

A THESIS

entitled

THE MELTING POINT OF SMALL CRYSTALS

by

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ABSTRACT

An experimental relationship between the melting temperature of a small crystal and its size is presented for each of the metals lead, bismuth and indium. The results are compared with theoretical predictions based on a thermodynamic model, and values for the crystal-liquid interfacial free energies are inferred.

Aggregates of small metallic crystals were prepared under vacuum in an electron diffraction camera by condensation from a molecular beam on to thin, amorphous substrate films. The melting temperatures of these deposits were determined by transmission electron diffraction - the melting being associated with the disappearance of the concentric sharp ring patterns characteristic of polycrystalline deposits. An electron microscope was used to obtain micrographs of each deposit, from which the size distribution of the crystallites could be obtained. Using these results in conjunction with the results of subsidiary experiments, it was possible to associate the melting temperature of a deposit with a particular crystallite size.

The solidification of a number of the deposits of lead and bismuth was also observed, and an experimental relationship between the solidification temperature of a crystallite and its size, for each of these metals, is compared with the predictions of nucleation theory.

The melting and solidification of deposits of lead and bismuth were investigated on two different amorphous substrates - carbon and silicon monoxide. Very similar results were obtained on the two substrates.

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CHAPTER 1

INTRODUCTION

1.1 Historical review of the size dependence of the melting and solidification temperatures of small crystals

The present thesis concerns the size dependence of the melting temperature of small crystals. The history of interest in this phenomenon is intimately bound up with developments in the broader context of the influence of surface on the physical properties of a material, and in particular with the dependence of the equilibrium vapour pressure on surface curvature. Some allusion to progress in this wider sphere is thus desirable.

From observations of capillary phenomena, Sir William Thomson (later Lord Kelvin) - see Thomson (1870) - deduced that the pressure of a vapour in equilibrium with its liquid, at a liquid surface concave with respect to the vapour, is less than that in equilibrium with a plane liquid surface at the same temperature. Using as a basis the work of Laplace, Thomson obtained the following expression for this difference:

$$p_1 - p_2 = - \frac{T d_v}{d_L - d_v} (1/r + 1/r') \quad (1-1)$$

where p_1 is the pressure of the vapour at the curved liquid surface

p_2 is the pressure of the vapour at the plane liquid surface

d_v is the density of the vapour

d_L is the density of the liquid

$1/r$ and $1/r'$ are the curvatures in the principle sections of the surface bounding liquid and vapour, reckoned positive when concave towards the vapour

and T is the "cohesive tension of the free surface, per unit of breadth".

The equation still bears his name.

In a classic work "On the Equilibrium of Heterogeneous Substances", Josiah Willard Gibbs (1876 - 1878) provided a framework for the thermodynamic study of the influence of surfaces on the equilibrium of a system.

J.J. Thomson (1888) considered the effect of surface tension on chemical equilibrium, upon solubility, and upon the freezing point. Although his examination of the effect of surface tension on the freezing point was purely qualitative and was made in ignorance of the vital role kinetic effects play in the phenomenon of freezing (see below), his work on the effect of surface tension upon the solubility was of importance both to problems on the influence of surface on melting and to the problem of freezing. Thomson investigated the equilibrium of a solution containing undissolved salt, and ascribed a surface tension T to the surface of the solution, and T' to the surface of the salt in contact with the solution. He then derived several equations for the increase $\delta\theta$ in the temperature which would produce the same effect as the surface tension. For instance, assuming the solution to be in the form of a spherical drop of radius a , and neglecting the surface tension of the salt in contact with the solution, he obtained

$$\delta\theta = - 2i \frac{\theta T}{qa}$$

where i and q are the increase in volume and heat absorbed, respectively, when unit mass of the salt dissolves and θ is the absolute temperature.

The lowering of the melting point of a material as a consequence of the reduction of the grain size was predicted by F.W. Kürster (1906), and following from Kürster's idea, Pawlow (1908, 1909a, 1910a) obtained an expression for the temperature at which a solid and liquid sphere of the same material and having identical masses, would be in equilibrium with the same vapour. Pawlow then attempted to observe the size dependence of the melting temperature of grains of salol - Pawlow (1910b), see also Pawlow (1909b) - though his findings have been discredited after the adverse criticism of Meissner (1920). An account of this early work on the influence of surface on melting has been given by Freundlich (1930), pgs. 144-145.

Using an elegant procedure proposed by Tammann, Meissner (op. cit.) observed the melting of thin lamellae of five low melting point organic compounds - azobenzene, myristic acid, tristearine, stearic acid, and p-chloraniline - which were sandwiched in the wedge-shaped space between a

flat metal bar and a convex cylindrical lens. With the axis of the lens parallel to the long axis of the bar, a known temperature gradient was established along the bar (and thus along the axis of the lens). This should, under ideal experimental conditions, produce isothermals perpendicular to the axis. If the melting point does not depend on thickness, the solid-liquid melting line should also be straight, perpendicular to the axis, and coinciding with the bulk melting point isothermal. If there is a dependence of the melting point on thickness, the melting line should deviate from the isothermal line, the deviation increasing with the decreasing thickness of the layer. The theoretical formula derived by Meissner to interpret his results has been criticised by Reiss and Wilson (1948), and the technique he employed has been greatly improved in the investigations made by Sill and Skapski (1956) on stearic and myristic acids.

Palatnik and Komnik (1960) investigated the melting points of thin condensed layers of tin and bismuth. A molecular beam of metal was condensed, under vacuum, onto a glass plate; and a screen, placed between the evaporator and the glass plate, was moved periodically during the condensation, producing steps in the deposit thickness. Then, without destroying the vacuum, the glass plate was heated from one end, and a stationary temperature gradient was obtained on it: the isotherms being almost straight lines intersecting the condensate perpendicularly to the steps. After cooling, the fusion boundary on each step was clearly visible as a result of a jump in the optical density of the condensate. However, in these experiments, no attempt was made to examine the actual nature of the deposit using replica or stripping techniques and electron microscopy; rather the size of the crystallites was inferred from the mean thickness of the deposit and certain doubtful assumptions concerning the mode of growth of the films. The interpretation of the jump in the optical density as representing the fusion boundary is also open to objection - see Fisher (1967) and Fisher and Anderson (1968).

A very important development in the investigation of the size dependence of the melting temperature of solids was the use of electron diffraction techniques to detect the melting of small crystalline particles. In the case of a polycrystalline deposit, the sharp ring diffraction pattern which is a manifestation of the long-range order of

the solid, gives way on heating to a diffuse halo pattern characteristic of the liquid - see § 4.2 - and the disappearance of the sharp ring pattern may be taken as a criterion of melting. Although several earlier observations of the fusion of vacuum condensed metallic deposits had been made using electron diffraction techniques, it was Takagi's investigations - see Takagi (1954) - on tin, lead and bismuth which first established that the melting temperature of a thin metallic deposit is substantially below the bulk melting temperature, and decreases as the mean thickness of the deposit decreases. Certain experimental deficiencies rendered Takagi's results unsuitable as a basis for detailed theoretical interpretation, and these deficiencies have been well indicated by Curzon (1960).

Blackman and Curzon (1959) - see also Curzon (op. cit.) - determined, from transmission electron diffraction observations, the melting temperatures of aggregates of very small crystallites of tin prepared by condensation in a vacuum. The aggregates were afterwards examined by means of an electron microscope and the size distribution of the crystallites of each deposit was found. A particular crystallite size, calculated from the size distribution, was then associated with the melting temperature of each deposit, though the criterion used to calculate the appropriate crystallite size was somewhat arbitrary. Wronski (1963, 1967) continued the work of Curzon on tin, and developed a sound criterion for the calculation of the crystallite size to be associated with the melting temperature of a deposit. The criterion was based on the results of subsidiary experiments, in each of which the electron diffraction patterns produced by a wholly-crystalline tin deposit and a wholly-molten tin deposit, having a known weight ratio, were superposed. That the results of Wronski's subsidiary experiments on tin were substantially different from the findings of the present investigations on lead and bismuth, may be a consequence of Wronski's technique of superposing the individually obtained diffraction patterns, rather than superposing the patterns on the same photographic emulsion as was done in the present work. Wronski further established that the melting temperature of tin crystallites is the same on both carbon and silicon monoxide substrates, within the limits of experimental error; as described below this was also found to be the case for deposits of lead and bismuth.

Gladkich, Niedermayer and Spiegel (1966) - see also Gladkich and Niedermayer (1965) and Gladkich, Hillecke and Niedermayer (1965) - investigated the structure of thin films of silver, copper, aluminium and germanium by means of transmission electron diffraction at 10^{-9} torr. The films were deposited on to carbon substrates suspended on a fine copper gauze, the gauze being welded over a 2 mm. diameter hole in a tantalum foil which could be heated electrically, the temperature of the tantalum foil in the neighbourhood of the 2 mm. hole being measured by a thermocouple. An observation of the melting of a silver film of thickness $800 \text{ \AA}$, made with a view to calibrating the thermocouple, yielded a melting temperature, as measured by the thermocouple, within 10°C of the bulk melting point of silver: this is surprising, since theoretical considerations - see below § 2.9 - indicate that with such an arrangement very large temperature differences are to be expected between the substrate and the thermocouple. The rate of evaporation of the metal from a U-shaped tungsten filament was measured by means of a quartz oscillator, and the deposit thickness on the carbon substrate was calculated by multiplying the evaporation rate by the time. As the authors point out, the fact that the condensation coefficient of metals is dependent on the temperature may result in the actual film thicknesses being less than quoted, in those cases where the substrate temperature was sufficiently high during the deposition.

Niedermayer et al. found that deposits of aluminium and germanium reacted with the carbon substrates on heating. Films of silver and copper condensed on to carbon substrates at 200°C gave rise immediately to diffraction patterns consistent with a polycrystalline aggregate. The dependence of the melting temperature of these films on the mean deposit thickness was investigated and the curves obtained were extrapolated to obtain a minimum melting temperature for the thinnest films: 550°C for silver and 670°C for copper. However, since the metallic deposits were not examined by electron microscopy, a correlation of the melting temperature with crystallite size was not possible. Moreover, the very high rate of evaporation of both the silver and copper deposits and the consequent uncertainty in the film thickness on melting, renders the validity of any extrapolation to small film thicknesses doubtful.

Measurements of the rate of evaporation of silver crystallites by Blackman, Lisgarten and Skinner (1968) indicate that at a pressure of 10^{-5} torr and a temperature of 772°C a $200\text{ \AA}$ crystallite completely evaporates in 30 sec.

Niedermayer et al. found that for a particular thickness of deposit, d , as measured by the quartz oscillator, the melting temperature, t_s , of films of silver was strongly dependent on the substrate temperature during deposition, t_u . However, it is difficult to evaluate the significance of their plots of t_s against t_u in view of the dependence of the condensation coefficient on the temperature. The condensation (or sticking) coefficient is a crude parameter which reflects poorly the complex processes of continuous nucleation and growth characteristic of the condensation of thin films from the vapour phase. It is not only dependent on the substrate temperature, but is also, under certain conditions, heavily dependent on the incident flux and the time which has elapsed since condensation commenced - see Hirth and Pound (1963), pg. 54 and pgs. 57 - 69. The sudden decrease in t_s for values of t_u above some 550°C has been interpreted by Niedermayer et al. as resulting from a retarded condensation at these substrate temperatures; and the gradual falling off of t_s for values of t_u below some 150°C as resulting from a decline in the crystallite size at these temperatures, presumably as a result of a decrease in the mobility of the atoms diffusing across the substrate surface.

The structure of layers of bismuth $150\text{ \AA}$ thick and produced by vacuum condensation on to carbon substrates, has been investigated by Hanszen (1966) in the electron microscope at 10^{-4} torr. The carbon substrate films were spread over a small hole in a tantalum strip which could be heated electrically, the experimental arrangement thus being similar to that used by Niedermayer et al. (op. cit.). As a technique for maintaining a thin film specimen at a known temperature, an arrangement of this kind in which the specimen is free to exchange radiation over a wide solid angle with material surroundings at room temperature is open to criticism. In addition, because of the relatively high electron beam currents, beam heating effects are likely to be large in the electron microscope. For deposits condensed at various substrate temperatures between 100 and 180°C and then cooled to 20°C , the

temperatures at which the deposits melted and resolidified during the (first) subsequent heating and cooling showed no apparent dependence on the substrate temperature during condensation and lay respectively in the ranges $230 - 250^{\circ}\text{C}$ and $90 - 70^{\circ}\text{C}$. The deposits were observed to melt over a finite interval of temperature and Hanszen attributed this to the size distribution of the particles in the layers. On remelting a deposit the melting temperature was found to be appreciably lower than on the first melting, lying in the range $180 - 220^{\circ}\text{C}$, while solidification occurred again in the range $90 - 70^{\circ}\text{C}$, the melting and solidification temperatures remaining unchanged on further heatings and coolings. Hanszen associated the change in the melting temperature with structural changes found to have occurred in the deposit after the first melting and resolidification. These structural changes were most marked for those deposits condensed at a low substrate temperature.

Recent theoretical investigations of the influence of surface on the melting of small crystallites have been made by Hanszen (1960) and Lacmann (1962) using a thermodynamic approach, and by Hill - see Hill (1963), pgs. 114 - 132 - from a thermodynamic and statistical viewpoint. Expressions for the dependence of the melting temperature of thin films on their thickness have been obtained by Weil (1964) thermodynamically, and by Wojtczak (1967) using a criterion for melting of vibrational instability similar to that of Lindemann (1910).

During the course of the present experiments, observations were made of the solidification temperatures of metallic deposits. In order to put this work into context, it is necessary to trace the events leading up to the present theory of nucleation in condensed systems.

The foundations for an understanding of the process of freezing and its associated supercooling phenomena (and also of crystallisation from solution and its associated supersaturation phenomena) were laid by de Coppet (1875) in terms of the kinetic theory of heat established by Clausius, Pfaundler, Dossios and Naumann. De Coppet explained spontaneous crystallisation of a liquid in the following manner:

"Considérons maintenant un liquide cristallisable refroidi jusqu'à son point de solidification. Si le liquide se trouve en présence d'un

cristal de la même substance, les molécules liquides de température suffisamment basse qui rencontreront le cristal déjà formé seront, en général, retenues par lui, et se déposeront à sa surface; mais, si le liquide n'est pas en contact avec un cristal de même espèce chimique, les choses pourront se passer tout autrement. Dans ce cas, la formation du premier élément cristallin exige la rencontre simultanée de plusieurs molécules liquides dans des conditions de mouvement toutes particulières

In a later paper de Coppet (1907) presented further experimental evidence and extended his ideas in response to the criticisms of Ostwald and others.

The supercooling of alloys of gold in the form of small metallic beads was reported by Van Riemsdyk (1880), who described the flash of light accompanying solidification and attributed it to the liberation of the latent heat of fusion. The paper contains many references to earlier work on supercooling, though there is no reference to the work of de Coppet. Unaware of the work of Van Riemsdyk, Mendenhall and Ingersoll (1908) observed the supercooling of particles of gold, palladium, platinum, silicon, rhodium and iridium. "Undercooling" of as much as 370 °C was observed with rhodium and platinum drops of 50 to 100 μ diameter, and the conspicuous "flashing" of the drops on solidification was again noted.

The ideas of de Coppet were further developed by Tammann (1903, 1922), Volmer and Weber (1926), Volmer (1929), Becker and Döring (1935), Becker (1938), and others. For an account of the early work see also Freundlich (1930), pgs. 457 - 463. Turnbull and Fisher (1949) derived an expression for the absolute rate of nucleation in condensed systems, by making use of the theory of absolute reaction rates. The evaluation by Turnbull and Fisher of the undetermined constant in Becker's equation for the rate of nucleation in condensed systems (i.e. liquid-solid or solid-solid transformations), coincided with the publication of a considerable amount of experimental work on nucleation in the freezing process. Vonnegut (1948) described the supercooling of aggregates of fine droplets of liquid tin, using originally X-ray diffraction and later a dilatometric method to detect the phase change. Schaefer (1949) gave an

account of the nucleation of aggregates of small droplets of water, Turnbull (1949) of mercury and gallium, and Turnbull (1950b) of mercury. Turnbull and Cech (1950) described the microscopic observation of the solidification of individual droplets (10 to 100 μ diameter) of a large number of different metals, including lead and bismuth; in the case of the higher melting point metals a sudden brightening ("blick") was used as the criterion of solidification. The available experimental results were discussed and interpreted in terms of homogeneous nucleation theory by Turnbull (1950c, 1950d) and a formulation for the frequency of heterogeneous nucleation was also discussed - Turnbull (1950a, 1950d). Further publications followed - see, for example, Pound and La Mer (1952), Turnbull (1952a, 1952b) - and the field was reviewed by Holloman and Turnbull (1953) and by Turnbull (1956).

Takagi (op. cit.) determined the solidification temperatures of her thin metallic deposits of tin, lead and bismuth and found appreciable supercooling. She calculated the solidification temperatures to be expected on the basis of the homogeneous nucleation theory of Turnbull and Fisher and their quoted data, and obtained higher values than those observed experimentally, though the discrepancy was small for lead. Blackman and Curzon (1959) made observations of the supercooling of aggregates of very small droplets ($\sim 100 \text{ \AA}$) of liquid tin using electron diffraction techniques. Curzon showed that the results could be adequately interpreted either in terms of homogeneous nucleation theory or of heterogeneous nucleation theory. However certain corrections to the free energy of formation of a critical nucleus within a droplet whose dimensions are comparable with the size of the critical nucleus - see Lacmann (1962) - were not considered by Takagi and Curzon.

Problems in both theoretical and experimental aspects of nucleation in the freezing process have latterly been discussed by Colligan, Loomis and Surprenant (1965), Gomersall, Shiraishi and Ward (1965), and at the Eighteenth Annual Conference of the Australian Institute of Metals - see Discussion (1965). In a number of instances supercoolings appreciably greater than those taken by Turnbull as representing the maximum degree of supercooling have been observed, and new (higher) values of the solid-liquid interfacial energies have been calculated from these on the basis

of homogeneous nucleation theory. Mannchen and Schuster (1966) - see also Mannchen (1964) - have recorded the supercoolings of bulk samples of high-purity bismuth and lead, and Frawley and Childs (1968a, 1968b) have investigated the influence of vibrations on the supercooling of pure bismuth and bismuth-tin alloys. Hanszen (1966) observed the solidification temperatures of vacuum condensed bismuth deposits, though no quantitative interpretation of the results was made and the actual deposit thicknesses or crystallite sizes were not stated. The solidification of thin films of silver condensed under vacuum at 10^{-9} torr has been observed by Niedermayer et al. (op. cit.), both during cooling, and at constant temperature during continuous condensation: a single curve was presented for the dependence of the solidification temperature on the (nominal) mean thickness of deposit, though certain difficulties exist concerning the actual deposit thicknesses (see above).

Recent theoretical work on nucleation in condensed systems includes the paper by Gindt and Kern (1968) where further references may be found.

1.2 Allied problems: experimental

The important parameter which may be estimated from the present experimental data on the size dependence of the melting and solidification temperatures of small metallic crystallites is the crystal-liquid interfacial free energy, σ_{CL} - see chapter 7. (For the purposes of the present discussion, the anisotropy of the crystal-liquid and crystal-vapour specific surface free energies - see § 6.3.1 - will be ignored.)

Solid-liquid interfacial energies in polyphase alloys have been measured relative to random, high-angle grain boundary energies, σ_{GB} , by dihedral angle measurement, and plots of σ_{CL}/σ_{GB} against composition allow the solid-liquid interfacial energies of pure metals to be inferred under certain assumptions. Values of σ_{CL} for aluminium and zinc derived in this way by Miller and Chadwick (1967) are greater by a factor of about 3/2 than the values obtained from maximum supercoolings by Turnbull on the basis of homogeneous nucleation theory.

The crystal-liquid, crystal-vapour and liquid-vapour specific surface free energies (at the melting point) - σ_{CL} , σ_C and σ_L ,

respectively - are related by the inequality

$$\sigma_{CL} \leq \sigma_C - \sigma_L \quad (1-2)$$

which is a consequence of the observation that every solid is completely wetted (contact angle zero) by its own liquid at the melting point - see Turnbull (1956), pg. 292 and Chadwick in Discussion (1965). Precise relationships between the quantities σ_{CL} , σ_C and σ_L have been deduced on theoretical grounds by Reiss and Wilson (1948), Skapski (1956) and Lacmann (1962), though it is the view of the present writer that in each case there are unjustified assumptions in the derivations.

Reliable experimental values of the liquid-vapour interfacial energies, σ_L , are available for most metallic melts - see, for example, Smithells (1967) and the review article by Flint (1965). The upper limit set to the solid-liquid interfacial energy, σ_{CL} , by the inequality (1-2) thus provides a check on the experimental estimates of σ_{CL} , when values for the solid-vapour interfacial energies, σ_C , have been obtained. Determinations of σ_C for metals have been made by Udin and others using the "wire-pulling" technique due originally to Berggren (1926) - for a review of this and other methods for measuring the surface energy of solid metals, see Greenough (1965). In recent observations of the rate of evaporation of small crystallites of silver by Blackman, Lisgarten and Skinner (1968), an appreciable increase of the vapour pressure was in evidence for crystallite radii less than $200 \text{ \AA}$, in accordance with the predictions of W. Thomson (1870): good agreement was obtained with theory with $\sigma_C = 1,130 \text{ ergs cm.}^{-2}$ - the value obtained for silver by Udin (1952).

The influence of surface energy effects on the structure of the solid phase has been reported by Bublik and Pines (1952). They observed the structure of unsupported thin films of the metals beryllium, chromium, cobalt, nickel and vanadium by transmission electron diffraction. Vanadium films of $60 - 70 \text{ \AA}$ mean thickness yielded a polycrystalline ring pattern characteristic of a face-centred-cubic structure, though when the vanadium films were about $100 \text{ \AA}$ thick, the diffraction rings of the normal body-centred-cubic structure of vanadium were obtained. The structure of thin films of beryllium, chromium, cobalt and nickel were

also found to depend on the mean thicknesses of the films. Recently Denbigh and Marcus (1966) have obtained molybdenum deposits having a fcc rather than the normal bcc structure, and Grigson and Dove (1966) using the scanning-electron-diffraction technique and filtered electrons have reported the formation of amorphous deposits of iron and germanium in the initial stages of growth.

1.3 Allied problems: theoretical

Most theoretical investigations of the influence of crystallite size on the temperature at which a crystallite melts have been made from a thermodynamic standpoint, and the thermodynamic approach is discussed in detail in chapter 6. However, a full insight into the process of fusion of a very small crystallite will only be possible when mechanisms of fusion in bulk materials are much better understood, and this itself will necessitate a more detailed knowledge of the structure of melts than we have at present. Statistical theories of liquids and statistical approaches to the melting problem are considered further in § 6.1.

Closely allied to the problem of applying statistical ideas to the melting of a small crystallite is recent statistical work on solid and liquid surfaces. Theories of the surface energy and surface tension of non-metallic crystalline solids have been reviewed by Benson and Yun (1967), and statistical theories of liquid surfaces by Ono and Kondo (1960).

It may be mentioned here that one of the most promising theories of melting is that due to Lennard-Jones and Devonshire (1939a, 1939b) based on the order-disorder theory of Bragg and Williams (1934, 1935a, 1935b) and Bethe (1935). The application of such a model to the melting of a small crystallite would involve an examination of disordering processes at the crystallite surface, and would thus be intimately bound up with the so-called "surface roughening" phenomenon. This problem has been treated by Burton, Cabrera and Frank (1951), Mullins (1959), Jackson (1959), Valenta and Sukiennicki (1966), and Karge, Heyer and Pound (1967).

The experiments described in this thesis concern the size dependence of the melting temperature of metallic crystallites. The possibility of formulating a mechanism of fusion for metals in terms of order-disorder processes is discussed in § 6.1. A consideration of the

properties of metal surfaces is complicated by the presence of conduction electrons, and here attention may be drawn to the extensive literature dealing with contributions to the surface energy of solid and liquid metals arising from the conduction electrons. A separate bibliography to this work is given in Appendix 3, and includes the papers by Stratton (1953a), Dupuis, Mazo and Onsager (1960) and Stratton (1962). These three papers on the surface specific heat of solids are relevant to the calculation of the total surface energy of a crystalline metal.

CHAPTER 2

DESCRIPTION OF THE APPARATUS

2.1 The electron diffraction camera

The diffraction of electrons by metallic deposits consisting of small crystals was observed during heating and cooling in a vertical electron diffraction camera. The camera was designed by Kehoe and Newman (1956) and part of it is shown schematically in figure 1.

The camera was pumped by a two inch diffusion pump backed by a rotary pump. A large vapour trap, cooled by liquid nitrogen and situated immediately above the diffusion pump, served to remove the considerable amounts of water vapour from the photographic film or plates used for recording. After completely dismantling, cleaning and reassembling the camera, it was possible to attain a pressure of 5×10^{-6} torr or better, after some eight hours pumping with ten feet or so of recording film in the film chamber. The pressure in the camera was measured by a Penning gauge situated immediately above the vapour trap: in this position the gauge was sufficiently far from the electron beam for its magnetic field not to distort the electron diffraction pattern. A "cold-finger" vapour trap made from a length of $\frac{1}{2}$ -inch, German-silver tube was fitted in the specimen chamber itself, and when filled with liquid oxygen this served to further reduce the water vapour in the immediate vicinity of the specimen - see figure 3.

In the electron gun, electrons drawn from an electrically-heated, tungsten, "hair-pin" filament were accelerated to 40 kilovolts, and those passing through a fine pin-hole in the anode were focussed on to a fluorescent screen by a magnetic lens. The specimen was situated approximately mid-way between the magnetic lens and the fluorescent screen. The screen could be raised to allow the electrons to pass into the film chamber below, patterns being recorded either on 70 mm. film, or plates. The electron beam intensity could be varied by varying the temperature of the tungsten filament and also by varying the bias on a cylinder situated between the filament and the anode. In the experiments here described, beam currents of 0.006 μ A or less were employed to avoid

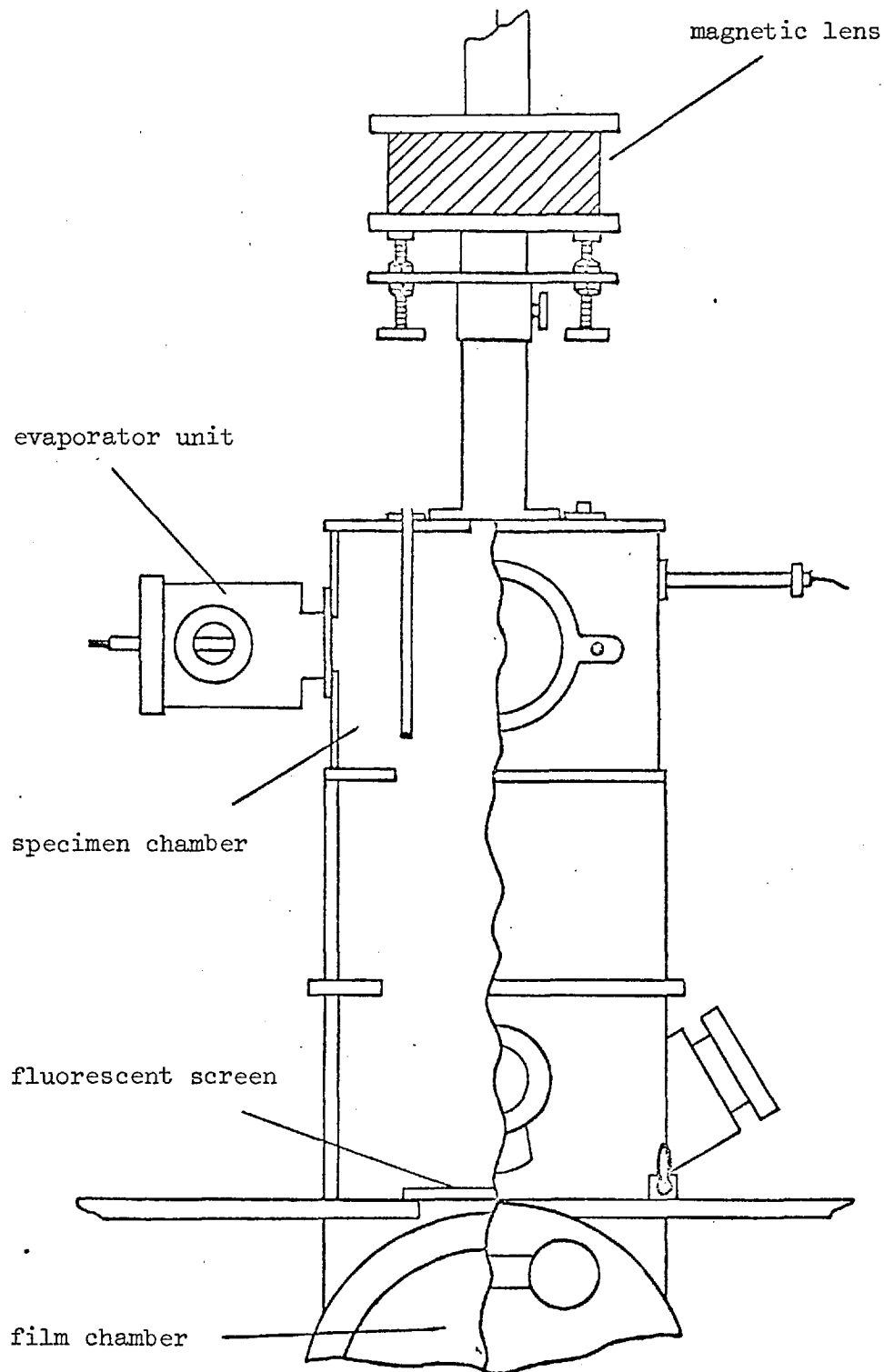


Figure 1. The electron diffraction camera

(scale: $\times \frac{1}{4}$)

heating the specimen by the beam. The beam diameter in the plane of the specimen was 0.6 mm., so that the current flux was about 2×10^{-6} amp. cm.⁻² or less.

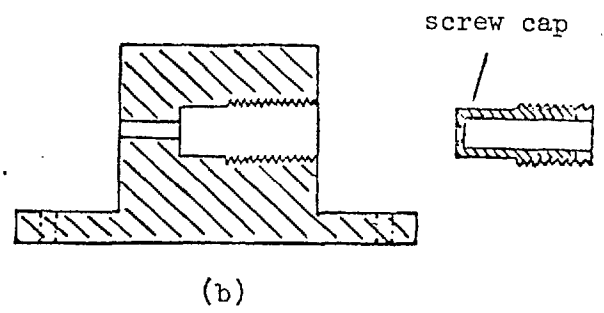
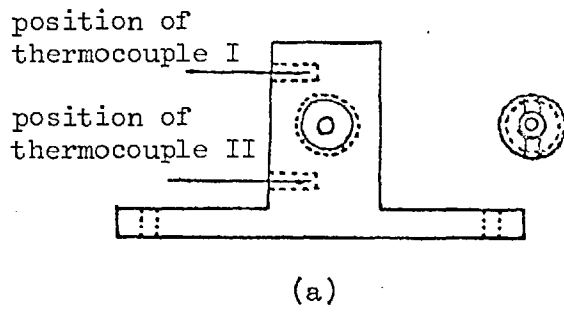
2.2 Measurement of the electron beam current

Except for the experiments described in § 3.4, the beam intensity was measured by inserting a Faraday cage (Curzon 1960) mounted on a sliding vacuum seal in the path of the beam immediately above the specimen - see figure 3. The current from the Faraday cage was fed directly into the input of a "Pye" D.C. amplifier of input impedance 3500 ohms, and the voltage developed across the input was observed, after amplification, on the meter of the amplifier. When the Faraday cage was correctly positioned, the reading on the meter was a maximum and remained unaltered by small adjustments of the Faraday cage in two perpendicular directions.

The Faraday cage behaves as a current source of very high impedance so that the current it delivers to the input of the amplifier should depend very little on the actual value of the input impedance provided this is small by comparison. Experimentally it was found that if a 15,000 ohm resistor was suddenly inserted in series with the input to the amplifier from the Faraday cage, the amplified voltage registered on the meter did not alter visibly indicating that the input current had not changed. The input current calculated from the voltage developed across the input of the amplifier was clearly a proper measure of the electron beam current, and (for example) an input of 35 μ V corresponded to a beam current of 0.01 μ A. The actual value of the input impedance of the amplifier on the range used was checked and found to be 3500 ohms to within 3%.

2.3 The specimen furnace

Each deposit of small crystals was prepared under vacuum inside the diffraction camera by horizontal evaporation on to a thin substrate film of carbon or silicon monoxide suspended on a copper electron microscope grid. The grid was held in a cylindrical cavity in a block of spectroscopically pure copper by means of a screw cap also of



Scale: (a), (b) and (c) x 2

(d) x 16

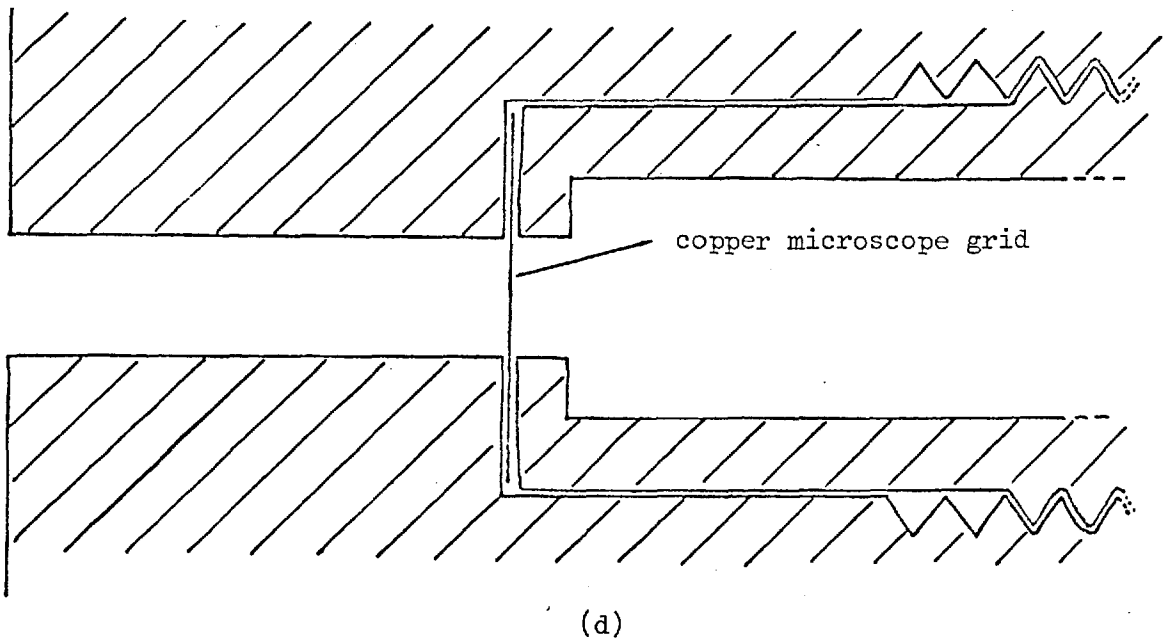
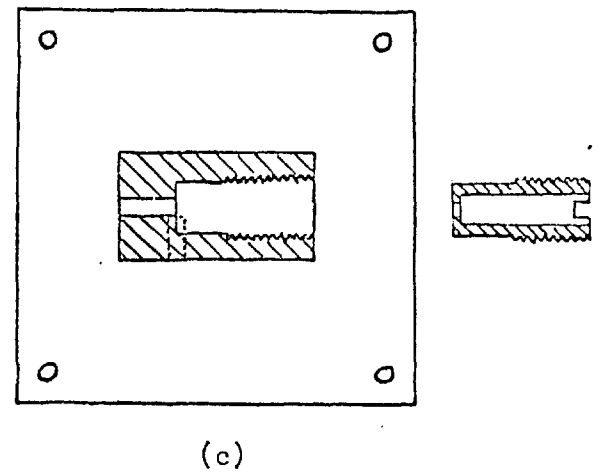


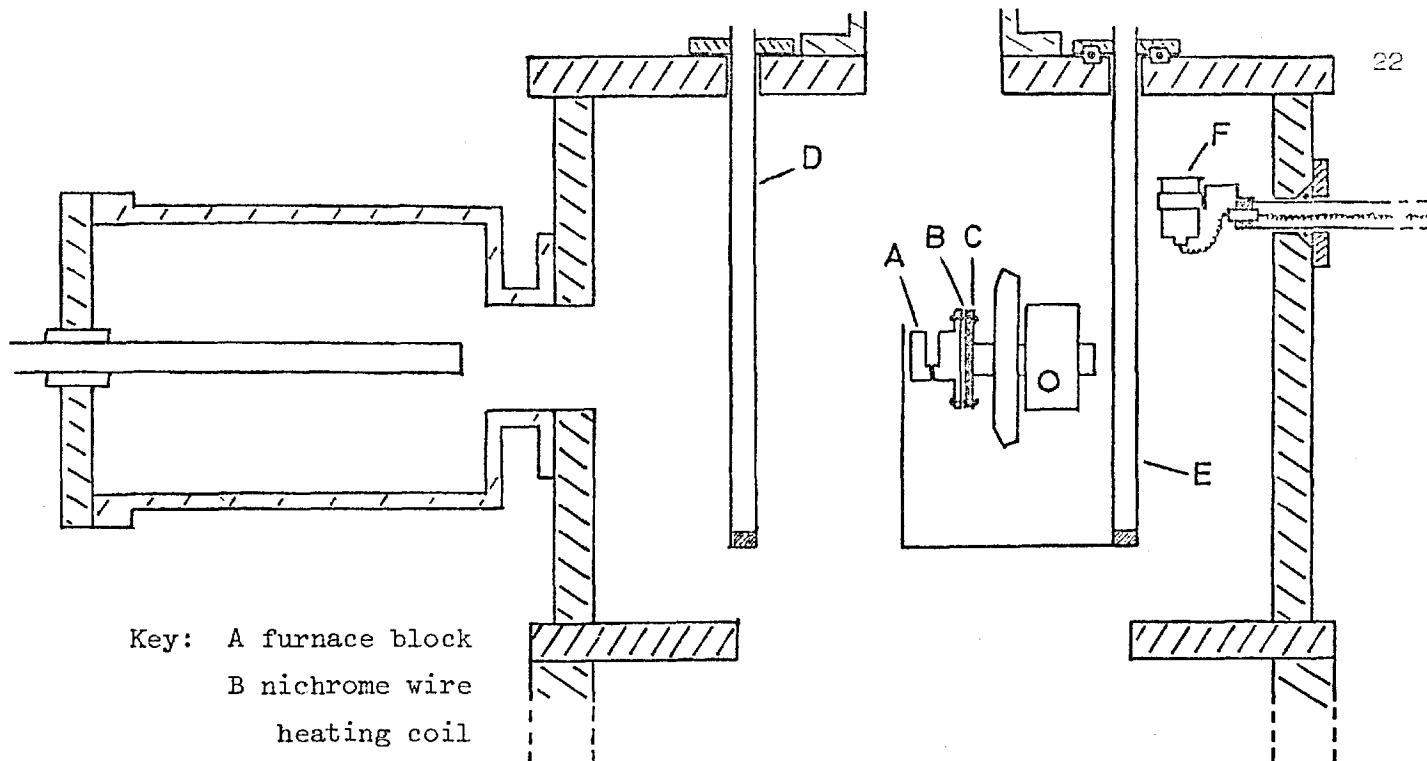
Figure 2. Copper block of furnace

spectroscopically-pure copper - see figure 2. The block could be heated by passing a current through a nichrome wire coil wound on a mica former, and insulated electrically from the block by a sheet of mica. Electrical and thermal insulation from the "specimen manipulator" on which the block was mounted was achieved by means of mica sheets (thickness ~ 4 mm.) - see figure 3.

The temperature of the copper block was measured at two points close to the position of the specimen by means of two copper-constantan thermocouples of identical material and total resistance (thermocouple I and thermocouple II - see figure 2), which had their hot junctions "hard soldered" into the bottom of two 1 mm. holes in the furnace. Very fine insulated wire was chosen (0.1 mm. diameter copper and 0.1 mm. diameter constantan) and was led out unbroken through vacuum seals in the "specimen manipulator". The cold junctions of these two thermocouples, together with the cold junction of a third thermocouple (thermocouple III) also of identical material, could be surrounded with a mixture of melting ice and water in the same beaker. The hot junction of thermocouple III was soft soldered onto the copper tag of a switch outside the camera. An all-copper switching system (to avoid additional thermoelectric e.m.f.s) made possible the connection of any of these three thermocouples across a "Unipivot" microammeter (f.s.d. 120 μ A). During the experiments the temperatures recorded by thermocouples I and II differed by no more than 1.5 $^{\circ}$ K. Such differences as arose were always consistent: with the furnace at room temperature the thermocouples read identically, but on heating the furnace, thermocouple I registered a slightly greater temperature than thermocouple II. This difference was independent of the rates of heating employed during the experiments, and depended solely on the temperature of the furnace, becoming noticeable at about 400 $^{\circ}$ K and increasing to some 1.5 $^{\circ}$ K at 600 $^{\circ}$ K.

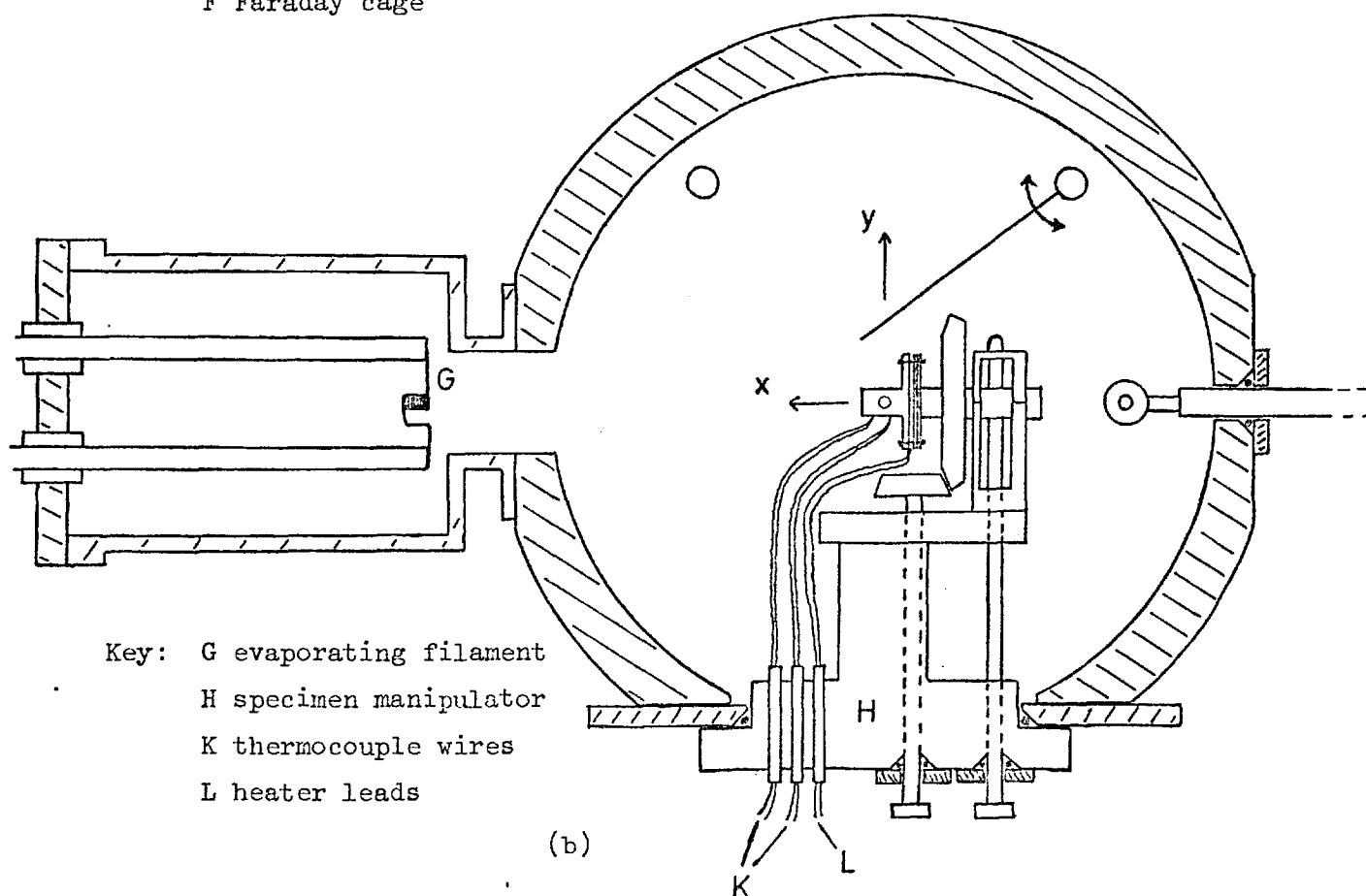
The maximum permissible current through the nichrome heating coil was about 3 amp., and a current of 1.4 amp. yielded an equilibrium furnace temperature of almost 450 $^{\circ}$ C. An analysis of the cooling curve of the furnace in vacuum showed that above 200 $^{\circ}$ C more heat was lost by radiation than by conduction.

A detailed discussion of the design features which made the furnace



Key: A furnace block
 B nichrome wire
 heating coil
 C mica insulation
 D "cold-finger" vapour trap
 E cooling device
 F Faraday cage

(a)



Key: G evaporating filament
 H specimen manipulator
 K thermocouple wires
 L heater leads

(b)

Figure 3. The specimen chamber (a) in elevation (b) in plan (to half scale)

suitable for maintaining a thin film (under vacuum) at a known temperature of some 600 °K is given in § 2.9.

2.4 The mounting of the furnace

The furnace was mounted - see figures 3 and 4 - on a specimen manipulator which has been described by Kehoe, Newman and Pashley (1954). This provided a lateral displacement of the furnace in the x-direction (in the present experiments this was only used once - in the initial positioning of the furnace) and rotations about the perpendicular axes x and y - see figure 3(b). At the start of each experiment - see § 3.2(ii) - the rotations about both axes were used to align the axis of the furnace and grid with the evaporating filament, an accuracy of $\pm 1/20$ radian being obtained by observations down the axis of the evaporating chamber. Once this alignment had been made and the camera pumped down, the rotation about the y-axis only was used - this rotation being obtained by turning the whole specimen manipulator about a greased 'O' ring vacuum seal. The axis of the furnace (and grid) could then be made to coincide accurately with either the evaporating filament or the electron beam, by means of a pointer on the outside of the specimen manipulator.

2.5 The cooling device

A second (see § 2.1) "cold finger" in the specimen chamber carried a length of thick copper wire and could be rotated about an 'O' ring vacuum seal to bring the wire firmly into contact with the furnace - see figure 3. By filling the cold finger with liquid oxygen, furnace temperatures down to -50 °C could be attained under vacuum, because of the good thermal insulation of the copper block. This device made possible the determination of the melting temperatures of deposits of indium which melted considerably below room temperature. It also made it possible to cool the furnace rapidly from any temperature, after the completion of a melting temperature determination, while maintaining the high vacuum: this saved time and reduced the risk of oxidation of the deposit particularly in experiments in which the same deposit was melted several times.

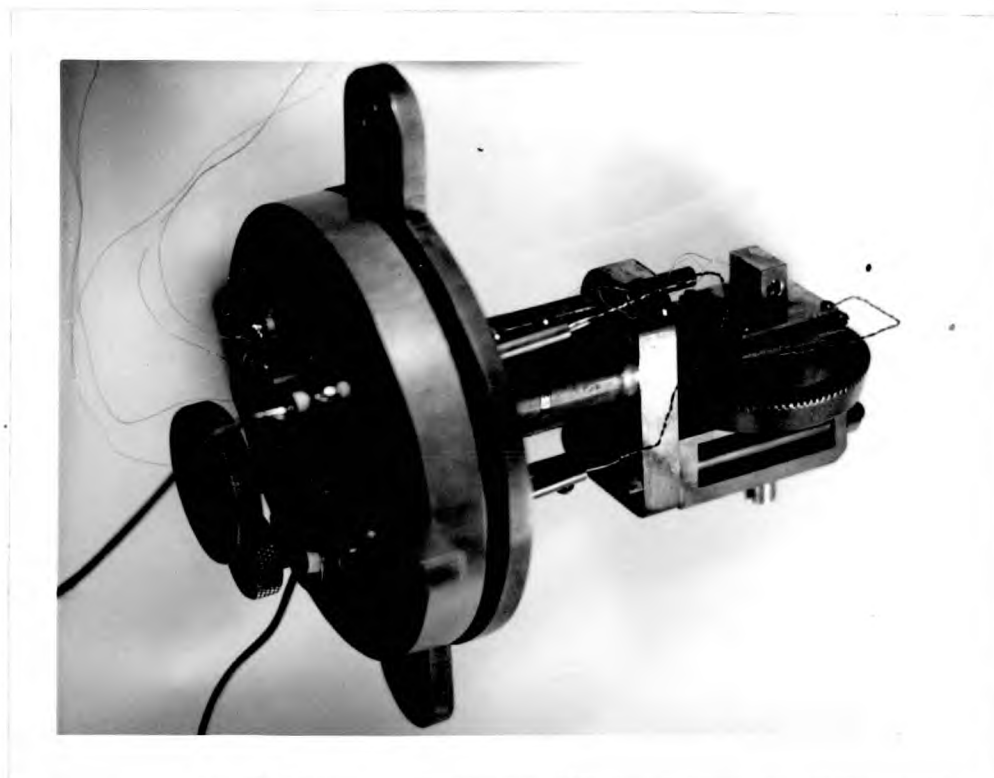


Figure 4. The specimen furnace mounted on the specimen manipulator.

2.6 The evaporator

This is shown in figures 1 and 3. Each metallic deposit was prepared under vacuum by the complete evaporation (horizontally) of a known weight of metal from a tungsten filament housed in the chamber of the evaporator, on to a carbon or silicon monoxide substrate film in the furnace at a fixed distance of 12.4 cm.

Provided certain precautions were taken (see below), the nature of the deposit depended only on the weight of metal evaporated and the substrate used (i.e. carbon or silicon monoxide); a particular weight of metal giving a deposit of definite mean thickness and consisting of small crystals of various sizes but having a definite size distribution. By varying the weight of metal evaporated, a series of deposits were obtained each of predictable mean thickness and size distribution of crystallites: weights from 0.4 mg. to 20 mg. were employed.

The precautions involved were:

- (i) melting the known weight of metal under vacuum into a small bead, which adhered to the filament, by passing a short current pulse through the filament. This was done prior to the alignment of the substrate with the filament.
- (ii) the careful choice of the evaporating filament. Two different tightly-wound tungsten filaments were used: a cylindrical one blanked at one end by means of a molybdenum sheet, for the evaporation of weights of 2 mg. or more; and a flat spiral one for the evaporation of weights of less than 2 mg. - see figures 7(a) and 7(b).

2.7 Details of the apparatus used for the experiments described in § 3.4

The experiments described in § 3.4 involved exposing a photographic emulsion to the electrons scattered from a specimen when a known electron beam was incident on the specimen for a known time. The experimental arrangement, with which this exposure time could be accurately measured and controlled within the limits 25 to 1/40 sec. and the beam current could be monitored immediately before and immediately after an exposure, is shown schematically in figure 5.

The electron beam was deflected from the centre of the specimen into the Faraday cage by passing a current through a pair of deflecting

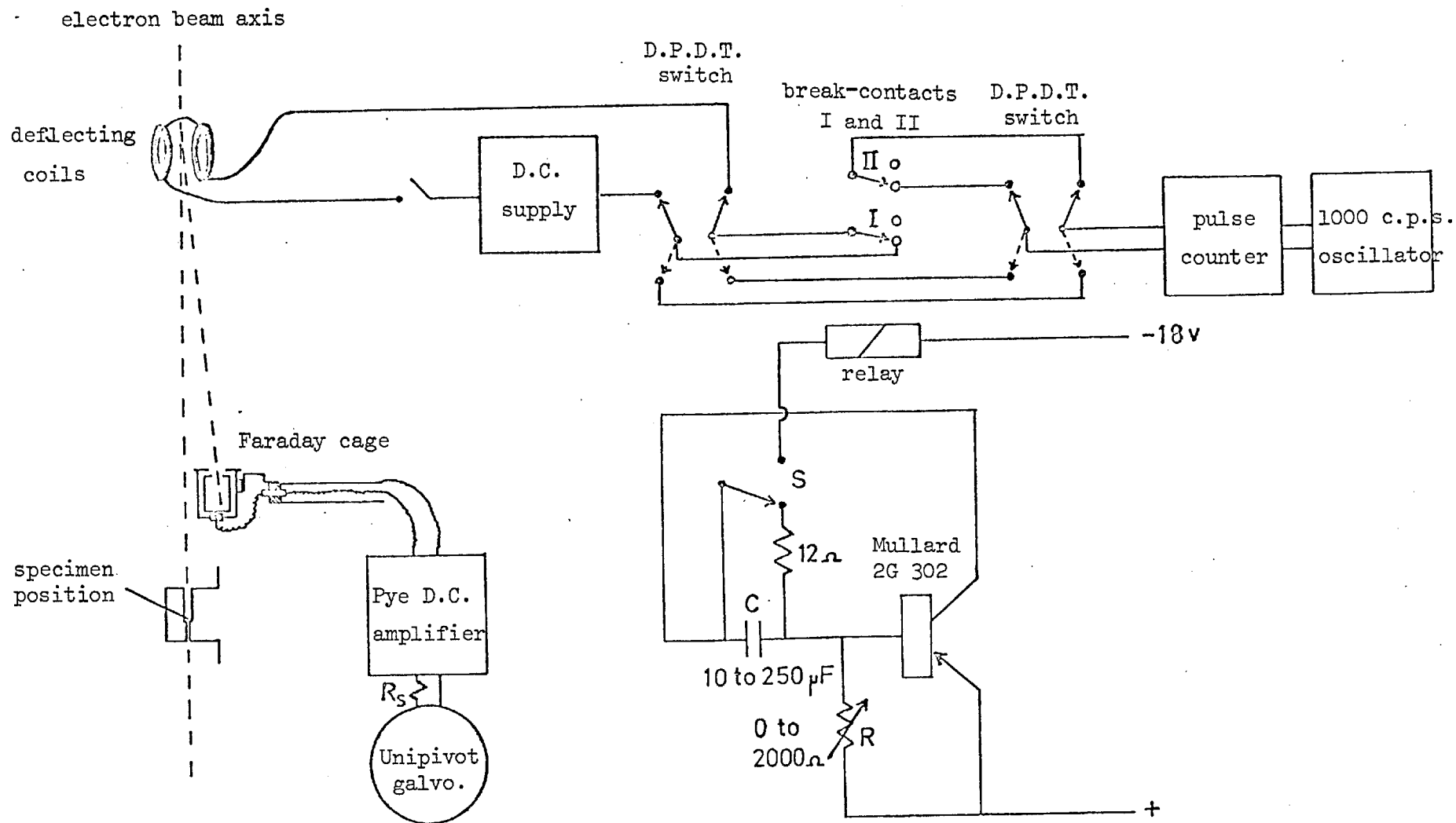
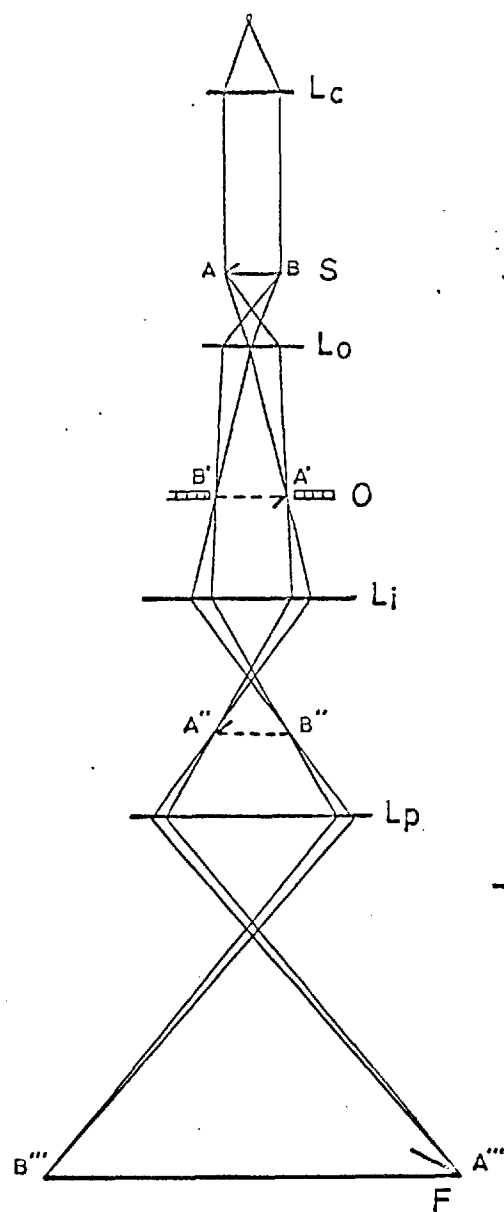


Figure 5. The apparatus used for making timed exposures (schematic)

coils. This current passed through one (break-contact I) of two break-contacts of a relay, so that when the relay was energised, the current to the deflecting coil was switched off and the electron beam was then incident upon the specimen. On throwing the two-way switch S, the relay could be energised for any period between 25 and $1/40$ sec. by suitable choice of the values of the capacitor C and the variable resistor R in the transistor biasing circuit. Any one of a number of capacitors, and any one of a number of variable resistors, could be switched into the biasing circuit of the transistor. By presetting the values of these capacitors and resistors it was possible to do an experiment which involved making several exposures of different, preselected times in a very short period. In this way the risk of oxidising a hot specimen was reduced.

The operation of the other break-contact (break-contact II) on the relay caused a counter to count the pulses from a 1000 c.p.s., maintained-tuning-fork oscillator. The time for which break-contact II was open was registered on the counter in thousandths of a second. The arrangement of double-pole, double-throw (D.P.D.T.) switches permitted break-contact I to be used to operate the counter instead of break-contact II (but not break-contact II to operate the deflecting current), so that the time for which the two sets of contacts were open, for a given setting of the transistor circuit, could be compared periodically. It was found that break-contact II consistently remained open for 5 thousandths of a second longer than break-contact I, no matter what the overall times involved, so this time was subtracted from the times recorded by the counter to obtain the exposure times of the specimen to the electron beam.

The output of the Faraday cage was fed directly into the Pye amplifier (see § 2.2), the output of which (up to 10 volts D.C.) was used to operate a "Unipivot" galvanometer (f.s.d. 120 μ A). The series resistor R_s was chosen to give a galvanometer deflection of 100 μ A for an input voltage to the amplifier of 20 μ V, that is for an electron beam current of 0.0057 μ A. When the Faraday cage was correctly positioned, the reading on the galvanometer was a maximum and remained unaltered by small adjustments of the Faraday cage in two perpendicular directions.



Key: L_c: condenser lens
 S : specimen
 L_o: objective lens
 O : objective aperture
 L_i: intermediate lens
 L_p: projector lens
 F : fluorescent screen



7(a)



7(b)

Figures 7(a) and 7(b).
 The evaporating filaments

Figure 6. Image formation in the
 electron microscope at high magnification

2.8 The electron microscope

The metallic deposits investigated in these experiments were examined in a J.E.M.-6A electron microscope. A ray diagram illustrating image formation in the electron microscope at high magnification is shown in figure 6.

2.9 The design features of a suitable furnace

Three furnaces were constructed during the course of these experiments - see figure 8 and § 2.9.2 - of which the second and third were of identical design. The first two were in stainless steel, chosen with a view to avoiding contaminating the films, and the third (the one finally used) was of "spec.-pure" copper, chosen both to avoid contamination and to attain a uniform furnace temperature.

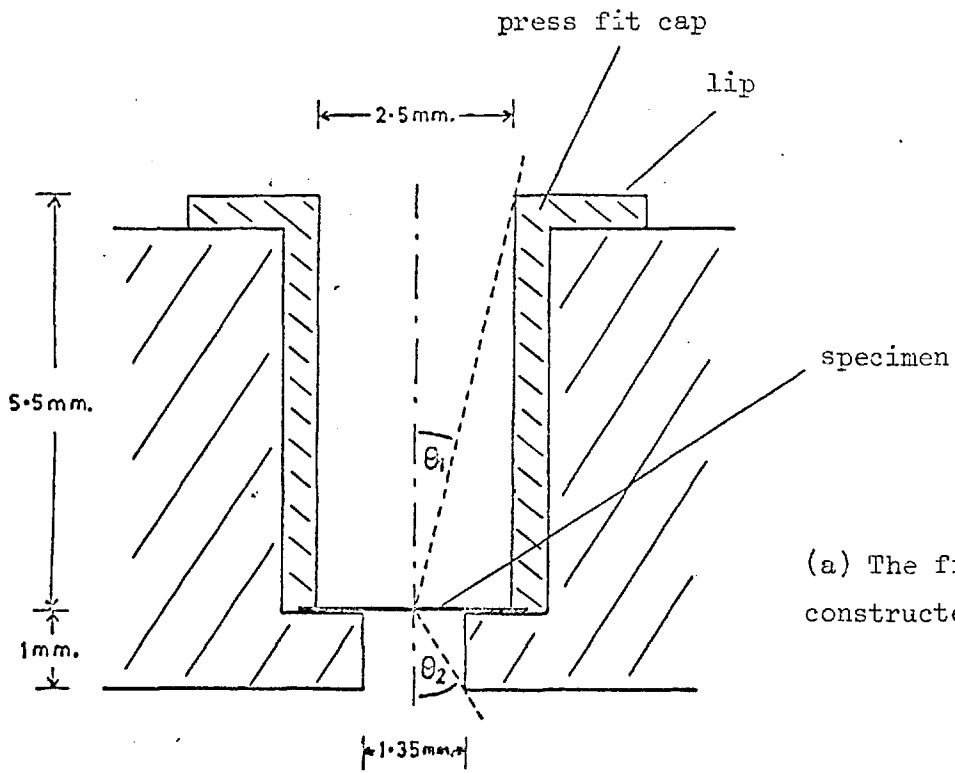
2.9.1 The factors which determine the temperature of a thin film

The design features of a furnace suitable for maintaining a thin film (under vacuum) at a known temperature of some 600°K are investigated by examining the factors which determine the temperature of a non-volatile, thin film under the three headings (i) radiation (ii) conduction and (iii) electron-beam heating.

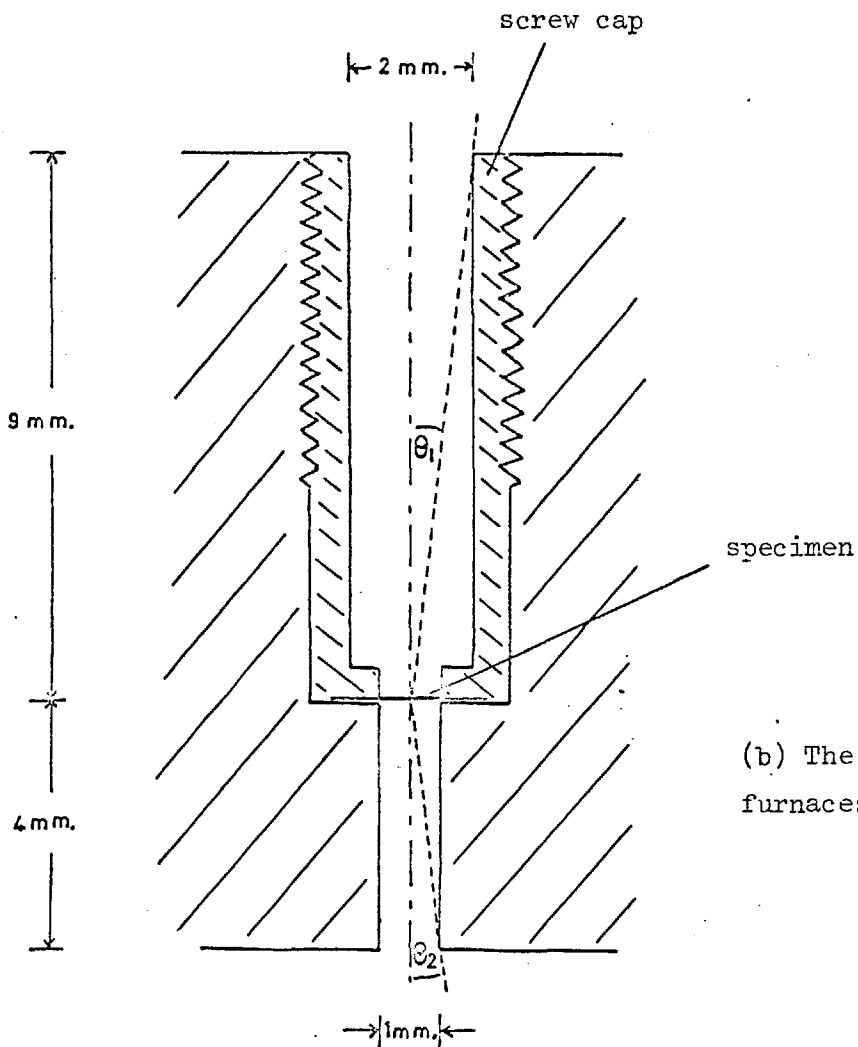
(i) Radiation

Consider a thin film supported on a microscope grid in a hot furnace within the evacuated electron diffraction camera. Suppose that the microscope grid and the furnace are both at a uniform temperature of $T_F^{\circ}\text{K}$ and that the camera is at a uniform temperature of $T_C^{\circ}\text{K}$.

We suppose that the design of the furnace is similar to those shown in figure 8 (a) and (b), so that the film "sees" the walls of the camera at room temperature through the ends of two cylindrical holes one above and one below the film. Consider a small element of the film of area δA , and let x_1 and x_2 be the fractions of the total solid angles of 2π steradians above and below the element, which the outer ends of the two cylinders subtend at the element. If the temperature of the element, $T_{ER}^{\circ}\text{K}$, is solely determined by radiative heat transfer, then in equilibrium



(a) The first furnace constructed (scale: x 10)



(b) The second and third furnaces constructed (scale: x 8)

Figure 8. Details of the design of the furnaces

$$2 e \delta A \sigma T_{ER}^4 = (1 - x_1) e \delta A \sigma T_F^4 + x_1 e \delta A \sigma T_C^4 + (1 - x_2) e \delta A \sigma T_F^4 + x_2 e \delta A \sigma T_C^4 \quad (2-1)$$

where e is the emissivity of the (two) surfaces of the film and σ is Stefan's constant.

If x is the fraction of the total solid angle of 4π steradians above and below the element, which the outer ends of the cylinders together subtend at the element, then

$$x = \frac{x_1}{2} + \frac{x_2}{2} \quad (2-2)$$

and equation (2-1) becomes

$$T_{ER}^4 = (1 - x) T_F^4 + x T_C^4 \quad (2-3)$$

Referring to figure 8, purely geometrical considerations lead to

$$x_1 = 1 - \cos \theta_1 \quad \text{and} \quad x_2 = 1 - \cos \theta_2$$

so that, for the first furnace

$$x = \frac{x_1}{2} + \frac{x_2}{2} = 0.012 + 0.086 = 0.098 \quad (2-4)$$

and for the second and third furnaces

$$x = 0.0070 \quad (2-5)$$

Using (now) the subscript 1 to refer to the first furnace and the subscript 2,3 to refer to the second and third furnaces, we may calculate the radiative-equilibrium temperature of a thin film:

When $T_F = 600^\circ\text{K}$ and $T_C = 293^\circ\text{K}$, from equation (2-3)

$$(T_{ER})_1 = 586.2 = 600 - 13.8^\circ\text{K} \quad (2-6)$$

$$(T_{ER})_{2,3} = 599.0 = 600 - 1.0^\circ\text{K} \quad (2-7)$$

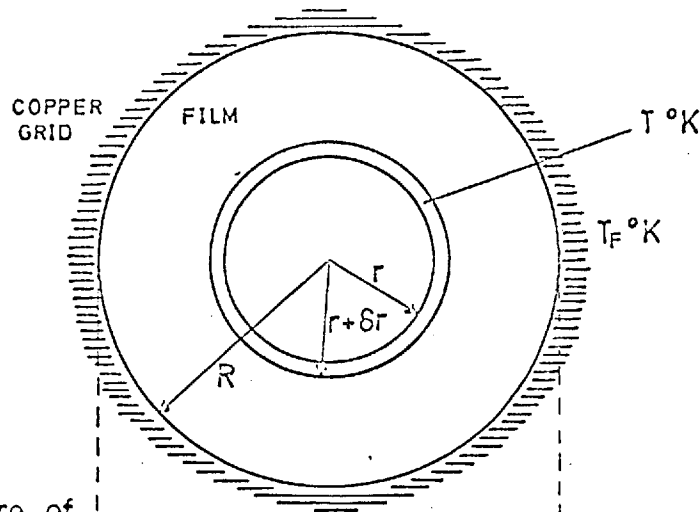


Figure 9(a). Thin film suspended over a circular hole in an electron microscope grid

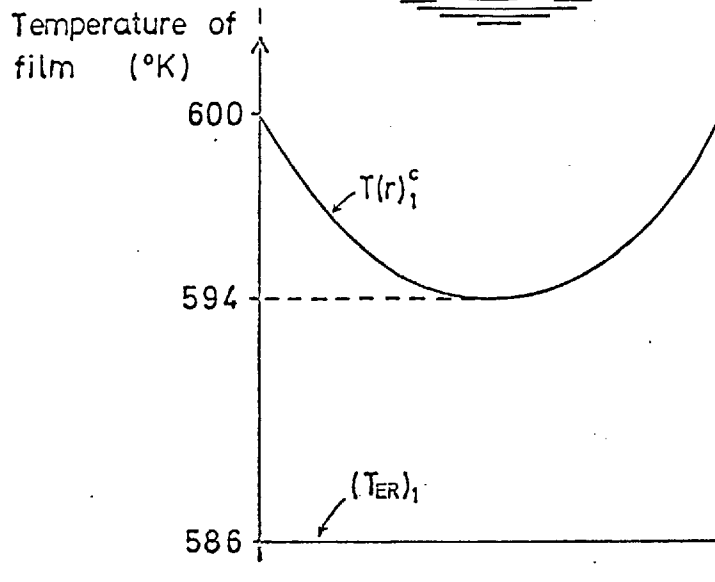


Figure 9(b). The temperatures of the film in the first furnace:
 $(T_{ER})_1$ neglecting conduction of heat
 $T(r)_1^C$ with conduction of heat

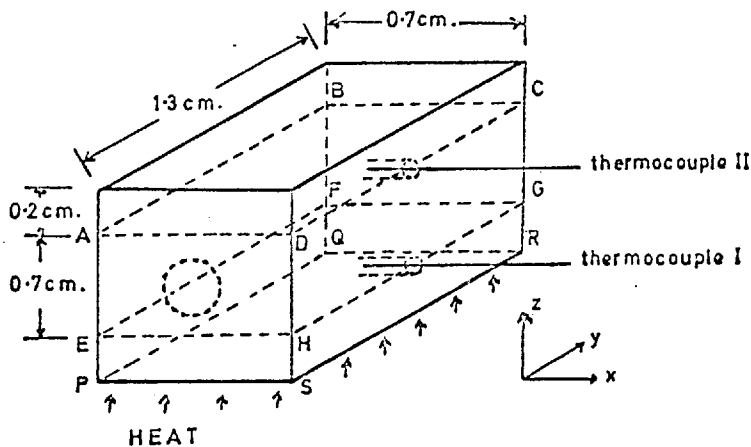


Figure 10. Conduction of heat in a radiating metal block

(ii) Conduction

When the camera is evacuated to 5×10^{-6} torr, loss of heat by the film to the residual gases in the vacuum is negligible. The effect of conduction of heat through the film is, however, important in determining the temperature of the thin film, as is shown below.

Let the thickness of the film (assumed uniform) be h , its thermal conductivity be K , and the radius of the hole (assumed circular) in the copper electron microscope grid on which the film is suspended be R .

Consider an element of the film at a temperature T °K in the form of an annulus having internal radius r and external radius $r + \delta r$ - see figure 9(a). The total heat lost by the annulus due to radiation exchange is

$$2e(2\pi r \delta r)\sigma \left[T^4 - (1-x)T_F^4 - xT_C^4 \right]$$

The heat conducted into the annulus is

$$K \left[2\pi(r + \delta r)h \right] \left(\frac{dT}{dr} \right)_{r+\delta r}$$

and the heat conducted out of the annulus is

$$K \left[2\pi rh \right] \left(\frac{dT}{dr} \right)_r$$

Thermal equilibrium requires

$$\begin{aligned} 2e(2\pi r \delta r)\sigma \left[T^4 - (1-x)T_F^4 - xT_C^4 \right] \\ = K2\pi h \left[r \left(\frac{dT}{dr} \right)_{r+\delta r} - r \left(\frac{dT}{dr} \right)_r + \delta r \left(\frac{dT}{dr} \right)_{r+\delta r} \right] \end{aligned}$$

$$\text{i.e.} \quad 2e\sigma \left[T^4 - (1-x)T_F^4 - xT_C^4 \right] = Kh \left[\frac{d^2T}{dr^2} + \frac{1}{r} \frac{dT}{dr} \right]$$

$$\text{i.e.} \quad \frac{d^2T}{dr^2} + \frac{1}{r} \frac{dT}{dr} - \frac{2e\sigma}{Kh} \left[T^4 - (1-x)T_F^4 - xT_C^4 \right] = 0 \quad (2-8)$$

with boundary conditions

$$r = R, T = T_F$$

(2-9)

$$r = 0, \frac{dT}{dr} = 0$$

The value of T in equation (2-8) always lies between the values T_{ER} and T_F , where T_{ER} is defined by equation (2-3). An analytic solution of equation (2-8) is, to the knowledge of this writer, unobtainable; but provided the temperature T_{ER} defined by equation (2-3) does not differ from T_F by more than a few percent (say some 10 °K), an approximate solution may be obtained as follows:

Put

$$T = T_{ER} + \Delta T$$

(2-10)

Then from equations (2-8) and (2-3) we obtain, approximately,

$$\frac{d^2 \Delta T}{dr^2} + \frac{1}{r} \frac{d \Delta T}{dr} - \frac{8e\sigma T_{ER}^3}{Kh} \Delta T = 0 \quad (2-11)$$

with boundary conditions

$$r = R, \Delta T = T_F - T_{ER}$$

(2-12)

$$r = 0, \frac{d \Delta T}{dr} = 0$$

(2-13)

As a solution of equation (2-11) try

$$\Delta T = r^c (a_0 + a_1 r + a_2 r^2 + \dots \text{to infinity}) \quad (2-14)$$

so that $\frac{d \Delta T}{dr} = a_0 c r^{c-1} + a_1 (c+1) r^c + a_2 (c+2) r^{c+1} + \dots$

and $\frac{d^2 \Delta T}{dr^2} = a_0 c(c-1) r^{c-2} + a_1 (c+1) c r^{c-1} + a_2 (c+2)(c+1) r^c + \dots$

Substituting into equation (2-11)

$$a_0 c(c-1) r^{c-2} + a_1 (c+1) c r^{c-1} + a_2 (c+2)(c+1) r^c + a_3 (c+3)(c+2) r^{c+1} + \dots$$

$$+ a_0 c r^{c-2} + a_1 (c+1) r^{c-1} + a_2 (c+2) r^c + a_3 (c+3) r^{c+1} + \dots$$

$$- \frac{8e\sigma T_{ER}^3}{Kh} a_0 r^c - \frac{8e\sigma T_{ER}^3}{Kh} a_1 r^{c+1} - \dots = 0$$

Equating coefficients of r^{c-2} to zero

$$c(c-1) + c = 0 \rightarrow c^2 = 0 \rightarrow c = 0$$

Equating coefficients of r^{c-1} to zero

$$(c+1)c + (c+1) = 0 \rightarrow (c+1)^2 = 0 \rightarrow c = -1$$

Equating further coefficients

$$a_2(c+2)^2 - \frac{8\epsilon\sigma T_{ER}^3}{Kh} a_0 = 0$$

$$a_3(c+3)^2 - \frac{8\epsilon\sigma T_{ER}^3}{Kh} a_1 = 0$$

$$a_4(c+4)^2 - \frac{8\epsilon\sigma T_{ER}^3}{Kh} a_2 = 0$$

etc.

If $c = 0$, then from equation (2-14), $\Delta T = a_0 + a_1 r + a_2 r^2 + \dots$, and the boundary condition (2-13) requires

$$a_1 = 0 \quad \text{and hence} \quad a_3 = 0 = a_5 = a_7 = \dots$$

so that $\Delta T = a_0 + a_2 r^2 + a_4 r^4 + \dots$

$$= a_0 \left[1 + \frac{1}{2^2} \left(\frac{8\epsilon\sigma T_{ER}^3}{Kh} \right) r^2 + \frac{1}{2^2} \frac{1}{4^2} \left(\frac{8\epsilon\sigma T_{ER}^3}{Kh} \right)^2 r^4 + \dots \right] \quad (2-15)$$

If $c = -1$, the boundary condition (2-13) leads to an expression identical to (2-15) except that a_0 is replaced by a_1 .

The required solution to equation (2-11) is therefore (2-15) which may be written

$$\Delta T = a_0 \left[1 + \sum_{n=1}^{\infty} \left(\frac{1}{n!} \right)^2 \left(\frac{2\epsilon\sigma T_{ER}^3}{Kh} \right)^n r^{2n} \right] \quad n = 1, 2, 3, \dots \quad (2-16)$$

with a_0 given by

$$r = R, \Delta T = T_F - T_{ER} \quad (2-17)$$

To obtain an idea of the magnitude of ΔT for each of the two designs of furnace and each of the substrates employed, appropriate figures will be taken for the quantities appearing in equations (2-16) and (2-17) :

Stefan's constant, σ	$= 0.567 \times 10^{-4} \text{ erg cm.}^{-2} \text{ }^{\circ}\text{K}^{-4} \text{ sec.}^{-1}$	
	$= \frac{0.567}{4.18} \times 10^{-11} \text{ cal. cm.}^{-2} \text{ }^{\circ}\text{K}^{-4} \text{ sec.}^{-1}$	
	Carbon	Silicon monoxide
Emissivity, e	0.95	0.70
Conductivity, K ($\text{cal. sec.}^{-1} \text{ }^{\circ}\text{K}^{-1} \text{ cm.}^{-1}$)	0.01	0.0026

(The figure taken for the thermal conductivity of silicon monoxide is that for fused silica.)

Let $T_F = 600^{\circ}\text{K}$, $T_C = 293^{\circ}\text{K}$, and $h = 200 \text{ \AA}$

The holes in the copper microscope grids on which the films were suspended were 0.010 cm. square, so take $R = 0.005 \text{ cm.}$

Making use of equations (2-6) and (2-7), the boundary condition (2-17) becomes for the first furnace

$$r = 0.005 \text{ cm.}, \Delta T = 13.8^{\circ}\text{K}$$

and for the second and third furnaces

$$r = 0.005 \text{ cm.}, \Delta T = 1.0^{\circ}\text{K}$$

Using subscripts 1 and 2,3 to denote the furnaces and superscripts C and SiO to denote the nature of the substrate, the expression (2-16) for ΔT becomes, in the four cases to be considered:

$$(\Delta T)_1^C = 7.83 \left| 1 + \sum_{n=1}^{\infty} \left(\frac{1}{n!} \right)^2 (2.597 \times 10^4)^n r^{2n} \right|$$

$$(\Delta T)_1^{\text{SiO}} = 3.56 \left| 1 + \sum_{n=1}^{\infty} \left(\frac{1}{n!} \right)^2 (7.356 \times 10^4)^n r^{2n} \right|$$

$$(\Delta T)_{2,3}^C = 0.55 \left| 1 + \sum_{n=1}^{\infty} \left(\frac{1}{n!} \right)^2 (2.770 \times 10^4)^n r^{2n} \right|$$

$$(\Delta T)_{2,3}^{\text{SiO}} = 0.24 \left| 1 + \sum_{n=1}^{\infty} \left(\frac{1}{n!} \right)^2 (7.849 \times 10^4)^n r^{2n} \right|$$

The approximate solutions of equation (2-8), in the four cases considered, may be written

$$T(r)_1^C = 586.2 + 7.8 \left| 1 + \sum_{n=1}^{\infty} \frac{(161r)^{2n}}{(n!)^2} \right| \quad (2-18)$$

$$T(r)_1^{SiO} = 586.2 + 3.6 \left| 1 + \sum_{n=1}^{\infty} \frac{(271r)^{2n}}{(n!)^2} \right| \quad (2-19)$$

$$T(r)_{2,3}^C = 599.0 + 0.5 \left| 1 + \sum_{n=1}^{\infty} \frac{(166r)^{2n}}{(n!)^2} \right| \quad (2-20)$$

$$T(r)_{2,3}^{SiO} = 599.0 + 0.2 \left| 1 + \sum_{n=1}^{\infty} \frac{(280r)^{2n}}{(n!)^2} \right| \quad (2-21)$$

In each of these last four equations, the first term on the R.H.S. represents the equilibrium temperature of an element of a film when only radiative heat exchange is considered. As can be seen (by putting $r = 0$) from equation (2-18), the actual temperature difference between the film and the furnace may be less than half that estimated when only radiative heat exchange is considered. The temperatures of a film in the first furnace, $(T_{ER})_1$ according to equation (2-6) and $T(r)_1^C$ according to equation (2-18), are shown in figure 9(b).

The calculations show that both conduction and radiation are important in determining the temperature of a thin film, and that it is impossible to estimate the temperature accurately without a knowledge of the thickness and emissivity of the film. It may be concluded that in order to minimise the uncertainty in the temperature of the film, the furnace should be designed so that the radiative-equilibrium temperature, T_{ER} , is as close as possible to the furnace temperature, T_F . It is thus desirable that the solid angle over which the film "sees" the walls of the diffraction camera should be very small.

(iii) Electron-beam heating

An experimental method was employed to ascertain the importance of beam heating in these experiments, and the findings are discussed in § 5.2.2.

The variation in temperature of a thin film under the influence of electron-beam heating has been examined by von Borries and Glaser (1943), Winkelmann (1956), and Gale and Hale (1961).

2.9.2 The three furnaces constructed

From the foregoing it is clear that a suitable furnace must have the following features:

- 1) The thin film should be able to "see" the diffraction camera over only a very small solid angle.
- 2) The thermal contact between the copper grid and the furnace should be good to minimise temperature differences between the grid and the furnace.
- 3) The temperature of all parts of the furnace "seen" by the film must be uniform and should be accurately measurable.

The first furnace constructed - see figure 8(a) - was such that the solid angle over which the film "saw" the diffraction camera was 1/10 of the total solid angle, yielding a radiative-equilibrium temperature some 14 °K below the furnace temperature at 600 °K as shown above. This meant that there was a comparatively large, unknown (temperature-dependent) difference in temperature between the film and the furnace. The specimen was held in a cylindrical cavity in the furnace by means of a press-fit cap which was later clamped: it is probable that the thermal contact between the copper microscope grid and the furnace was adequate, at least when the press-fit cap was clamped. The temperature of the furnace was measured by two thermocouples firmly clamped into the bottom of a 1 mm. diameter hole, and so placed as to be within 2 mm. of the specimen position. Continual checks were made to see that the thermocouples were firmly clamped into the hole, and further evidence of their good thermal contact with the furnace was provided by the identity of their readings. The copper and constantan wires used were extremely fine insulated wires and heat losses along the wires should have been small. However, it was found impossible to obtain even consistent results with this furnace (discounting the uncertainty in the absolute value of the temperature) in that apparently similar lead deposits consisting of fairly large crystallites (some 200 Å radius) showed melting temperature discrepancies

of some 15°K . It was also found that the thermocouples recorded lower melting temperatures, though still unreproducible, if the press-fit cap was clamped down, indicating that this reduced the temperature difference between the thermocouples and the deposit. The lack of reproducibility experienced with the first furnace probably arose from differences in temperature between the cap and the rest of the furnace. The press-fit cap had a large radiating area in the form of a lip - see figure 8(a) - and the whole furnace was constructed in stainless steel, a relatively poor conductor of heat.

The second furnace constructed was identical in design to that finally used - see figures 2 and 8(b) - but was in stainless steel. The solid angle of camera "seen" by the film was cut down to $7/1000$ of the total solid angle, yielding a radiative-equilibrium temperature only 1°K below the furnace temperature at 600°K . A screw cap was introduced and the bottom of the cap was shaped - as shown in figure 2(d) - to "bite" the copper grid, thus ensuring good thermal contact between the copper grid and the furnace. The possibility of the cap being at a different temperature from the rest of the furnace was minimised by having a large area of screw thread in firm contact with the furnace block, and reducing the area of the cap from which heat is lost by radiation. There were two thermocouples (of fine copper and constantan wire) "hard soldered" into holes close to the specimen position, and separated by a distance of 0.7 cm . It was found that on heating the furnace to 600°K , a temperature difference of 15°K developed between these two thermocouples under conditions of thermal equilibrium; and that a rate of heating of 10°K per minute produced an additional difference of 1.5°K . The calculations below substantiate these findings. The furnace was therefore regarded as unsuitable in that feature 3) enumerated above was not realised.

The third furnace constructed, which was the one used for the experiments described here, was made entirely from "spec.-pure" copper. As described in § 2.3 above, thermocouple I registered a slightly greater temperature than thermocouple II, which difference was independent of the rates of heating employed during the experiments, and depended solely on the temperature of the furnace, becoming noticeable at about 400°K and increasing to some 1.5°K at 600°K . Insofar as features 2) and 3) above

were realised for this furnace, equations (2-20) and (2-21) show that the temperature of a thin film should differ from the recorded furnace temperature by less than 1°K .

It can be shown that under the conditions prevailing in the present experiments, latent-heat losses arising from the evaporation of the metallic deposits are negligible compared with the quantities of heat exchanged by radiation and conduction.

The findings indicated above concerning differences between the temperatures registered by thermocouples I and II may be understood semi-quantitatively in terms of a simplified model, in which the second and third furnaces are represented as solid blocks heated from one end, PQRS, as shown in figure 10:

We first estimate the temperature differences to be expected between thermocouples I and II when the second and third furnaces are maintained in thermal equilibrium at 600°K . Suppose the temperature, T_{II} , at the position of thermocouple II is 600°K , and that the temperature, T_I , at the position of thermocouple I does not differ from this by more than a few degrees. The net heat lost from the surfaces of the block above the section ABCD is, neglecting radiative heat gains, approximately

$$e(1.3 \times 0.7 + 2 \times 1.3 \times 0.2 + 2 \times 0.7 \times 0.2)\sigma T_{II}^4$$

where e is the emissivity of the surface

and σ is Stefan's constant.

In equilibrium, this must be equal to the heat conducted upwards through the section ABCD, and assuming that the temperature gradient, $\frac{dT}{dz}$, is uniform over the section ABCD, we obtain

$$\left(\frac{dT}{dz}\right)_{ABCD} = - \frac{e(1.3 \times 0.7 + 2 \times 1.3 \times 0.2 + 2 \times 0.7 \times 0.2)\sigma T_{II}^4}{K \times 1.3 \times 0.7}$$

where K is the thermal conductivity of the block.

Similarly, in equilibrium, the temperature gradient over the section EFGH, assumed uniform, is approximately

$$\left(\frac{dT}{dz}\right)_{EFGH} = - \frac{e(1.3 \times 0.7 + 2 \times 1.3 \times 0.9 + 2 \times 0.7 \times 0.9)\sigma T_{II}^4}{K \times 1.3 \times 0.7}$$

Taking $T_{II} - T_I$ to be equal to the average value of these temperature gradients multiplied by the separation (0.7 cm.) of the thermocouples in the z-direction, we obtain

$$T_I - T_{II} = \frac{3.11}{1.3} \frac{e\sigma}{K} 600^4 \quad (2-22)$$

Using the following values for the physical constants appearing in equation (2-22):

Stefan's constant, $\sigma = 5.67 \times 10^{-12}$ joule cm.⁻² °K⁻⁴ sec.⁻¹

	stainless steel	copper
thermal conductivity, K (watts cm. ⁻¹ °K ⁻¹)	0.15	3.89
emissivity, e	0.8	0.8

we find, for the second furnace: $T_I - T_{II} = 9.4$ °K

and for the third furnace: $T_I - T_{II} = 0.36$ °K

We secondly estimate the temperature differences to be expected between thermocouples I and II when the temperatures of the furnaces are increasing at a rate of ω °K per minute. Under these circumstances, the heat absorbed by the metal lying above a section mid-way between ABCD and EFGH is

$$(1.3 \times 0.7 \times 0.55)\rho C \frac{\omega}{60} \text{ cal. sec.}^{-1}$$

where ρ is the density of the metal in gm. cm.⁻³

and C is its specific heat in cal. °K⁻¹ gm.⁻¹

Assuming that the temperature gradient, $\frac{dT}{dz}$, is uniform over the section considered, and ignoring radiative heat losses, we obtain

$$\frac{dT}{dz} = - \frac{1}{K \times 1.3 \times 0.7} \times (1.3 \times 0.7 \times 0.55)\rho C \frac{\omega}{60} \text{ °K cm.}^{-1}$$

so that, approximately,

$$T_I - T_{II} = \frac{1}{156} \frac{\rho C}{K} \omega \text{ °K} \quad (2-23)$$

Using the following values for the physical constants appearing in equation (2-23):

	stainless steel	copper
density, ρ (gm. cm. ⁻³)	7.81	8.93
specific heat, C (cal. °K ⁻¹ gm. ⁻¹)	0.13	0.098
thermal conductivity, K (cal. sec. ⁻¹ cm. ⁻¹ °K ⁻¹)	0.036	0.931

when $\omega = 10$ (°K per minute), then
for the second furnace:

$$T_I - T_{II} = 1.81 \text{ } ^\circ\text{K}$$

and for the third furnace: $T_I - T_{II} = 0.060 \text{ } ^\circ\text{K}$

The agreement between the figures estimated and those observed may be regarded as satisfactory in view of the approximate nature of the calculations.

CHAPTER 3

DETAILS OF EXPERIMENTAL PROCEDURES

3.1 Preparation of the substrate films

The vacuum deposits of lead, bismuth and indium, whose melting and solidification temperatures were determined, were made onto thin, continuous films of carbon or silicon monoxide supported by copper electron microscope grids.

The silicon monoxide films were prepared as follows: 3 mgm. of silicon monoxide (the "Select Grade" manufactured by "Kemet") were evaporated upwards from a cylindrical filament onto cleaved mica surfaces at a distance of 12 cm. The evaporation was carried out in a conventional evaporation plant at a pressure of some 4×10^{-5} torr, and with the filament at a yellowish-red heat (the optimum temperature for the evaporation is some 1200°C - see Holland (1956), pg. 487). A number of 3.05 mm. diameter, copper microscope grids were placed with the polished side of each grid uppermost on a piece of copper mesh immersed beneath the surface of distilled water in a petry dish, and a silicon monoxide film was "floated off" from the mica substrate onto the surface of the water by immersing the mica obliquely. The mesh was raised, thus supporting film across the mesh and grids, and covered until dry. The grids were afterwards transferred to numbered positions in dust-proof boxes for storage.

Carbon films were prepared by the deposition, under vacuum, of carbon - from a carbon arc between "spec.-pure" carbon electrodes - onto cleaved mica surfaces at a distance of 14 cm. Short current pulses (from a relay) were passed through the carbon electrodes, so that by counting the number of pulses, the same thickness of film could always be produced. Carbon substrates were prepared from the films as described above.

The thicknesses of both the carbon and silicon monoxide films obtained in this (controlled) way should not have varied appreciably over the course of the experiments, and were the minimum which would withstand the effects of the electron beam in the electron microscope without breaking up. By keeping the thicknesses of the substrates to a minimum, it

was found possible to detect the sharp-ring, electron-diffraction patterns of crystalline deposits having mean thicknesses of as little as $1 \text{ \AA}$ against the diffuse, "halo" patterns produced by the amorphous carbon and silicon monoxide films. However, with these very thin deposits, only the halo patterns could be seen on examining the fluorescent screen and so the success or otherwise of an attempt to determine the melting point was not known until after the photographic record had been examined.

3.2 Determination of the melting temperature

In the course of each determination of the melting and solidification temperatures of a metallic deposit the following operations were performed:

- (i) A chip of the metal being investigated was cut from a "spec.-pure" rod to the required weight, and was melted into a small, shiny bead on one of the two tungsten filaments described in § 2.6. This was done in the evaporating chamber of the electron diffraction camera, at a pressure of some 2×10^{-5} torr and with the axis of the filament vertical, by raising the temperature of the filament to a dull-red heat and allowing it to cool immediately. Time was allowed for the filament to become quite cold, and dry nitrogen was admitted into the camera.
- (ii) A copper grid with a substrate film suspended on it was then inserted into the cylinder of the furnace with the substrate film uppermost (i.e. with the polished side of the grid uppermost - c.f. § 3.1) and the furnace cap was screwed down onto the grid until just tight. The axis of the evaporating filament was set horizontal and the axis of the furnace aligned with it as described in § 2.4. The orientation of the specimen manipulator (as registered by the pointer) was noted, so that the alignment could later be reproduced perfectly when the camera was under vacuum - see (vii) below.
- (iii) The camera was pumped down with several feet of photographic recording film in the film chamber, wound loosely to allow the free escape of water vapour from the emulsion, to a pressure of 5×10^{-6} torr. The pressure was monitored throughout the experiment and did not change appreciably on heating the furnace. As the removal of water vapour from the film required some eight hours of pumping with liquid nitrogen in the

large vapour trap above the diffusion pump, it was found convenient to pump overnight on sufficient film for two or three melting point determinations. The film was maintained dry by admitting only dry nitrogen into the camera between experiments: this reduced the pumping time required to attain 5×10^{-6} torr to only 1 or 2 hours.

(iv) The specimen manipulator was rotated to align the axis of the substrate with the electron beam, and three diffraction patterns of the substrate were taken. The appearance of any sharp rings on these patterns would indicate contamination of the substrate prior to the experiment, but in general only the diffuse halos of the substrate were to be seen.

(v) The cold junctions of the three copper-constantan thermocouples - see § 2.3 - were surrounded with a mixture of pure melting ice and water, and it was checked that the reading of thermocouple III was consistent with room temperature. At this stage thermocouples I and II always read identically and registered a temperature close to room temperature.

(vi) The furnace was heated to some 350°C to evaporate any volatile impurities from the surface of the substrate.

(vii) After cooling to the required temperature for the evaporation, the specimen manipulator was rotated into the orientation previously noted (see (ii) above) to bring the substrate axis into coincidence with the evaporating filament. The "cold-finger" vapour trap in the specimen chamber was filled with liquid oxygen in order to further reduce the partial pressure of water vapour in the neighbourhood of the specimen, and thus to reduce oxidation during and after the formation of the metallic deposit. The evaporation of the whole of the investigated material was then achieved rapidly by passing a fixed current through the tungsten filament which attained a steady white heat very quickly. During the evaporation, the residual pressure in the camera (5×10^{-6} torr or better, as registered on the Penning gauge) was observed, and usually there was no visible change. If the evaporation was made with the substrate at a temperature above room temperature, the substrate and deposit were afterwards cooled to room temperature (or below) using the cooling device described in § 2.5.

(viii) The electron beam was switched on and stabilised at about 5×10^{-9} amp., and the supply current registered by the H.T. generator

was noted. This current was monitored throughout the melting, and provided a sensitive check on the constancy of the beam current. The furnace axis was aligned with the beam, and the diffraction pattern photographed. The pressure was noted.

(ix) The furnace was heated until the crystalline ring pattern (initially clearly visible on the fluorescent screen for all but the thinnest films) had almost disappeared - indicating that a large part of the deposit was molten and giving rise only to the diffuse halos characteristic of the liquid metal. Photographs were then taken at temperature increments of either 2.4°C or 1.2°C , the current to the furnace heater being adjusted to give a convenient, steady rate of heating of some 3°C per minute or 1.5°C per minute, respectively. The larger temperature increment and faster rate of heating were used when a depression of the melting point of more than about 20°C was expected. The length of each exposure was normally 30 sec. Thermocouple I was used to measure these temperatures, but two or three checks of the "simultaneous readings" (observed in quick succession) of thermocouples I, II, and III were made. Photographs were taken until it was thought that the ring pattern from the crystalline material should have completely disappeared; the pressure was then noted and the beam current measured - see § 2.2.

(x) If the solidification temperature was to be determined, the furnace was allowed to cool naturally, photographs being taken at intervals of 13°C in most cases. Otherwise, to minimise oxidation, the furnace was cooled rapidly to room temperature or below, using the cooling device described in § 2.5.

(xi) The diffraction pattern of the solidified deposit was photographed at room temperature.

(xii) In cases where more than one determination of the melting temperature of a particular deposit was to be made, the operations described from (ix) to (xi) were repeated.

3.3 The admission of hydrogen

Having in mind the possibility of the reduction of any surface layer of oxide on the metallic crystallites, the influence of a small partial pressure of hydrogen on the melting and solidification

temperatures of metallic deposits was investigated.

The hydrogen used was supplied in a 1 litre flask as "Grade X" by the British Oxygen Co. Ltd. Several hours before an experiment, a small quantity was released from the flask into a pyrex U-tube which had previously been evacuated by direct connection to the camera. The U-tube was surrounded by liquid nitrogen, and the hydrogen left to dry. The pure, dry hydrogen was admitted into the specimen chamber of the camera through a needle valve, prior to the formation of a deposit by evaporation; and the pressure was maintained constant to within 10 % for the duration of the experiment. The pressures of hydrogen employed (as registered on the Penning gauge) were between twice and ten times the pressure of the residual gases in the camera. Larger pressures were not tried, because of the possibility of a temperature difference developing between the deposit and the furnace as a consequence of the conduction of heat by the hydrogen.

3.4 Superposition of the electron diffraction patterns obtained from a metallic deposit when it is wholly crystalline and when it is wholly liquid

The diffraction patterns from a metallic deposit (and its substrate) when the deposit was wholly crystalline and from the same deposit when it was wholly molten, were superposed in various proportions on photographic emulsion, in order to find the proportion in which the crystalline, sharp-ring pattern could only just be detected on the developed plate. In order to interpret the melting experiments, this proportion was taken to be equal to the proportion by weight of solid crystallites in a partially-molten deposit of the same mean thickness when the crystalline pattern could only just be detected. A full discussion of this interpretation is given in § 4.4.

In the course of each determination of the proportion of the crystalline pattern which could just be detected in superposition with the liquid pattern from the same deposit, the following operations were performed (for details of the apparatus see § 2.7) :

- (i) As in (i) of § 3.2
- (ii) As in (ii) of § 3.2

(a) Exposure times and beam currents chosen prior to the experiment:

	Solid pattern exposure		Liquid pattern exposure		Exposure to solid pattern as a % of the total exposure
	Exposure time (secs.)	Amplified * beam current (μ A)	Exposure time (secs.)	Amplified * beam current (μ A)	
Plate 1	0.125	25	~ 25 (24.97)	100	~ 0.125 (0.125)
Plate 2	0.25	25	~ 25 (24.94)	100	~ 0.25 (0.25)
Plate 3	0.125	100	~ 25 (24.88)	100	~ 0.50 (0.50)
Plate 4	0.25	100	~ 25 (24.75)	100	~ 1.00 (1.00)
Plate 5	0.75	100	~ 25 (24.25)	100	~ 3.00 (3.00)

(b) Actual experimental record:

Exposure to solid pattern						Exposure to solid pattern as a % of the total exposure
	Before exposure Unipivot "zero reading" (μ A)	Amplified beam current * (μ A)	Exposure time** as registered on counter (secs.)	After exposure Amplified beam current * (μ A)	Unipivot "zero reading" (μ A)	
Plate 1	0	$24\frac{1}{2}$	0.123	25	0	0.120
Plate 2	1	25	0.251	25	0	0.246
Plate 3	$\frac{1}{2}$	$99\frac{1}{2}$	0.122	$99\frac{1}{2}$	1	0.467
Plate 4	0	99	0.252	100	0	0.985
Plate 5	0	101	0.759	100	0	2.88
Exposure to liquid pattern						
Plate 1	$\frac{1}{2}$	99	24.96	97	0	
Plate 2	0	99	24.94	98	1	
Plate 3	1	100	24.90	100	1	
Plate 4	3	101	24.94	103	3	
Plate 5	1	103	24.80	104	0	

* As registered on Unipivot: $100 \mu\text{A} \equiv$ an electron beam current of $0.0057 \mu\text{A}$ - see § 2.7.

** Note that 0.005 secs. must be subtracted from the times shown, to obtain the actual exposure times - see § 2.7.

Table 1. Data from a superposition experiment

- (iii) Five Kodak N50 quarter plates were mounted in the plate holder in the electron-diffraction camera, and the camera was pumped down for several hours with liquid nitrogen in the large vapour trap above the diffusion pump until a pressure of 5×10^{-6} torr was attained.
- (iv) As in (v) of § 3.2, or sometimes the cold junctions of the three thermocouples were immersed in water at room temperature.
- (v) As in (vi) of § 3.2
- (vi) The particular exposure times to be used were chosen - see table 1(a) - and preset as described in § 2.7.
- (vii) As in (vii) of § 3.2
- (viii) The electron beam was switched on, the furnace axis was aligned with the beam, and the beam was centred on the specimen. The set zero of the Pye amplifier was adjusted so that the Unipivot galvanometer registering the output read zero. The current to the deflecting coils was switched on, and the position of the Faraday cage adjusted so that the electron beam fell centrally into the Faraday cage. The temperature of the furnace (room temperature or below), as recorded on thermocouple I, was noted.
- (ix) The resistor and capacitor appropriate to the first exposure time were switched into the transistor biasing circuit. The electron beam was stabilised so that the Unipivot galvanometer read 100 μ A (or sometimes 33 μ A, 25 μ A, 20 μ A) corresponding to a beam current of 0.0057 μ A.
- The deflecting current was switched off, the centring of the electron beam on the specimen checked, and the "zero reading" of the Unipivot galvanometer noted (some small departure from zero was often noticable as a result of amplifier drift). The deflecting current was switched on again, the fluorescent screen raised, the beam current as registered on the Unipivot noted, and the switch S - see figure 5 - thrown to make the first exposure. After the exposure the beam current was noted, the fluorescent screen lowered, and the time registered on the counter recorded. The deflecting current was switched off, the "zero reading" of the Unipivot noted, and the beam centring checked. The next photographic plate was rotated into the exposure position.
- (x) The operations described in (ix) were repeated until all the five plates had been exposed - typical data are shown in table 1(b).

(xi) The furnace was heated to somewhat above the melting point of the bulk metal: the heater current was adjusted to maintain a constant temperature, and the temperature noted. Each of the five plates was exposed a second time (to the diffraction pattern from the wholly-molten deposit) using the same procedure as in (ix) - typical data are shown in table 1(b).

In some instances, the photographic plates were first exposed to the diffraction pattern from the wholly-molten deposit, and then (after cooling the deposit again) to the diffraction pattern from the wholly-crystalline deposit.

3.5 Observation of the crystallites

After examining the melting and solidification of a deposit, or after a superposition experiment, the specimen was transferred as quickly as possible to the J.E.M.-6A electron microscope to be photographed.

In mounting the specimen in the electron microscope care was taken to see that its distance from the objective lens was always the same. Throughout the experiments an accelerating voltage of 80 kV was employed. The intermediate lens current was always set to the same value for each micrograph, and then cycled from zero to this value four times so as to arrive at a definite point in the hysteresis cycle of the lens. In this way the micrographs were taken at a reproducible magnification, and this magnification (approximately $\times 50,000$ on the plate) was determined periodically using the method described by Skinner (1967, 1969).

Several micrographs (usually eight) were taken of each deposit, and these were equally spaced over the whole circular area (1 mm. in diameter) covered by the deposit. For each deposit two, three or four (usually three) of these micrographs, well spaced out, were chosen and enlargements of these were printed on 15" x 12", Grade IV, "Kodak" bromide paper. The enlargements were made at linear magnifications of precisely $\times 16$, $\times 10$, $\times 8$, or $\times 6$ (corresponding to overall magnifications of approximately 800,000; 500,000; etc.), the smaller magnifications being used for the deposits having the larger crystallites.

3.6 Measurement of the crystallite sizes

The images of the crystallites on the enlargements (see § 3.5) were measured using one or other of two transparent, perspex stencils. One stencil, manufactured by Faber-Castell, had a series of circular holes drilled in it with diameters (nominally) from 1 to 35 mm. in 1 mm. intervals. The other stencil, used only to measure the deposits consisting of very small crystallites, was specially prepared, and had a series of circular holes with diameters (nominally) from 1 to 16 mm. in $\frac{1}{2}$ mm. intervals. The mean of two perpendicular diameters was found for each hole, from measurements taken with a travelling microscope: these means were used in all calculations.

On each enlargement a continuous thin red line was drawn backwards and forwards, so as to join together all of the crystallites visible; the order in which the crystallites were joined being unimportant, so long as the line passed only once through each crystallite. The size of each crystallite was then measured in turn, by moving along the line with one of the stencils, and the sizes were recorded immediately on a tape recorder. The recording was then played back, and a histogram of the crystallite diameters was constructed directly by recording each size in the appropriate column. The above methods were found to be extremely valuable in reducing the strain involved in making measurements on some 200,000 individual crystallites.

CHAPTER 4

EXPERIMENTAL DATA OBTAINED.

4.1 Size and volume distributions of the crystallites in the deposits and the mean thicknesses of the deposits

Some typical micrographs of metallic deposits whose melting was observed are shown in figures 11 to 18. Histograms showing the size distributions, $n(R)$, of the crystallites of these specimens and obtained as indicated in § 3.6, are shown in figures 11(a) to 18(a).

Each of these histograms is the sum of two, three or four histograms representing the distribution of crystallites on two, three or four equal, but widely separated, areas of the deposit. To illustrate this, two other widely separated areas of the deposit shown in figure 15 are shown in figure 19, and histograms of the size distributions of the crystallites on these three areas taken separately are shown in figure 19(a). The sum of these three histograms is the histogram shown in figure 15(a). Except in a few instances, the histograms obtained from different areas of the same specimen were very similar.

As can be seen from the micrographs, most of the crystallites appear circular when viewed perpendicular to the substrate. However, by breaking the substrate carrying the deposit, before its insertion into the electron microscope, in such a way as to produce folds, it was possible to observe the profiles of the crystallites viewed parallel to the substrate. For those crystallites sufficiently large for their profiles to be clearly seen (those greater than some $100 \text{ \AA}$ radius), it was found that (at room temperature) the forms of the profiles of both large and small crystallites of the same material were similar. The profiles suggested that the crystallites approximated to segments of spheres, with the flat surfaces on the substrate. This wetting of the substrate by the metals, producing cap-like structures, is discussed further and illustrated in § 5.3. It is assumed here that the crystallites approximate to segments of spheres having a constant contact angle with the substrate independent of the crystallite size and dependent only on the particular metal and substrate employed.

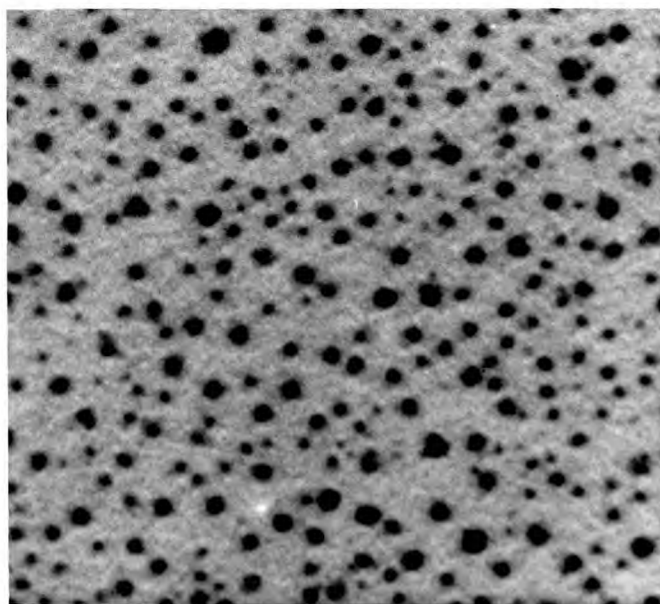


Figure 11. Electron micrograph ($\times 400,000$) of a lead deposit (on silicon monoxide) of nominal mean thickness $2.15 \text{ \AA}$.

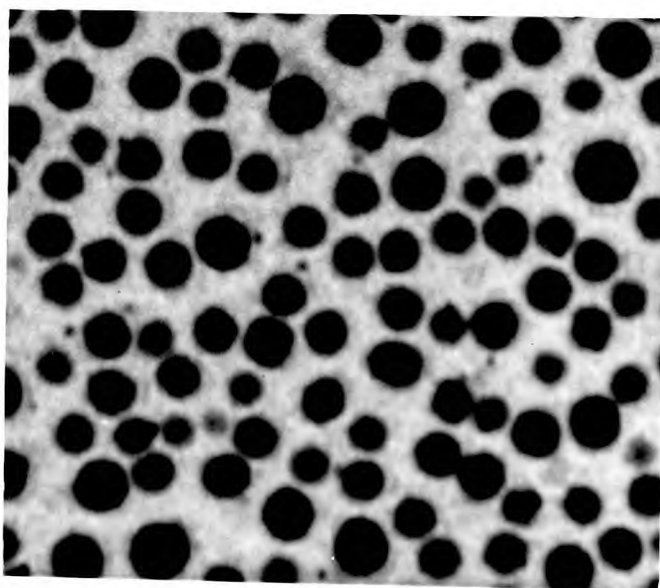


Figure 12. Electron micrograph ($\times 400,000$) of a lead deposit (on carbon) of nominal mean thickness $28.7 \text{ \AA}$.

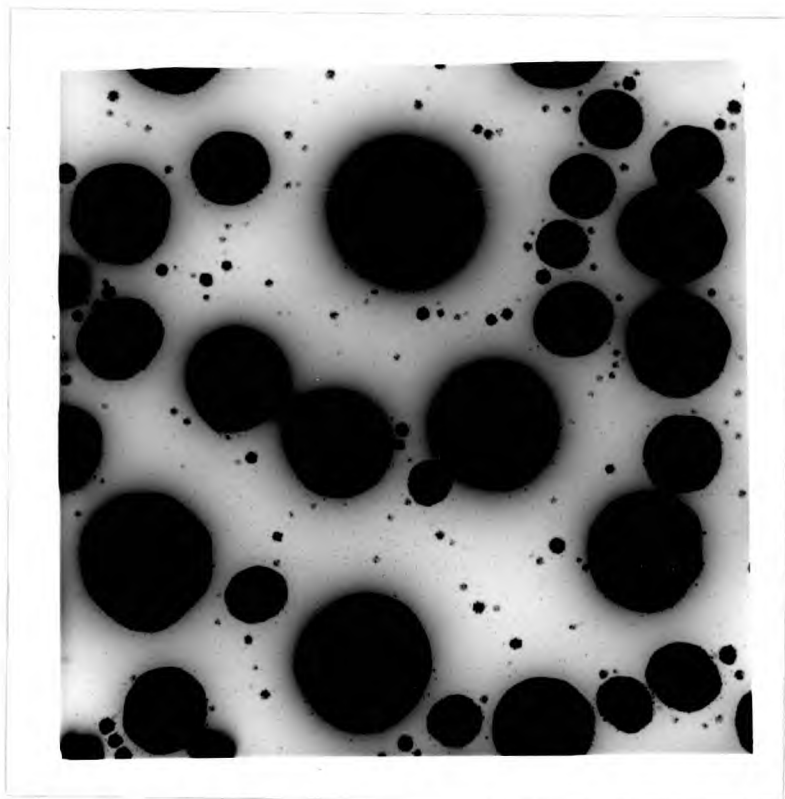


Figure 13. Electron micrograph ($\times 100,000$) of a lead deposit (on carbon) of nominal mean thickness $325 \text{ \AA}$.

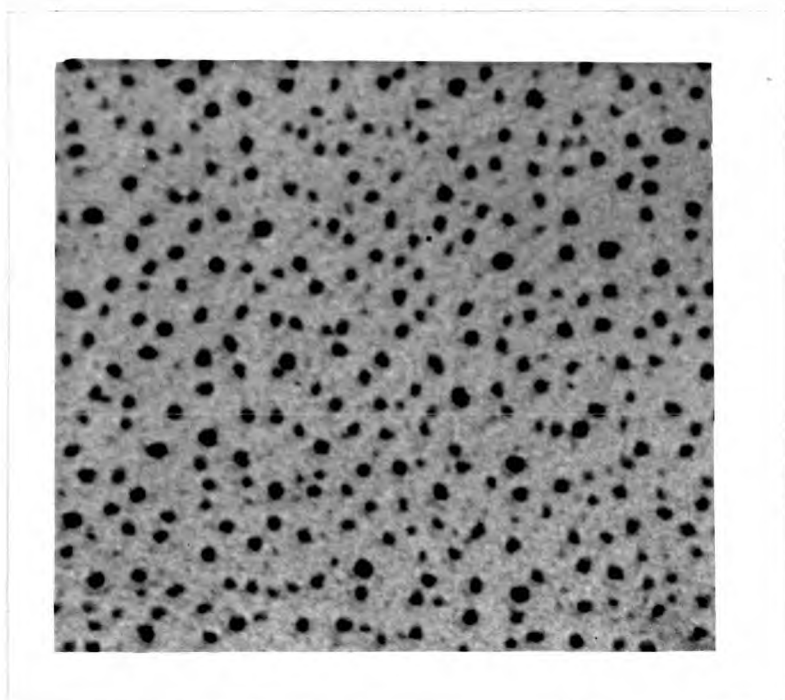


Figure 14. Electron micrograph ($\times 400,000$) of a bismuth deposit (on carbon) of nominal mean thickness $1.61 \text{ \AA}$.

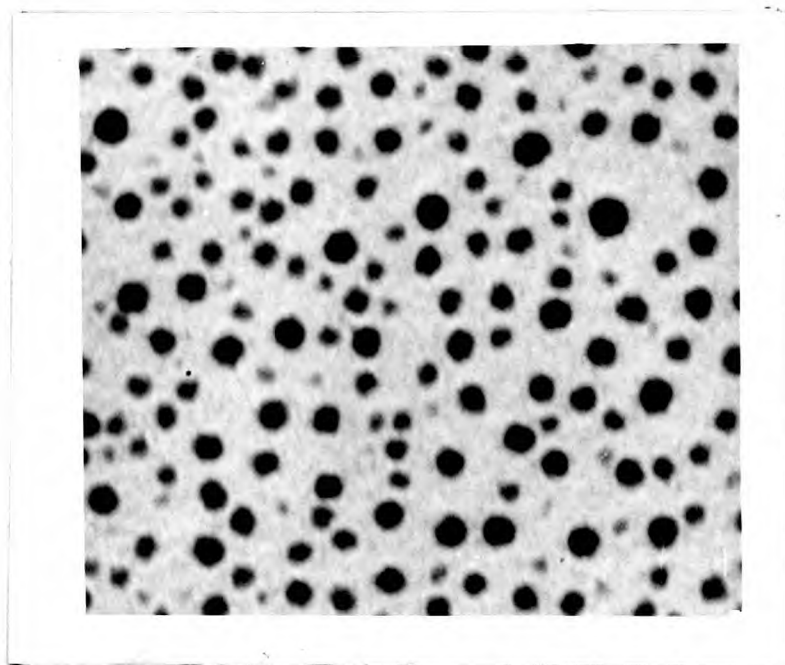


Figure 15. Electron micrograph ($\times 400,000$) of a bismuth deposit (on carbon) of nominal mean thickness $7.71 \text{ \AA}$.

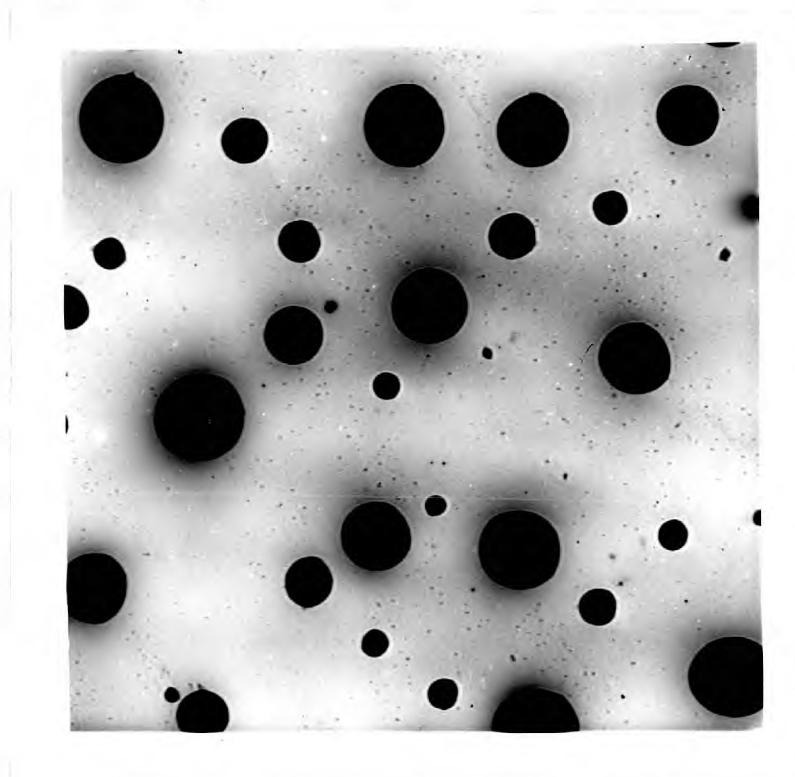


Figure 16. Electron micrograph ($\times 100,000$) of a bismuth deposit (on carbon) of nominal mean thickness $75.6 \text{ \AA}$.

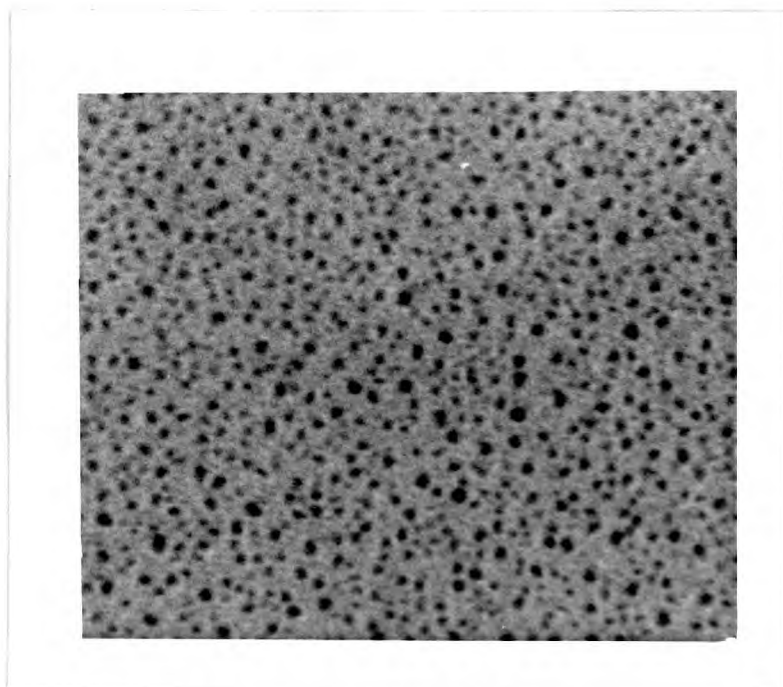


Figure 17. Electron micrograph ($\times 400,000$) of an indium deposit (on carbon) of nominal mean thickness $1.13 \text{ \AA}$.

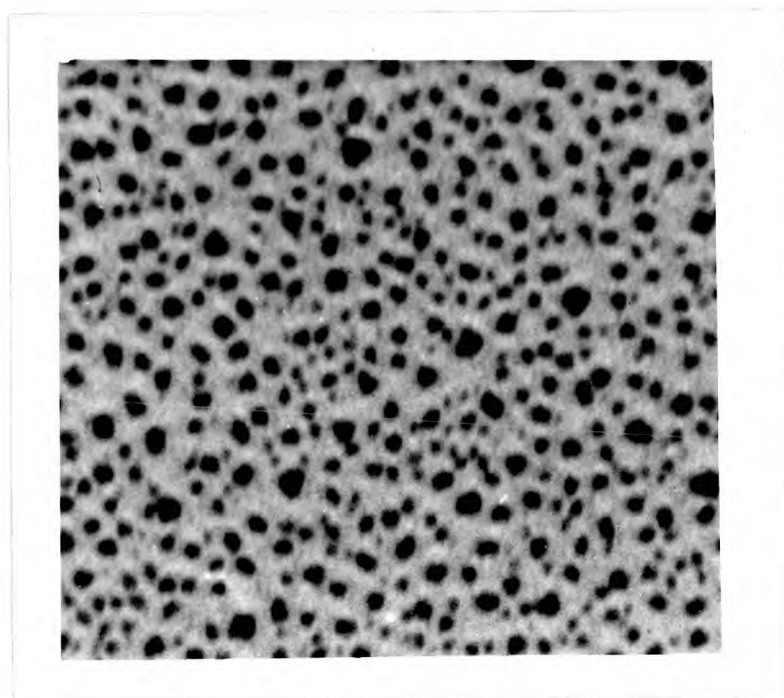


Figure 18. Electron micrograph ($\times 400,000$) of an indium deposit (on carbon) of nominal mean thickness $3.82 \text{ \AA}$.

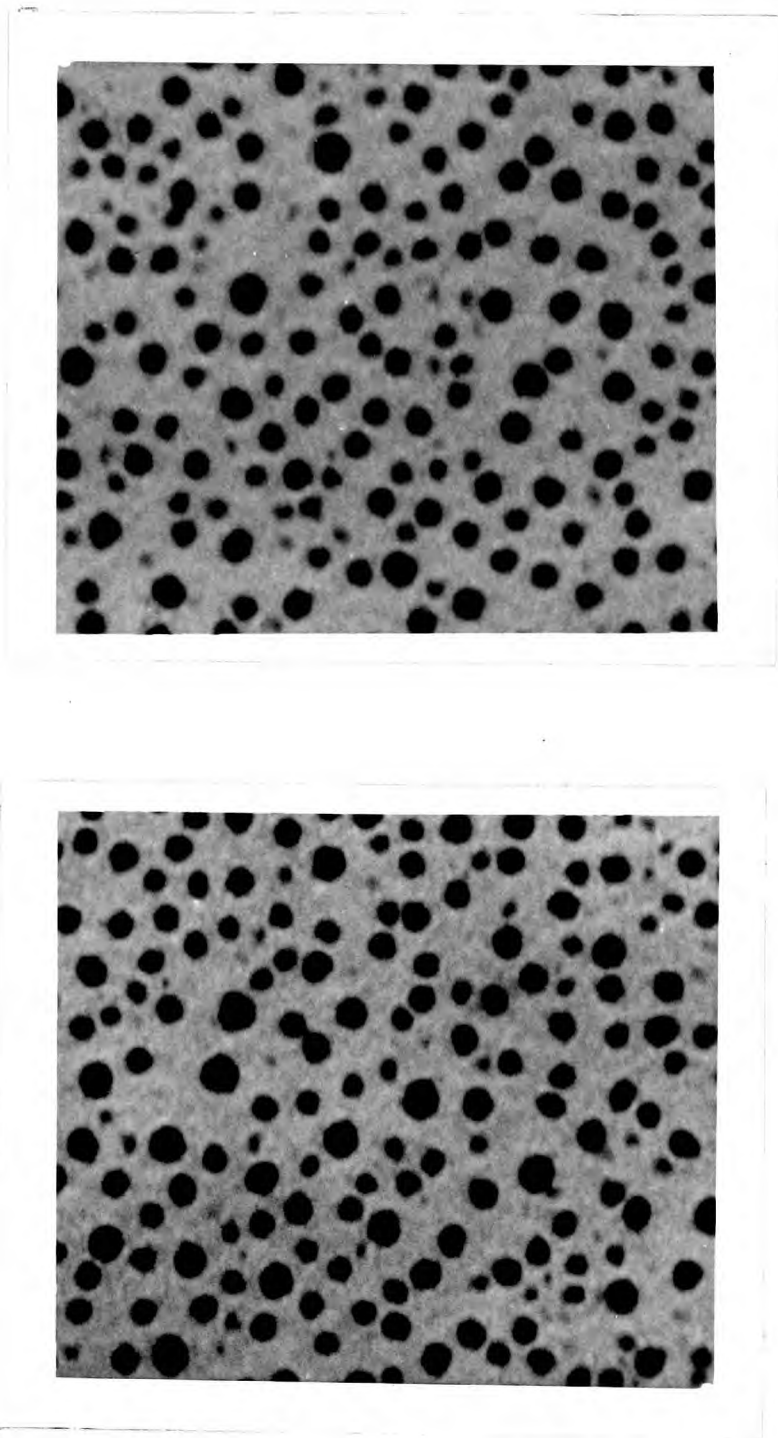


Figure 19. Electron micrographs ($\times 400,000$) of two other widely separated areas of the deposit shown in figure 15.

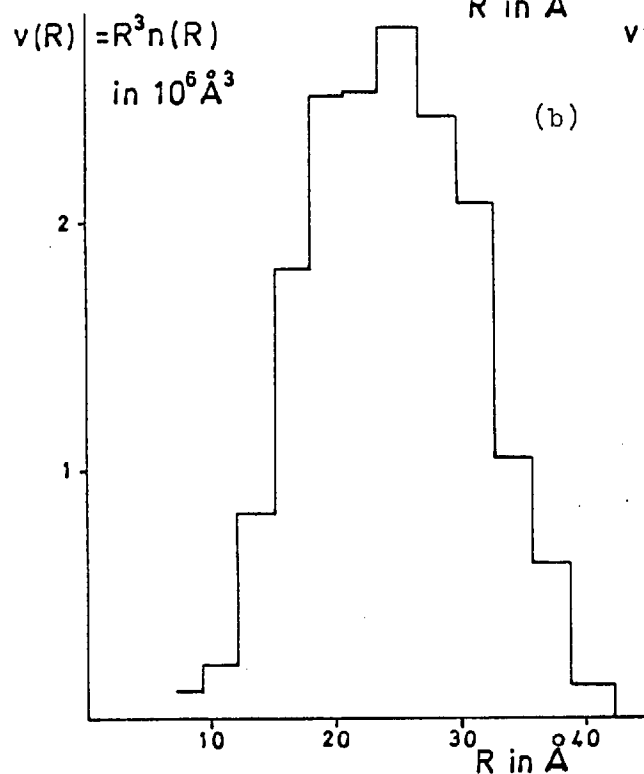
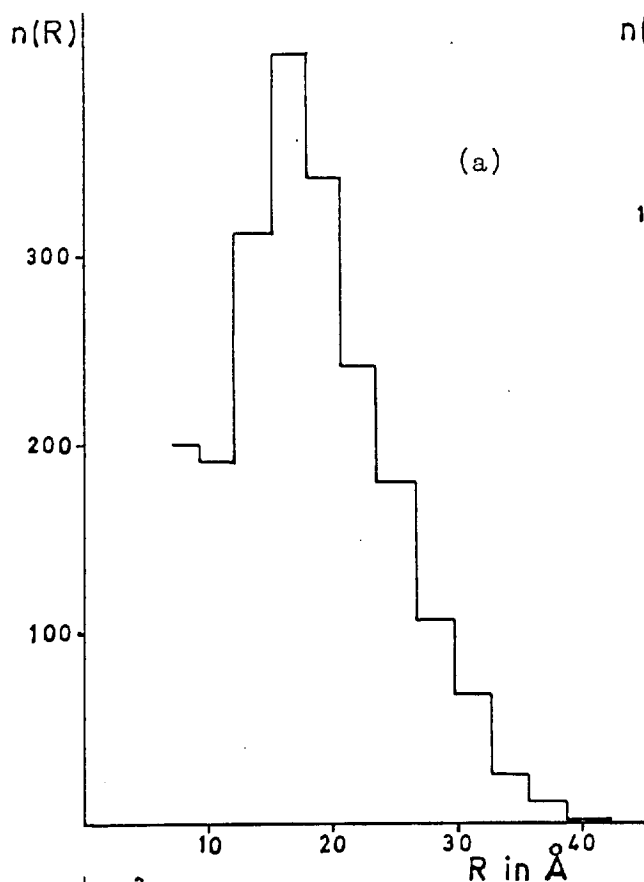


Figure 11 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $33.3 \times 10^6 \text{ Å}^2$ area of the deposit shown in figure 11.

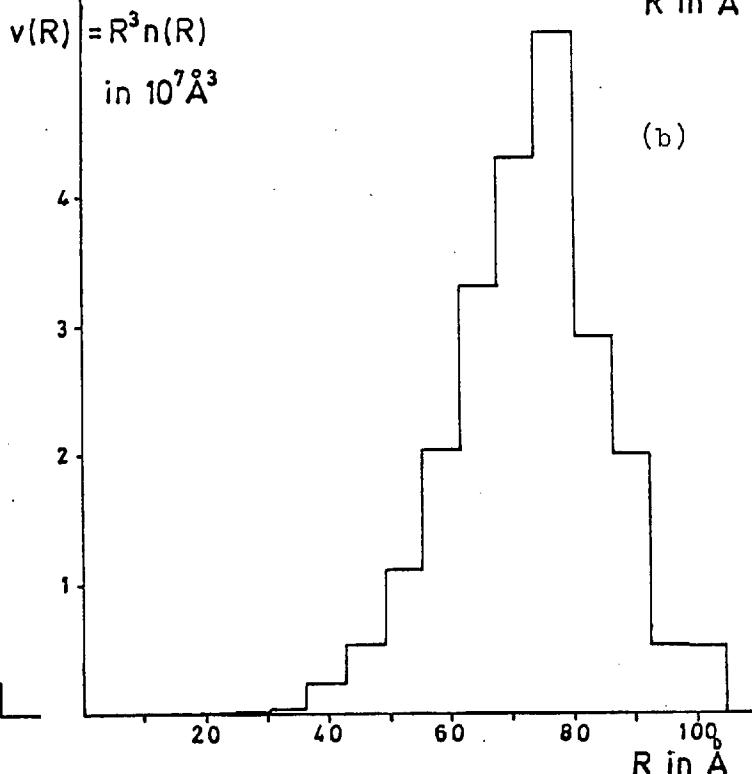
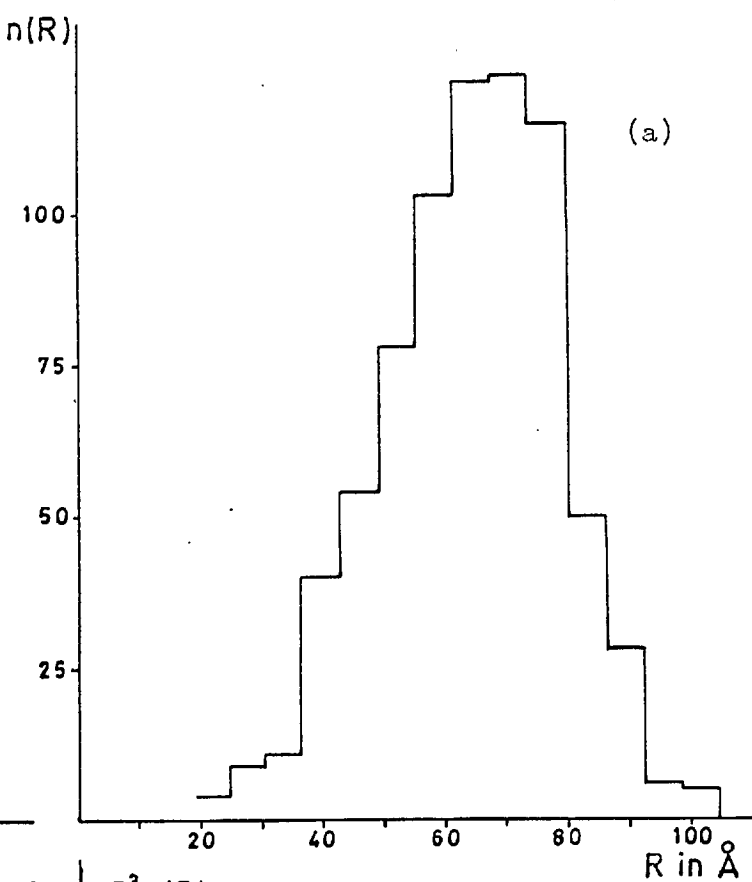


Figure 12 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $33.3 \times 10^6 \text{ Å}^2$ area of the deposit shown in figure 12.

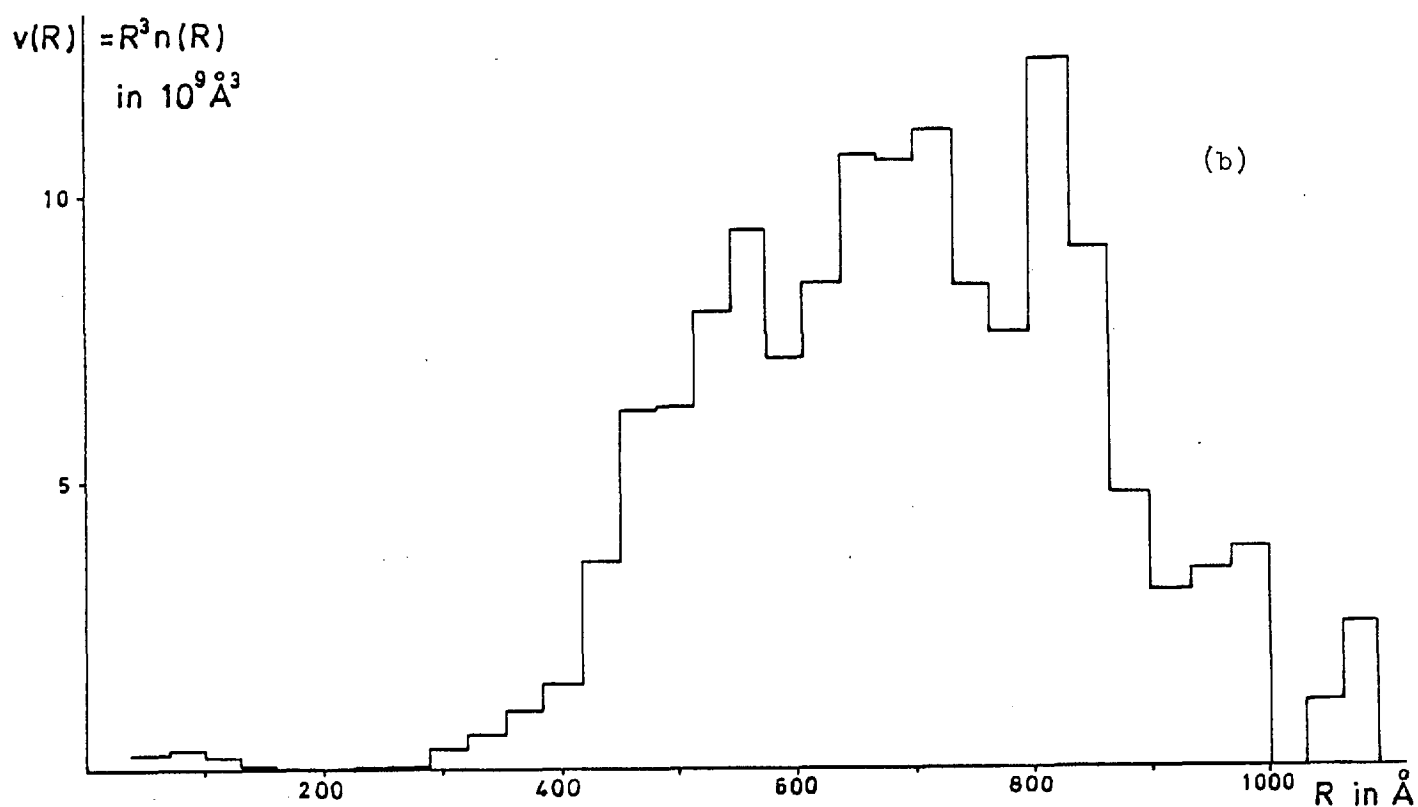
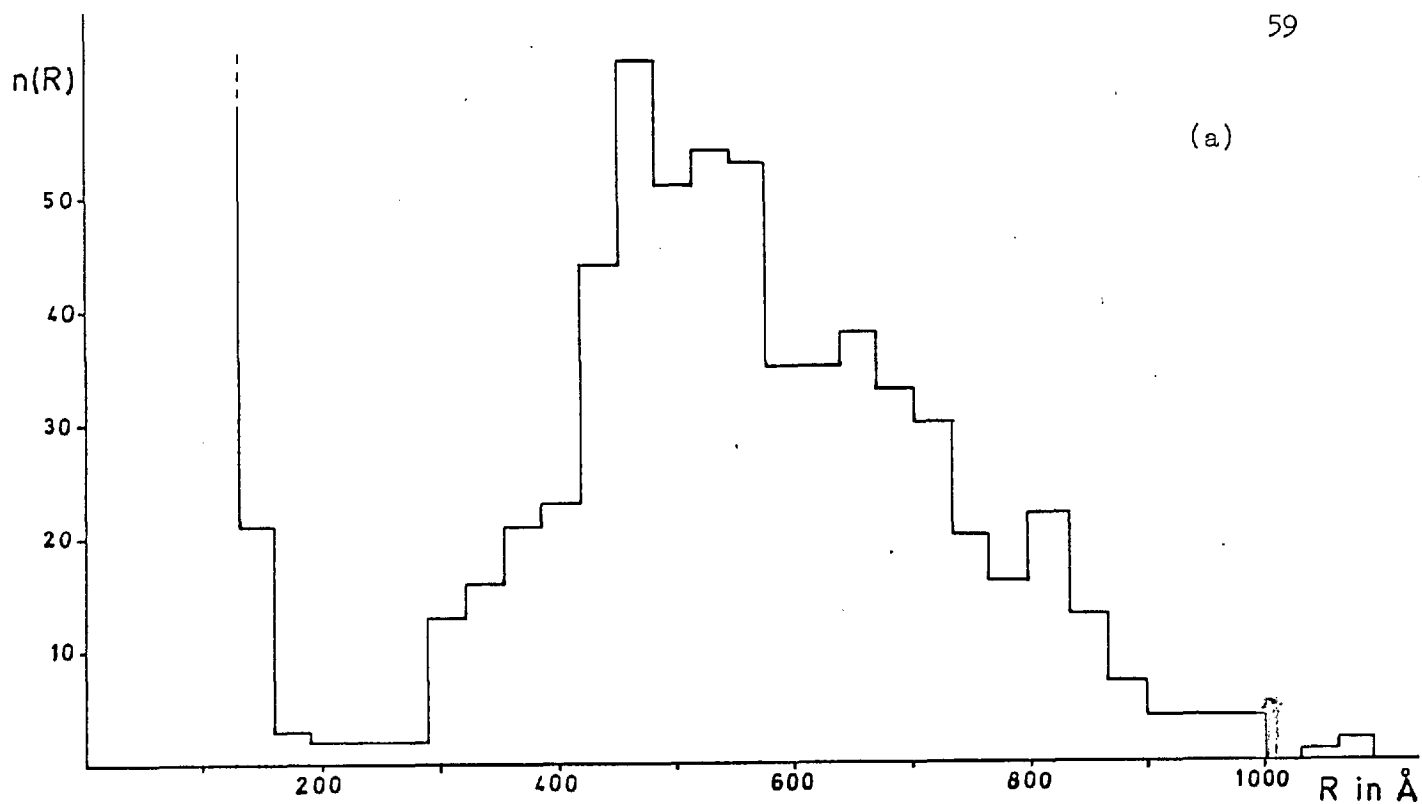


Figure 13 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $18.2 \times 10^8 \text{\AA}^2$ area of the deposit shown in figure 13.

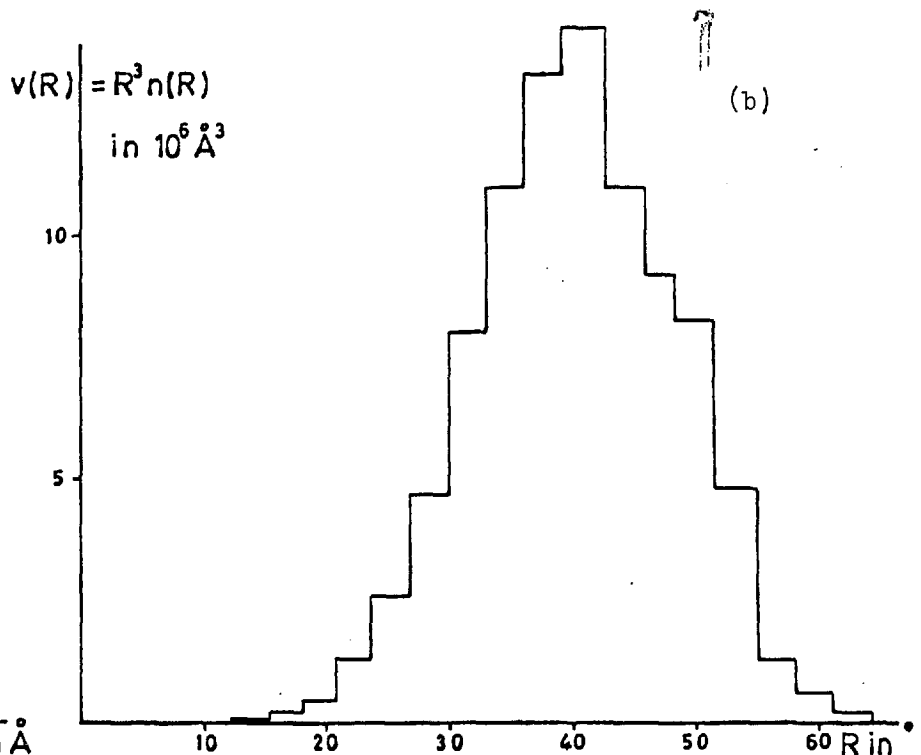
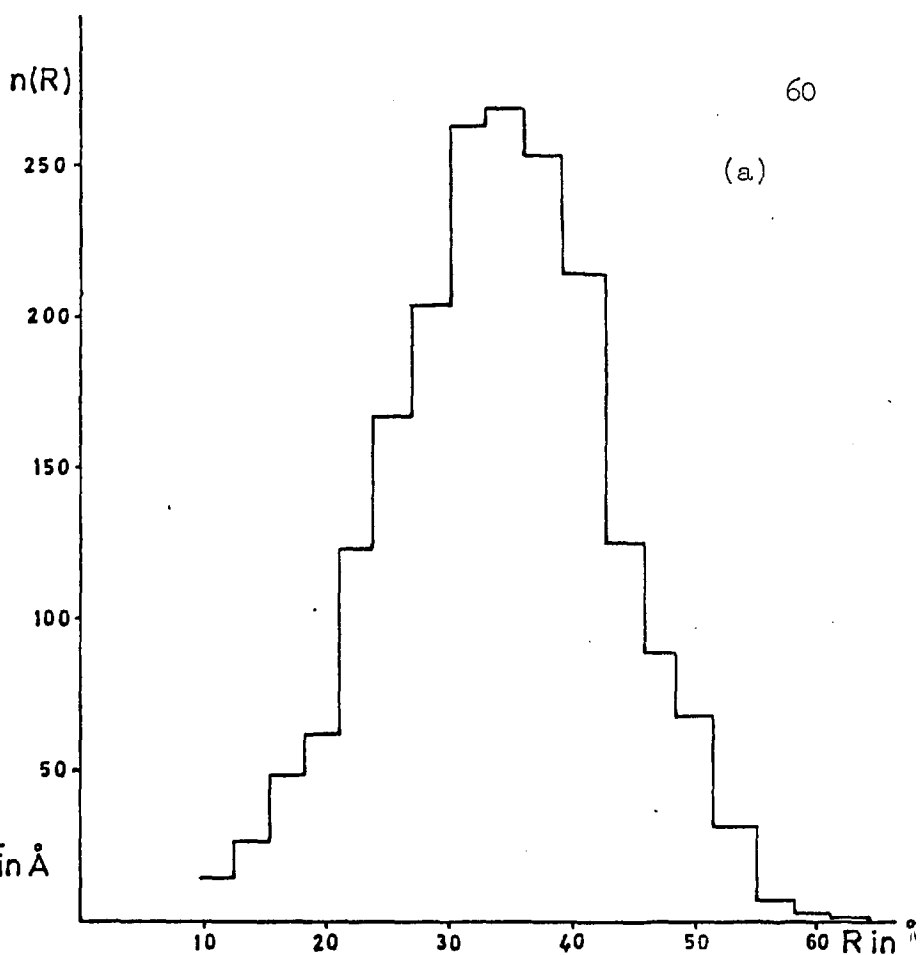
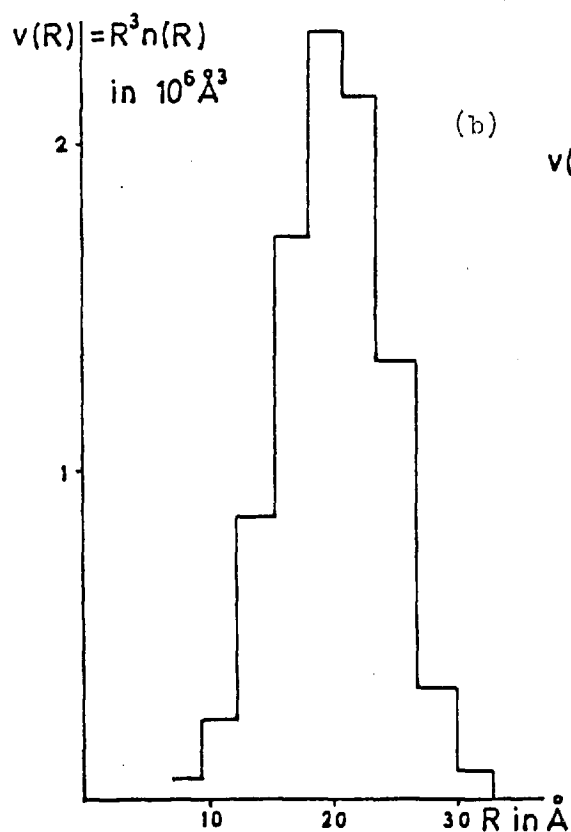
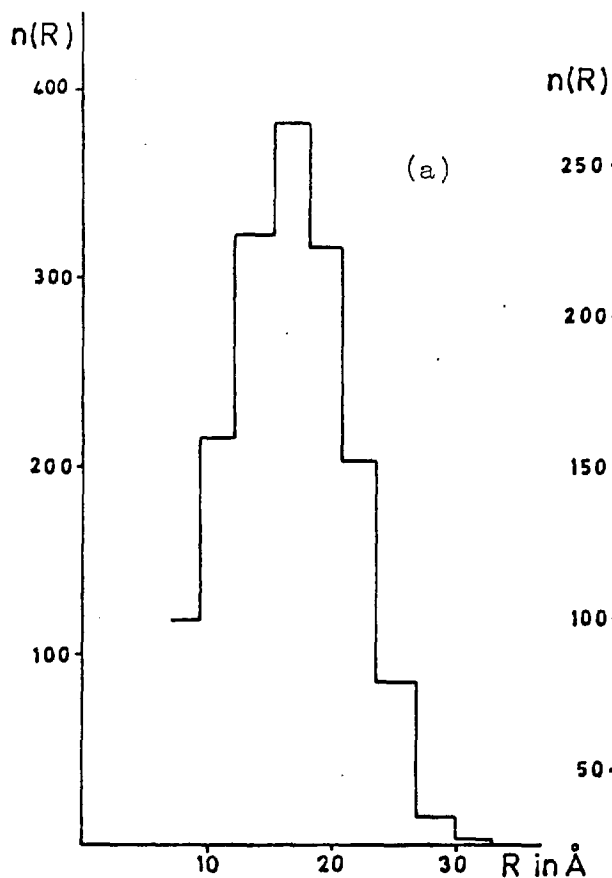


Figure 14 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $23.8 \times 10^6 \text{ Å}^2$ area of the deposit shown in figure 14.

Figure 15 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $49.8 \times 10^6 \text{ Å}^2$ area of the deposit shown in figure 15.

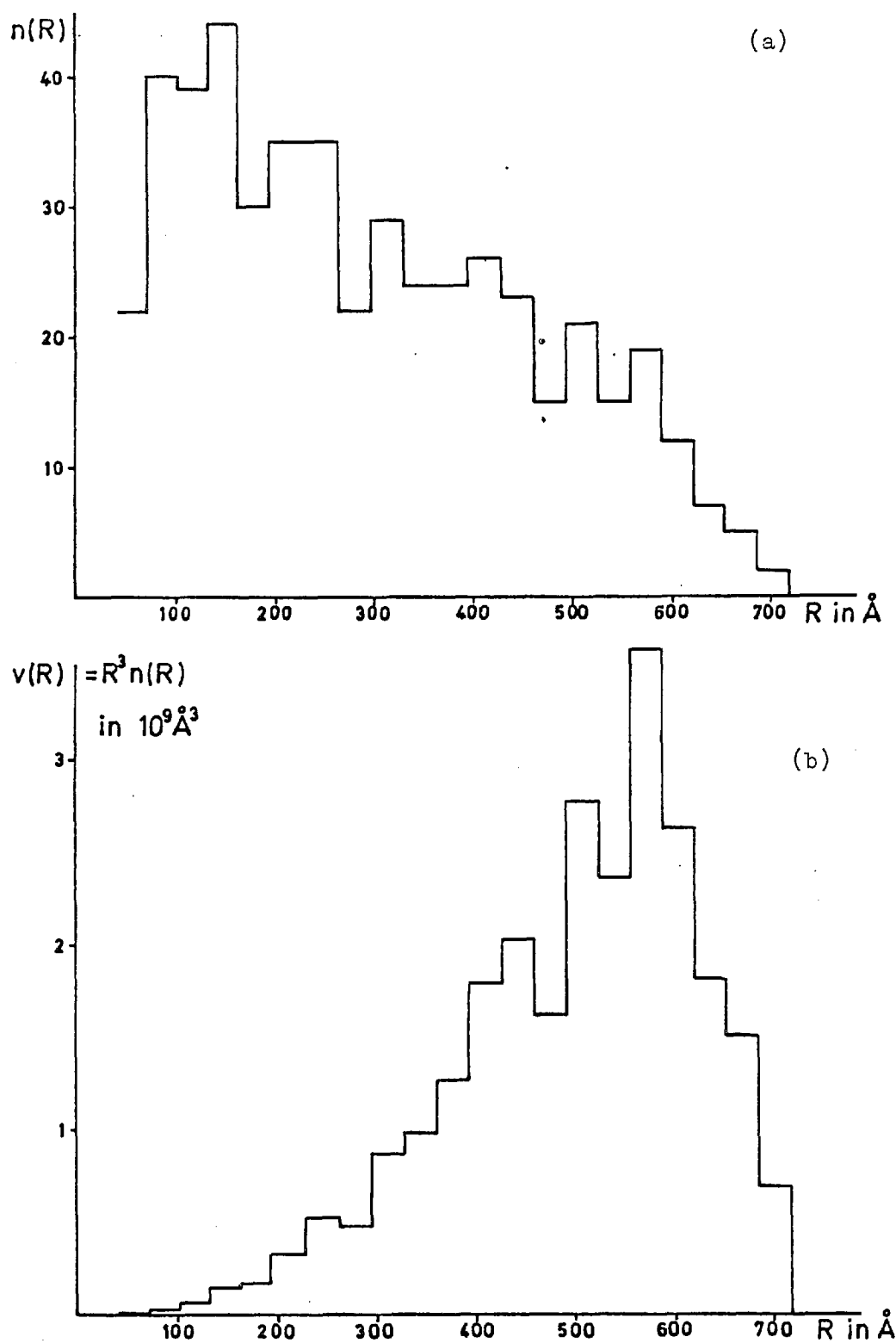


Figure 16 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $14.2 \times 10^8 \text{\AA}^2$ area of the deposit shown in figure 16.

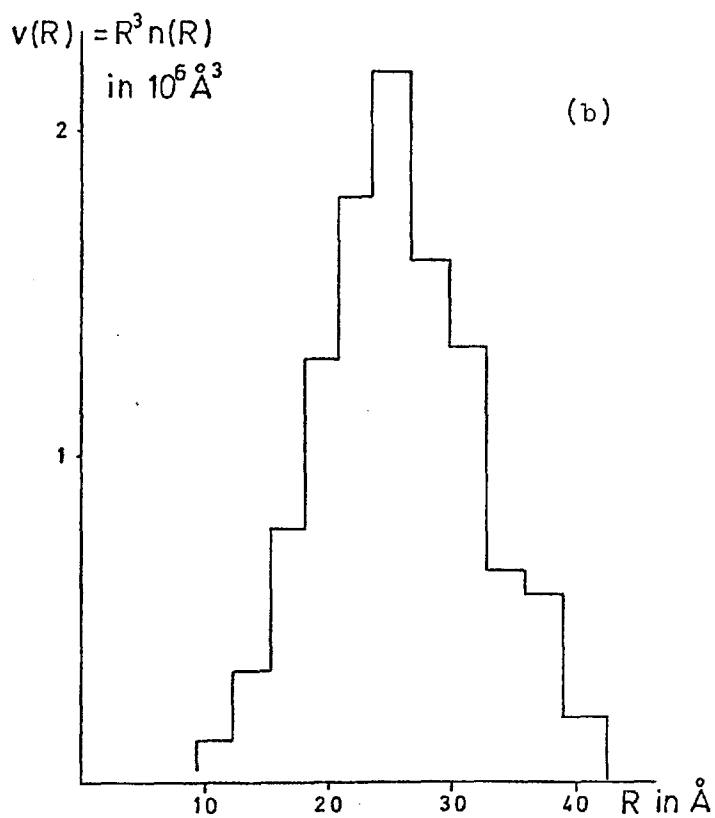
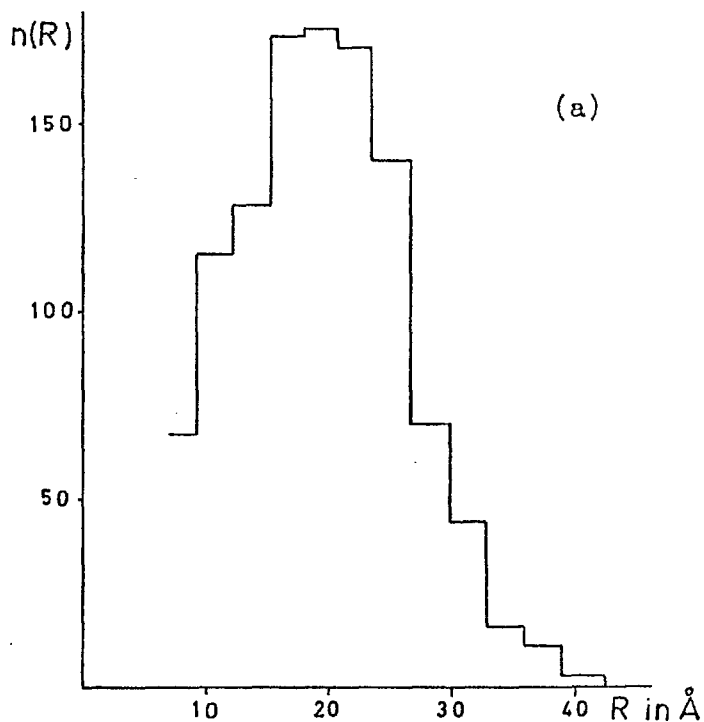
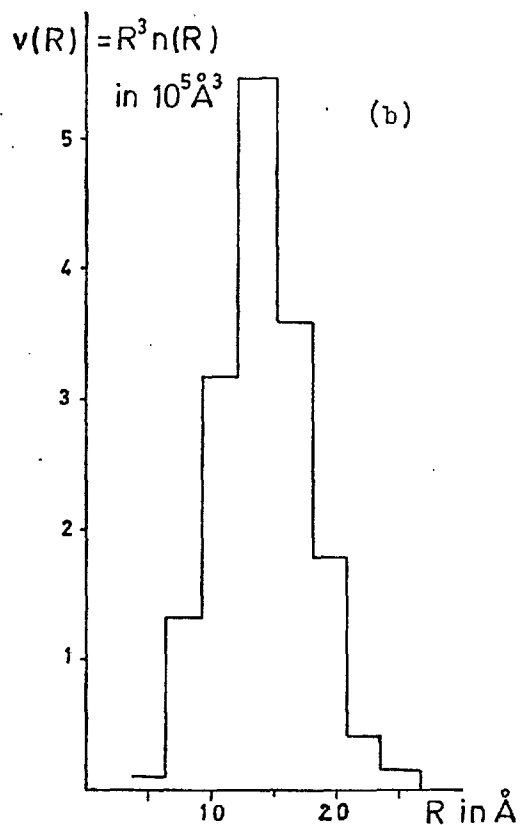
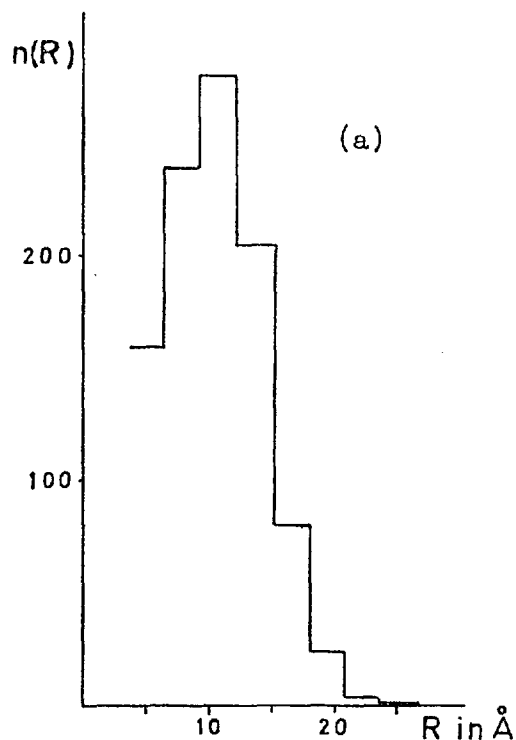


Figure 17 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $5.95 \times 10^6 \text{ Å}^2$ area of the deposit shown in figure 17.

Figure 18 (a) and (b). Histograms of the size distribution, $n(R)$, and volume distribution, $v(R)$, of the crystals from a $12.0 \times 10^6 \text{ Å}^2$ area of the deposit shown in figure 18.

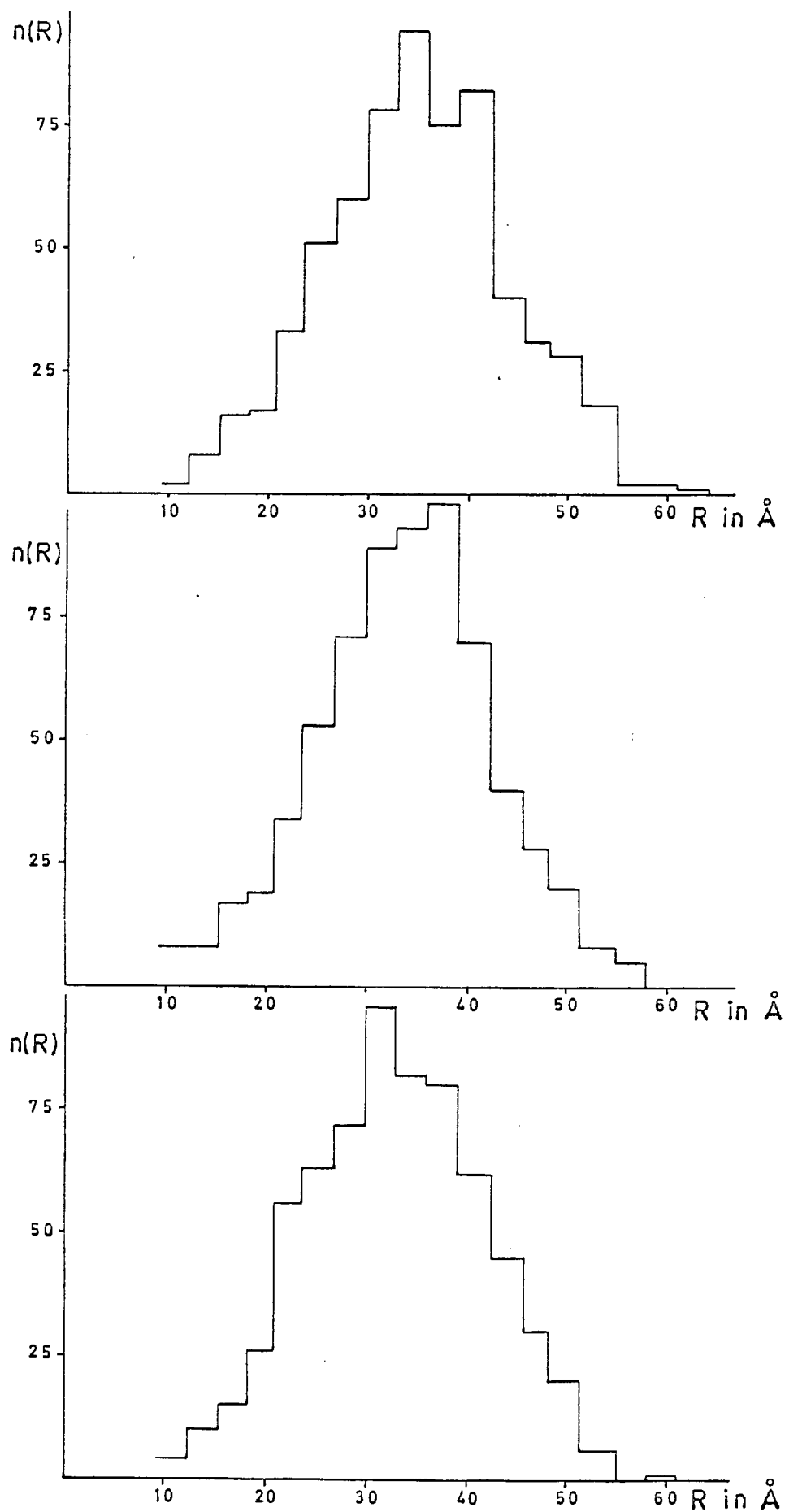


Figure 19(a). The size distributions, $n(R)$, of the crystals from three, widely-separated, equal areas (each of $16.6 \times 10^6 \text{\AA}^2$) of a bismuth deposit. Portions of these three areas are shown in figures 15 and 19, and the sum of the three histograms is the histogram shown in figure 15(a).

For the combinations of materials investigated it was found experimentally that a contact angle, $\theta > 90^\circ$ was appropriate. For such a spherical, cap-shaped crystallite having contact angle, θ , with the substrate - see figure 20 -

$$\begin{aligned} h &= R + R \sin(\theta - 90^\circ) \\ &= R(1 - \cos \theta) \end{aligned}$$

so that the volume of the cap is

$$\pi h^2 \left(R - \frac{h}{3}\right) = \frac{\pi}{3} R^3 (1 - \cos \theta)^2 (2 + \cos \theta)$$

where R is the observed radius of the crystallite when viewed perpendicular to the substrate.

Consider a size-distribution histogram of all the crystallites occupying an area A of a metallic deposit, the number of crystallites having a radius equal to R (within the limits of one interval of the histogram) being $n(R)$. Then the distribution function

$$V(R) = kR^3 n(R) \quad (4-1)$$

where $k = \frac{\pi}{3} (1 - \cos \theta)^2 (2 + \cos \theta) \quad (4-2)$

is a histogram representing the volume distribution of the crystallites. Further the total volume of all the crystallites is

$$\sum_{R=0}^{\infty} kR^3 n(R)$$

and therefore the mean thickness of the deposit is

$$\frac{k}{A} \sum_{R=0}^{\infty} R^3 n(R)$$

In the particular case when the contact-angle $\theta = 180^\circ$ (no wetting), so that the crystallites are spherical, then $k = \frac{4\pi}{3}$.

From each size-distribution histogram, $n(R)$, a histogram

$$v(R) = R^3 n(R) \quad (4-3)$$

which is proportional to the actual volume distribution, was computed. In

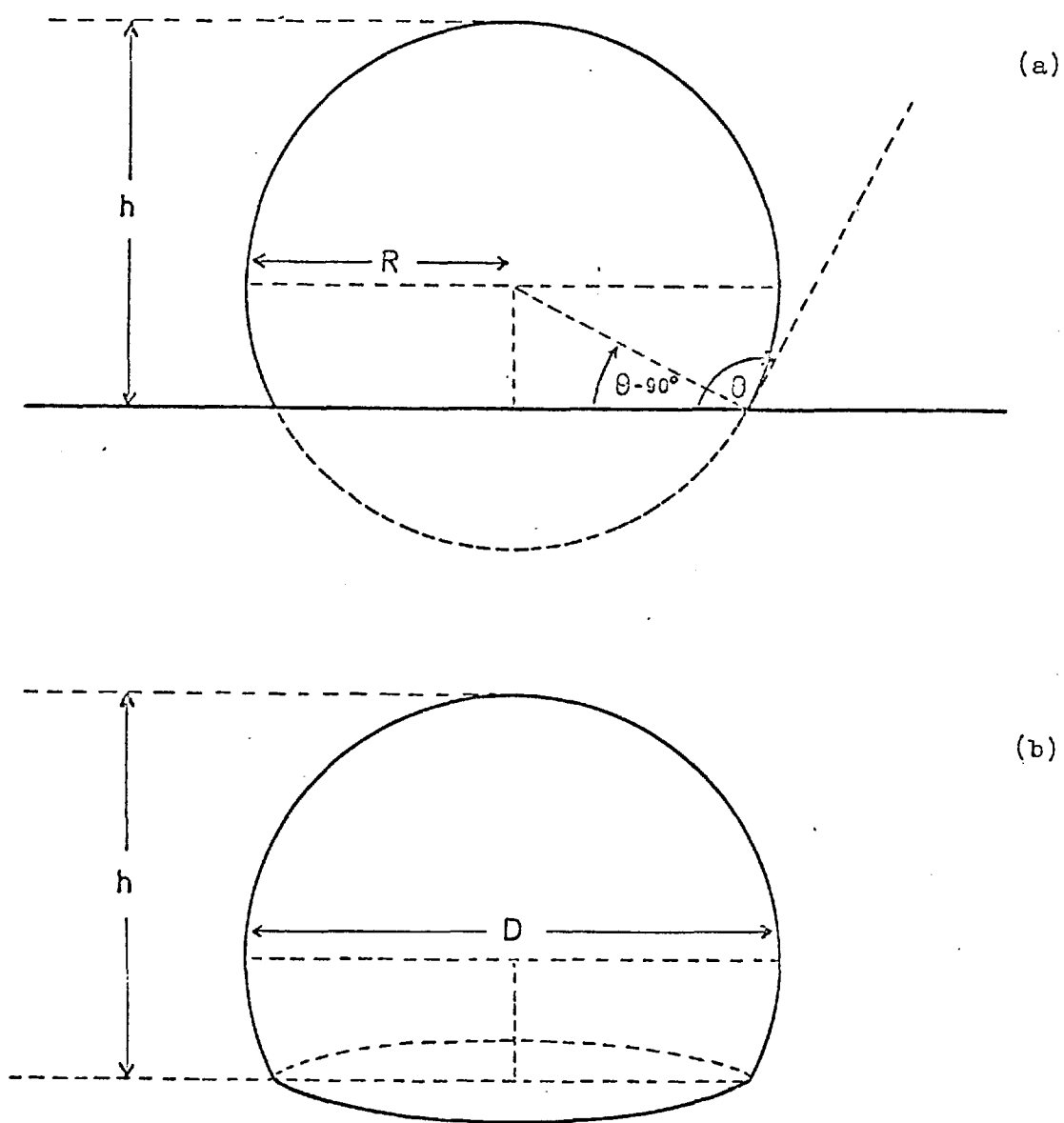


Figure 20 (a) and (b). A spherical, cap-shaped crystallite having contact angle θ ($> 90^\circ$) with the substrate

addition the area A was determined accurately, and the quantity

$$z = \frac{4\pi}{3} \frac{1}{A} \int_{R=0}^{\infty} R^3 n(R) \quad (4-4)$$

was calculated. This last quantity, which will be referred to as the "nominal mean thickness", represents the mean thickness of the deposit on the assumption that the crystallites were spherical.

The size distribution, $n(R)$, volume distribution, $v(R)$, and nominal mean thickness, z , were found for every deposit whose melting was observed or on which superposition experiments were made. The distributions $v(R)$ computed from the histograms of figures 11(a) to 18(a) are shown in figures 11(b) to 18(b).

4.2 The melting and solidification temperatures

The amorphous carbon and silicon monoxide films, used as substrates, gave rise to diffuse, "halo", electron-diffraction patterns - see figure 21. Immediately after deposition onto a substrate at (or in some instances below) room temperature, each of the three metals investigated in these experiments - lead, bismuth and indium - gave rise to a sharp-ring, electron-diffraction pattern characteristic of a randomly-oriented, polycrystalline deposit - see figures 22(a) to 26(a). Every experiment in which the melting and solidification of a metallic deposit were observed yielded a photographic record, which consisted of a series of electron-diffraction patterns of the deposit (and its substrate) taken at small increments of temperature during heating and cooling.

On heating a deposit, the sharp-ring pattern gradually gave way to a diffuse, "halo" pattern as the deposit melted. However, the rings visible in the initial pattern did not all disappear at the same time: in general, the "high index" (large radius) rings disappeared first, and before the crystalline pattern disappeared altogether, only one or two of the rings in the original pattern could be detected. The disappearance of these last rings was used as the criterion of the melting of the deposit. The photographic record was examined and two patterns were chosen, one of which was the last pattern on which a ring (or rings) of the crystalline pattern could be detected, and the other (in many instances the same pattern) was the first pattern which could be distinguished from the

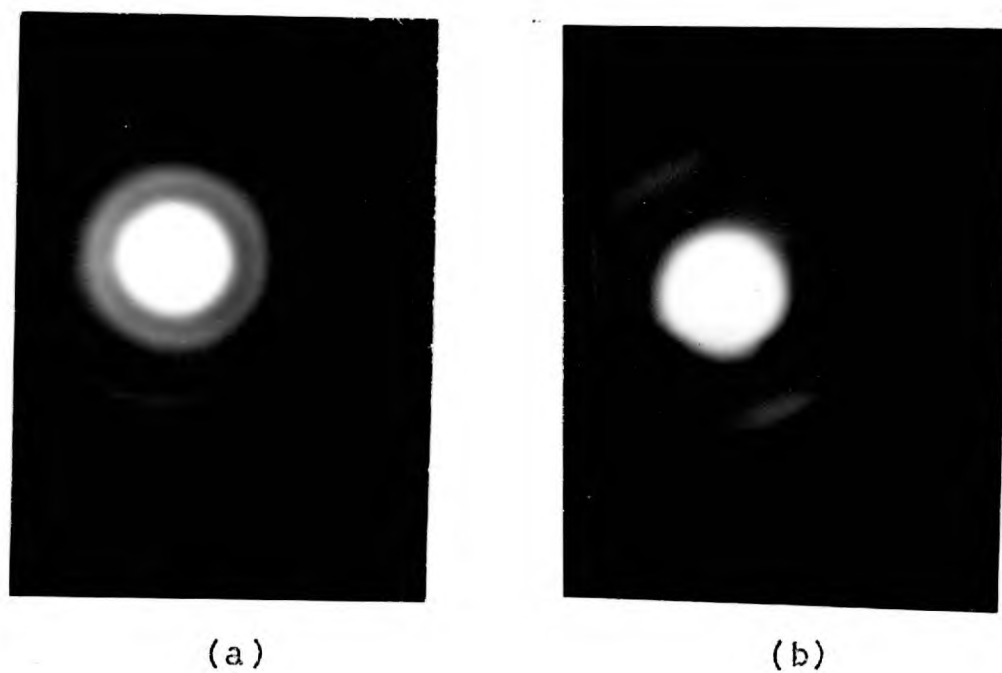
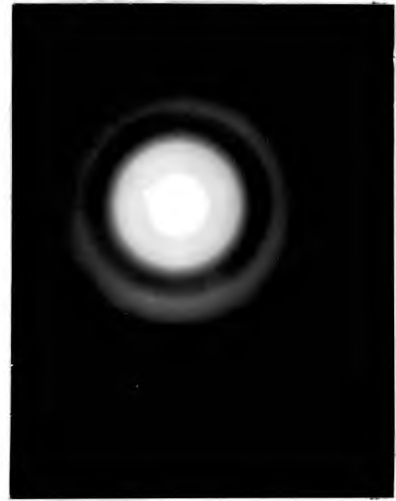


Figure 21. Transmission electron diffraction patterns produced by the amorphous substrate films (a) carbon (b) silicon monoxide.



(a)

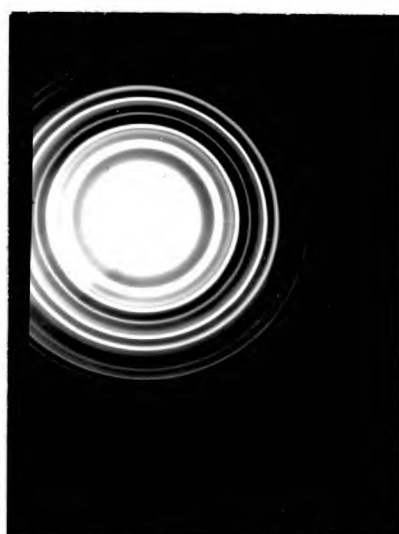


(b)



(c)

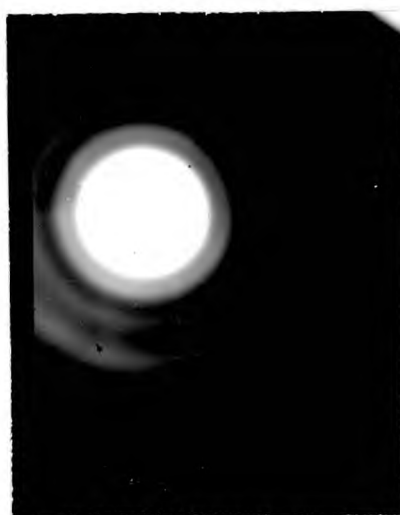
Figure 22. Transmission electron diffraction patterns of a lead deposit (on silicon monoxide) of nominal mean thickness $12.8 \text{ \AA}$ at the temperatures (a) $30.0 \text{ }^{\circ}\text{C}$ (b) $299.8 \text{ }^{\circ}\text{C}$ (c) $311.9 \text{ }^{\circ}\text{C}$.



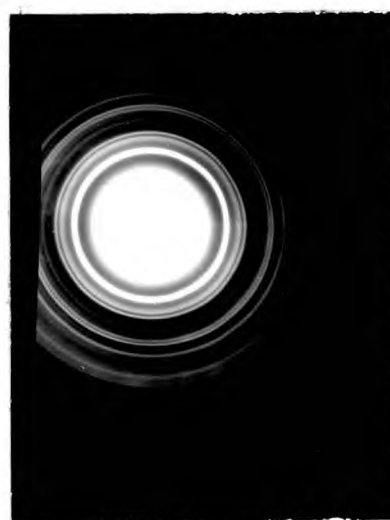
(a)



(b)

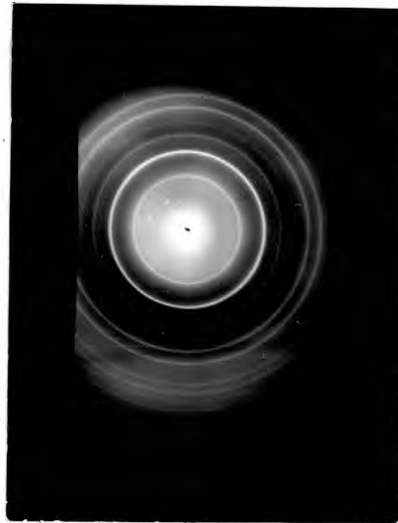


(c)

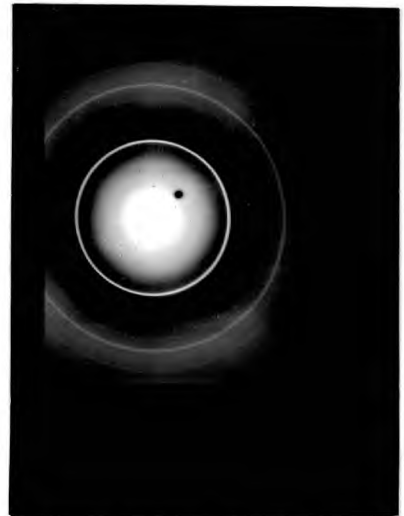


(d)

Figure 23. Transmission electron diffraction patterns of a bismuth deposit (on carbon) of nominal mean thickness $36.1 \text{ \AA}$ at the temperatures (a) 23.0°C (b) 276.9°C (c) 281.5°C (d) 15.0°C (after resolidification).



(a)



(b)



(c)

Figure 24. Transmission electron diffraction patterns of a bismuth deposit (on silicon monoxide) of nominal mean thickness $27.0 \text{ \AA}$ at the temperatures (a) $25.8 \text{ }^{\circ}\text{C}$ (b) $270.5 \text{ }^{\circ}\text{C}$ (c) $285.2 \text{ }^{\circ}\text{C}$.



(a)

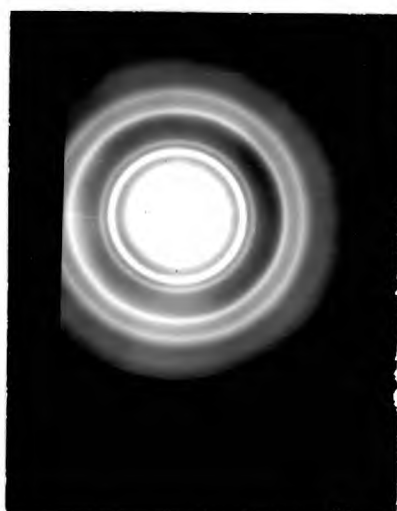


(b)

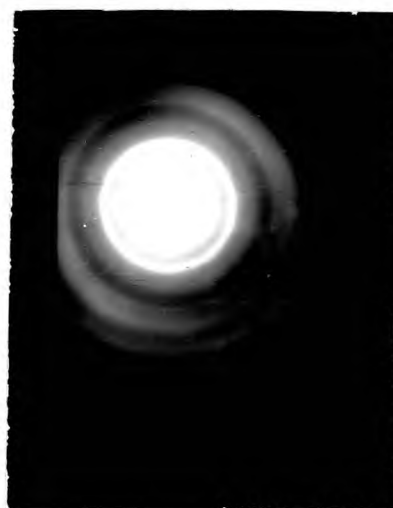


(c)

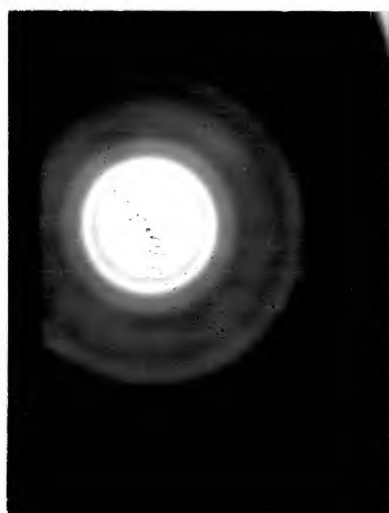
Figure 25. Transmission electron diffraction patterns of a bismuth deposit (on carbon) of nominal mean thickness $1.61 \text{ \AA}$ at the temperatures (a) 24.8°C (b) 127.8°C (c) 150.5°C .



(a)



(b)



(c)

Figure 26. Transmission electron diffraction patterns of an indium deposit (on carbon) of nominal mean thickness $3.82 \text{ \AA}$ at the temperatures (a) $-7.4 \text{ }^{\circ}\text{C}$ (b) $49.0 \text{ }^{\circ}\text{C}$ (c) $70.7 \text{ }^{\circ}\text{C}$.

diffuse patterns obtained at higher temperatures. The "melting temperature of the deposit" was taken to be the mean of the two temperatures at which these exposures were made - see further § 5.2.3.

On cooling a molten deposit, solidification did not occur until a temperature was reached appreciably below that at which the deposit had melted. The reappearance of the complete crystalline pattern on solidification occurred over a smaller temperature interval than its disappearance on melting; nevertheless, the last rings of the crystalline pattern to disappear on melting were the first rings to reappear on solidification. The reappearance of these first rings was used as the criterion of solidification. The "solidification temperature of the deposit" was considered to be that temperature at which rings of the crystalline pattern first became detectable.

On examining the photographic record of solidification, there was, in most instances, little doubt between which two (successive) diffraction patterns solidification had begun (this was a consequence of the relatively large temperature intervals between successive exposures - see § 3.2(x)). In these instances, a particular solidification temperature was not assigned; rather the solidification temperature was regarded as lying within a temperature interval - that defined by the temperatures at which the two exposures were made. However, in a few instances, a diffraction pattern was found on which rings of the crystalline pattern could only just be detected: in these instances the solidification temperature was taken to be the temperature at which that particular exposure was made.

The melting and solidification temperatures ascribed to the lead, bismuth and indium deposits are shown in tables 2, 3 and 4 (pgs. 94-98). A number of the deposits of lead and bismuth were melted and resolidified twice or three times. The first-, second- and third-melting temperatures are indicated by the Roman numerals I, II and III, and the first-, second- and third-solidification temperatures (where observed) by SI, SII and SIII. The melting and solidification temperatures pertaining to each deposit are presented in the order in which they were observed.

(i) Lead

The polycrystalline ring patterns obtained from the lead deposits

were consistent with the accepted face-centred-cubic structure of crystalline lead - see appendix 1. On heating a deposit, the last rings to disappear were the (111), the (220) and the (311), and the disappearance of these last two (the $\sqrt{8}$ and $\sqrt{11}$ rings) was used as the criterion of melting. On resolidification, the (220) and (311) were amongst the first rings to appear. Typical patterns from the melting and solidification of a lead film are shown in figure 22. The (220) and (311) reflections are, respectively, the rings ~ 2.6 cm. and ~ 3.1 cm. diameter visible in figure 22. After depositing a lead film at room temperature, melting it, and cooling again to room temperature, the final pattern was indistinguishable from the initial pattern.

It was found that if a deposit was melted twice or three times, the melting temperatures were in close agreement - see table 2. The melting temperature decreased with the mean thickness of the deposit: a deposit having a (nominal) mean thickness $\sim 100 \text{ \AA}$ melted only a few degrees below the melting point of bulk lead (327.4°C), whereas a deposit of (nominal) mean thickness $\sim 2 \text{ \AA}$ melted $150\text{--}200^\circ \text{C}$ below the bulk melting point. The uncertainty in the melting temperature increased as the film thickness decreased, both because the disappearance of the crystalline pattern occurred over a larger temperature interval, and because the crystalline pattern obtained became less sharp and less intense.

(ii) Bismuth

The polycrystalline ring patterns obtained from the bismuth deposits were consistent with the accepted rhombohedral structure of the solid phase of bismuth which is stable (in bulk form) at ordinary pressures - see appendix 1. However, the ring patterns produced by a bismuth deposit immediately after condensation and by the same deposit after melting and resolidification, exhibited some differences in the relative intensities of the rings. These are illustrated for a deposit of bismuth on carbon in figure A1.3 of appendix 1 (compare also patterns (a) and (d) of figure 23). Differences were also evident between the relative intensities of the diffraction rings obtained, immediately after deposition, from deposits (of comparable thickness) of bismuth on carbon and of bismuth on silicon monoxide - compare figures 23(a) and 24(a). These variations must have reflected structural differences in the

deposits - see § 5.4.1.

Notwithstanding these variations in the diffraction patterns produced by the bismuth deposits, on heating crystalline bismuth deposits the last ring to disappear was the $(\bar{1}\bar{1}0)$, except for the very thinnest films when the (110) could still be detected after the disappearance of the $(\bar{1}\bar{1}0)$. (The indices employed are those of the rhombohedral system - see appendix 1.) On solidification, the $(\bar{1}\bar{1}0)$ and the (110) were always amongst the first rings to appear. Typical patterns from the melting and solidification of bismuth deposits are shown in figures 23 to 25. The $(\bar{1}\bar{1}0)$ is the ring ~ 2.0 cm. diameter visible in figures 23 and 24, and the (110) is the ring ~ 1.4 cm. diameter visible in figures 24 and 25.

If a bismuth deposit was melted twice or three times, the melting temperatures decreased on successive meltings (with the exception of three of the thinnest deposits), typically by some 10°C - see table 3. For those bismuth deposits having a nominal mean thickness less than some $15 \text{ \AA}$, the first-melting temperature was found to decrease with the mean thickness of the deposit: a deposit having a (nominal) mean thickness $\sim 15 \text{ \AA}$ melted within a few degrees of the melting point of bulk bismuth (271.3°C), whereas a deposit having a (nominal) mean thickness $\sim 1 \text{ \AA}$ melted some $100\text{--}150^\circ\text{C}$ below the bulk melting temperature. Eleven of the twelve first-melting temperatures, ascribed to the twelve deposits examined having a nominal mean thickness $> 15 \text{ \AA}$, were a few degrees above the melting temperature of bulk bismuth.

(iii) Indium

The polycrystalline ring patterns obtained from the indium deposits were consistent with the accepted body-centred-tetragonal structure of crystalline indium - see appendix 1. On heating a deposit, the last rings to disappear were the (101) , the (200) and the (211) , and the disappearance of these last two was used as the criterion of melting. Typical patterns from the melting of an indium film are shown in figure 26. The (200) and (211) reflections are, respectively, the rings ~ 2.8 cm. and ~ 3.3 cm. diameter visible in figure 26. On heating deposits of indium it was found that a polycrystalline ring pattern, identified as that of indium sesquioxide - see appendix 1, began to appear at some 100°C . Further heating up to the melting point of bulk indium (157°C)

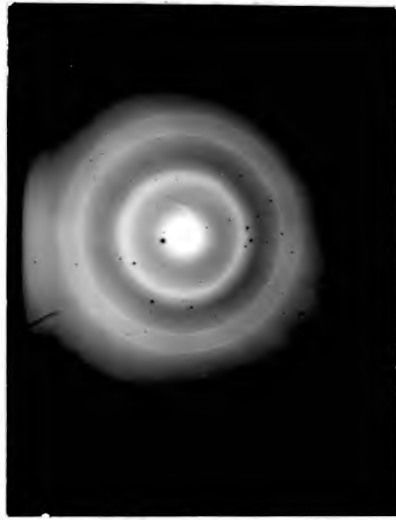
resulted in the complete oxidation of even relatively thick deposits. Below 85°C , however, no evidence of the formation of indium sesquioxide was obtained, and the melting temperatures ascribed to the deposits in table 4 are all below this temperature. Attempts to provoke the resolidification of deposits of indium, which had melted below 85°C , by cooling to -50°C for up to 30 minutes (using the cooling device) failed: however, the presence of the liquid-indium halos on the final pattern (at -50°C) was quite evident on comparison with the pattern produced by the carbon substrate before deposition.

Over the range of deposit thicknesses investigated - (nominal) mean thicknesses from 1 to 4×10^{-6} cm - the melting temperature decreased with the mean thickness of the deposit from some 70°C to some 0°C .

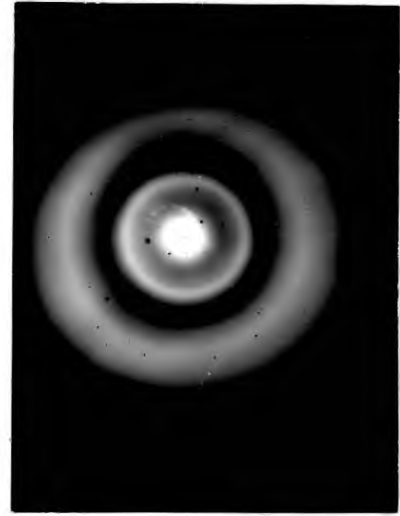
4.3 Superposition experiments and the limiting detectable exposure to the crystalline pattern as a percentage of the total exposure

Each superposition experiment, conducted as described in § 3.4, yielded a set of five diffraction patterns, the exposure to the crystalline pattern as a percentage of the overall exposure, denoted below by P, changing by a factor of 2 or 3 from one plate to the next - compare table 1. Prints of typical composite patterns are shown in figures 27 to 29. For deposits of lead and bismuth, the gradual disappearance of the rings of the crystalline pattern on progressing to smaller values of P was similar to the disappearance of the pattern on melting: in particular, the last rings of the crystalline pattern to disappear were the same. The rings ~ 2.6 cm. and ~ 3.1 cm. diameter visible in figure 27(b) are, respectively, the (220) and (311) reflections of crystalline lead. The ring ~ 2.0 cm. diameter visible in figure 28 (a) and (b) (and also in figure 29(a)) is the (110) reflection of crystalline bismuth. The ring ~ 1.4 cm. diameter visible in figure 29 (a) and (b) is the (110) reflection of crystalline bismuth. No attempt was made to obtain superposition results for indium, because it had been previously found that films of indium of any thickness oxidised rapidly when heated up to the bulk melting point (under the vacuum conditions prevailing in these experiments).

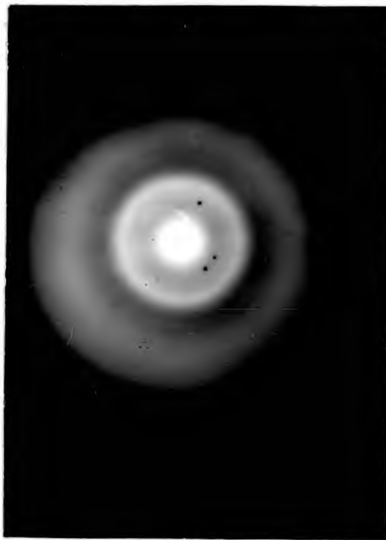
The exposure of a photographic emulsion to the diffraction pattern



(a)

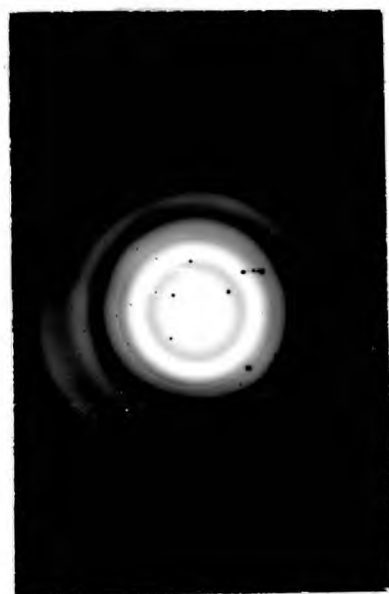


(b)

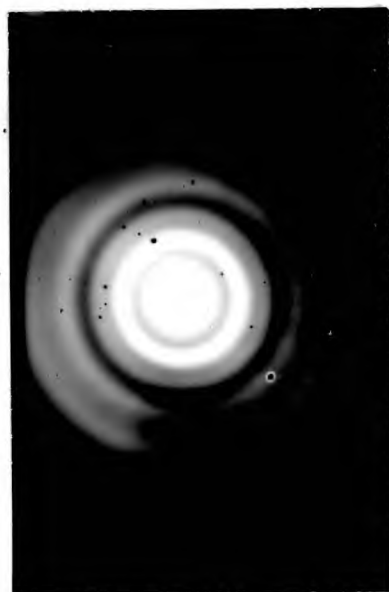


(c)

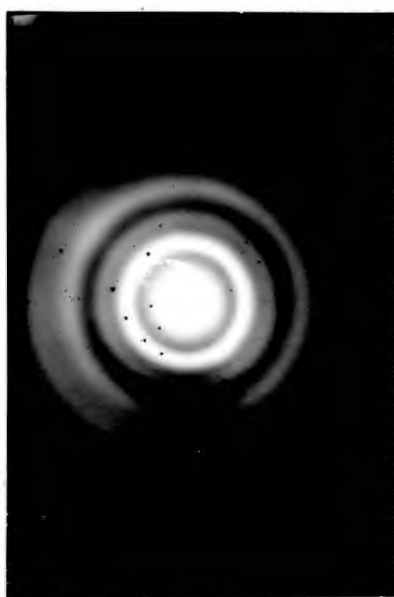
Figure 27. Composite (crystalline and liquid) transmission electron diffraction patterns from a lead deposit (on silicon monoxide) of nominal mean thickness $91.7 \text{ \AA}$. The exposure to the crystalline pattern as a percentage of the overall exposure was (a) 12.3 % (b) 1.87 % (c) 0.298 %.



(a)

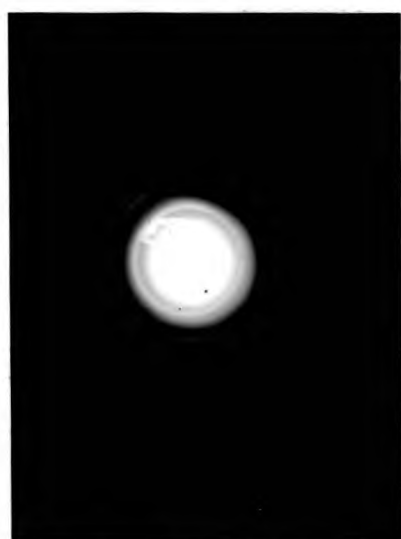


(b)

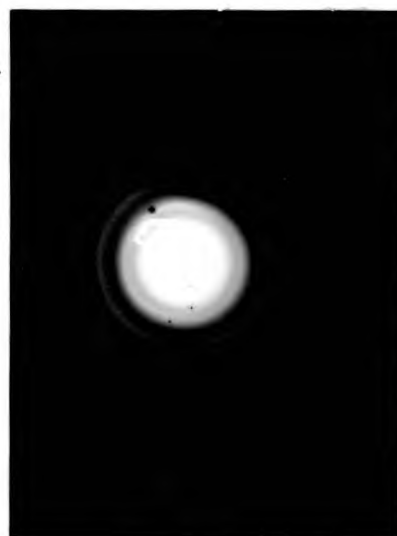


(c)

Figure 28. Composite (crystalline and liquid) transmission electron diffraction patterns from a bismuth deposit (on carbon) of nominal mean thickness $28.6 \text{ \AA}$. The exposure to the crystalline pattern as a percentage of the overall exposure was (a) 0.298 % (b) 0.125 % (c) 0.0609 %.



(a)



(b)



(c)

Figure 29. Composite (crystalline and liquid) transmission electron diffraction patterns from a bismuth deposit (on carbon) of nominal mean thickness $0.77 \text{ \AA}$. The exposure to the crystalline pattern as a percentage of the overall exposure was (a) 8.40 % (b) 4.00 % (c) 1.96 %.

from a wholly-crystalline deposit and its substrate, as a percentage of the overall exposure of the emulsion to the patterns from the wholly-crystalline and wholly-liquid deposit, which renders the crystalline sharp-ring pattern only just detectable on the developed emulsion, will be denoted by P_{CE} and referred to as the "limiting detectable exposure". The limiting detectable exposure will clearly depend upon the thickness of the deposit, the thickness of the substrate, the nature of the emulsion, the overall exposure and the degree of development. The accelerating voltage on the electron gun (40 kV) and the geometrical arrangement of the electron diffraction camera ("camera length" ~ 40 cm.) were the same throughout the experiments. A "Kodak" N50 photographic plate was found to be suitably exposed, if subjected for 25 sec. to the electrons scattered from a specimen upon which the beam current of $0.0057 \mu A$ indicated in § 2.7 was incident; this same overall exposure was employed for all the superposition experiments.

A series of superposition experiments were carried out with lead deposits of different thicknesses on carbon substrates. Each set of five plates was examined on either three or four separate occasions: upon each examination two consecutive plates were chosen from each set, such that rings of the crystalline pattern could be detected upon the first but not on the second. If the crystalline pattern could only just be detected on the first, then a weight of 2 was ascribed to the percentage, P , corresponding to this plate; whereas if the crystalline pattern was clearly detectable on the first, then a weight of 1 was ascribed to each of the two percentages corresponding to the two plates. When all of the examinations, which were spaced over an interval of some three months, had been completed, the weights ascribed to each of the discrete percentages, P , of a particular set of plates were added up and reduced to their simplest ratio. A plot of these discrete percentages (excluding the unweighted ones), together with their weightings, against the nominal mean thickness of the deposit, z , on a log-log scale is shown for lead on carbon in figure 30. Each vertical group of points corresponds to one deposit, and the numbers beside the points indicate the weight to be given to each point within its own group. The "centre of gravity" of each group of points was considered to be the best value obtainable for the

limiting detectable exposure, P_{CE} , for that experiment.

The centre of gravity, P_{CE} , of each group of points was found and plotted against the nominal mean thickness, z , on a log-log scale - see figure 31. It was found that the dependence of $\log P_{CE}$ on $\log z$ could be represented well by a straight line, and a least-mean-square straight line was fitted to the data. Also shown in figure 31 are results for bismuth on carbon, bismuth on silicon monoxide and lead on silicon monoxide.

The points in figures 30 and 31 marked with the letter L are results of experiments in which the emulsion was exposed to the pattern from the wholly-molten deposit first, and to the pattern from the resolidified deposit afterwards. All other points refer to experiments in which the emulsion was first exposed to the pattern from the crystalline deposit (immediately after its deposition). In the case of lead on carbon, the two "L-results" are in close agreement with the other results, and were included in the calculation of the least-mean-square fit. However, the results of two "L-experiments" with bismuth on carbon (only one is shown, as no crystalline pattern could be detected on any of the five plates of the other) suggest that if the emulsion is exposed to the pattern from the resolidified deposit, a longer exposure to the solid pattern is required to render it detectable. This is in accord with the qualitative observation that the intensity of a number of the strongest rings in the pattern from an unmelted deposit of bismuth on carbon is greater than their intensity in the pattern from the resolidified deposit - compare patterns (a) and (d) of figure 23.

A least-mean-square straight line was fitted to the five results (excluding the result marked L) for bismuth on carbon. A straight line was drawn through the two results obtained for bismuth on silicon monoxide. For lead on silicon monoxide, a line was drawn through the one result obtained parallel to the line for lead on carbon.

The extent of each continuous line in figure 31 corresponds to the range of z -values over which melting-temperature determinations were made (with that particular combination of materials).

Superposition experiments were performed in which one of the five plates was exposed only to the pattern from the wholly-molten deposit,

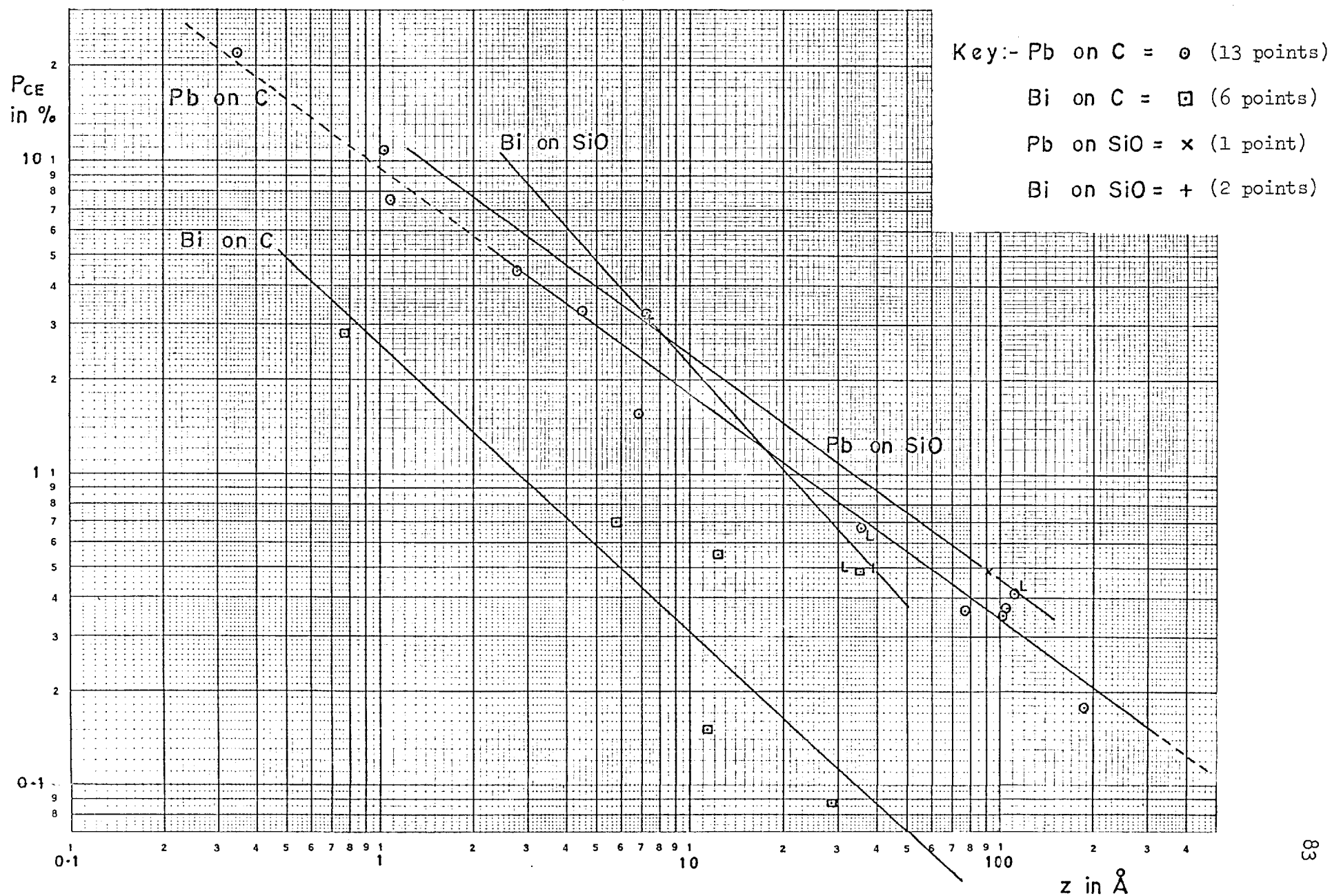


Figure 31. Data illustrating the dependence of the "limiting detectable exposure", P_{CE} , on the deposit thickness, z

but for such a time as to receive the same overall exposure as the other four: in each case it was found that no difference could be detected between the pattern on this plate and one of the composite patterns on which the crystalline pattern could not be detected. In other experiments, one plate was exposed only to the pattern from the wholly-crystalline deposit, and for a time equal to, or somewhat shorter than, the shortest crystalline exposure employed for the composite patterns. It was found, in each case, that rings of the crystalline pattern could be detected on this plate, whereas longer crystalline exposures could not be detected when part of a composite pattern. For example: a limiting detectable exposure, P_{CE} , of 0.087 % was ascribed to the deposit of bismuth of nominal mean thickness $28.6 \text{ \AA}$, from which composite patterns are shown in figure 28. One plate was exposed only to the electrons scattered from this unmelted, crystalline deposit, when a beam current of $0.0057 \times 0.195 \text{ \mu A}$ was incident on it for a time 0.033 sec. It was found that rings of the crystalline pattern could be detected on this developed plate, although this solid exposure, if part of a composite pattern, would correspond to a value of P of 0.026 %. This finding indicates that the disappearance of the crystalline pattern - see figure 28 - was not due to a failure to expose the plates.

4.4 The association of a particular crystallite radius with the melting temperature of a deposit

It was observed - compare § 4.2 - that when a metallic deposit, consisting of crystallites of varying radii, was heated, the crystalline diffraction pattern did not disappear suddenly at a definite temperature, but gradually over a finite interval of temperature. Further, the complete disappearance of the crystalline pattern occurred at ever lower temperatures, as the sizes of the crystallites composing the deposit decreased. These findings can be explained on the assumption that the melting temperature of a crystallite decreases (monotonically) with decreasing crystallite size; moreover, this assumption can be justified theoretically by the application of thermodynamics to a model of a crystallite melting - see § 6.3.

This leads to the following picture of the melting of a metallic

deposit: as the deposit is heated, the smallest crystallites melt first, and as the temperature is increased, so larger and larger crystallites melt. At any given temperature, all the original crystallites which were greater than a certain size - the size which melts at this temperature - remain solid. Eventually a temperature is reached at which the crystallites which remain only just diffract sufficient electrons for the crystalline pattern to be detectable (on a photographic emulsion): the radius of the crystallites which are melting at this temperature will be denoted by R_m and referred to as the "melting radius", and the volume of the crystallites remaining at this temperature, as a percentage of the volume of all the original crystallites, will be denoted by P_{CV} and referred to as the "limiting detectable volume".

With this picture of the melting of a deposit, if the "melting temperature" has been determined and the volume distribution of the crystallites composing the deposit has been found, then a knowledge of the limiting detectable volume, P_{CV} , is sufficient to determine the size (the melting radius, R_m) of the crystallites which were melting at this temperature - for further details see § 5.1. Because the thickness of the substrates was kept constant throughout the experiments - see § 2.1 - and the emulsion used for the superposition experiments was similar to that of the recording film, the limiting detectable exposure, P_{CE} , for any deposit can be inferred from the nominal mean thickness of the deposit and the data of figure 31. If the two percentages P_{CV} and P_{CE} can be identified, then each melting experiment yields a crystallite size and its melting temperature. The remainder of this section is devoted to a justification for identifying these two percentages.

In order to investigate the factors which affect the visual detectability of a "sharp ring" on a developed emulsion, certain facts concerning the physiology of the eye and the response of photographic emulsions to electrons must be examined.

The optical density, D , of a processed emulsion is defined as

$$D = \log_{10} \left(\frac{1}{T} \right)$$

where T is the fraction of incident light transmitted by the emulsion (its "transmission")

It is a physiological fact that over the range of tones conveniently viewed by the eye, differences in density are perceived and interpreted as proportional differences in contrast.

It has been established - see Valentine (1966), and Hall (1966), pgs. 171-176 - that for a wide variety of photographic emulsions, the response to electrons in the energy range 40-120 kV is consonant with a "single-hit" process of latent image formation. For a particular emulsion, degree of development and electron energy, the density of the processed emulsion, D , is directly proportional to the exposure (over the range of densities usually employed - more specifically, the approximation is good up to densities of $\frac{1}{4}D_s$ where D_s is the saturation density). It is implied also, of course, that the reciprocity law holds - i.e. the density is dependent only on the product of the exposure time, t (sec.), and the intensity of exposure, I (amp./sq. cm.). We may write

$$D = kIt$$

where k is a constant depending upon the emulsion, the degree of development and the electron energy.

If, for a particular emulsion, degree of development and electron energy, D_1 and D_2 are the densities corresponding to exposures $I_1 t_1$ and $I_2 t_2$, then

$$D_2 - D_1 = D_1 \frac{I_2 t_2 - I_1 t_1}{I_1 t_1} \quad (4-5)$$

This important result means that the density difference, and therefore contrast, of the processed emulsion is dependent only on the ratio of the exposures and the density of the processed emulsion - it does not depend explicitly on the actual exposures or degree of development (within broad limits), nor on the particular emulsion employed. Moreover, the contrast of an emulsion exposed to a single electron image depends only on the relative intensities of the various parts of the image and on the final processed density; and when exposed and processed to the same final density, all emulsions will have exactly the same contrast - see Valentine (1966), pg. 190.

Consider a specimen consisting of an amorphous substrate of uniform

thickness and mass per unit area m , on which is deposited an aggregate of metallic crystallites having a mean mass per unit area of M .

(a) Suppose this specimen is at a temperature T °K, and that the deposit is partially molten such that a proportion p_a by weight of the whole still remains solid. Suppose that a photographic emulsion is exposed for a time t sec. to the electrons scattered from the specimen when an electron beam of i amp. is incident on a uniform area of the specimen.

In accordance with kinematic theory, we may represent the total flux of electrons per unit area per second at any point of the emulsion - the electron intensity, $I_C(\theta, T)$, in amp./sq. cm. - arising from scattering by the polycrystalline metal, by an expression of the form .

$$I_C(\theta, T) = K_g F_C(\theta, T) p_a M i$$

where K_g is a geometrical constant depending on the distance of the emulsion from the specimen

θ is the scattering angle corresponding to the point in question and $F_C(\theta, T)$ is a function characteristic of the particular metal and its temperature, T , and largely independent of the distribution and sizes of the crystallites provided they are small enough for the kinematic approximation to hold.

In a similar way, the electron intensities $I_L(\theta, T)$ and $I_S(\theta, T)$ arising from scattering by the liquid metal and by the substrate, respectively, may be represented by expressions of the form

$$I_L(\theta, T) = K_g F_L(\theta, T) (1 - p_a) M i$$

and

$$I_S(\theta, T) = K_g F_S(\theta, T) m i$$

The total flux of electrons per unit area scattered from the specimen as a whole to any point on the emulsion - the exposure, $E_a(\theta)$, in coulombs/sq. cm. - is thus

$$E_a(\theta) = K_g \left[F_C(\theta, T) p_a M + F_L(\theta, T) (1 - p_a) M + F_S(\theta, T) m \right] i t$$

Discounting the dependence of the functions F_C , F_L and F_S on the

temperature, we may write

$$E_a(\theta) = K_g \left\{ (F_C(\theta) - F_L(\theta)) M p_a + F_L(\theta) M + F_S(\theta) m \right\} it \quad (4-6)$$

(b) Suppose that a photographic emulsion is exposed, successively, to the electrons scattered when an electron beam of i_1 amp. falls on the wholly-crystalline specimen at a temperature T_1 °K for a time t_1 sec., and then an electron beam of i_2 amp. falls on the wholly-molten specimen at a temperature T_2 °K for a time t_2 sec.

The overall exposure, $E_b(\theta)$, is

$$E_b(\theta) = K_g \left\{ F_C(\theta, T_1) M + F_S(\theta, T_1) m \right\} i_1 t_1 \\ + K_g \left\{ F_L(\theta, T_2) M + F_S(\theta, T_2) m \right\} i_2 t_2$$

Defining p_b by

$$p_b = \frac{i_1 t_1}{i_1 t_1 + i_2 t_2}$$

and discounting the dependence of the functions F_C , F_L and F_S on the temperature, we may write

$$E_b(\theta) = K_g \left\{ (F_C(\theta) - F_L(\theta)) M p_b + F_L(\theta) M + F_S(\theta) m \right\} (i_1 t_1 + i_2 t_2) \quad (4-7)$$

Comparison of equations (4-6) and (4-7) shows that if

$$i_1 t_1 + i_2 t_2 = it \quad (4-8)$$

and

$$p_b = p_a$$

then the photographic emulsions in the two cases (a) and (b) receive identical overall exposures. Moreover, if the emulsions are similar, and provided that the reciprocity law holds, they will have identical latent images.

Suppose that two emulsions are exposed as indicated in (a) and (b),

and that on processing them, it is found that rings of the crystalline pattern can just be detected on each, then

$$p_a = \frac{P_{CV}}{100} \quad \text{and} \quad p_b = \frac{P_{CE}}{100} \quad (4-9)$$

(i) Suppose that the emulsions are similar, that they were similarly processed, and that the exposures were such as to satisfy equation (4-8), then we may infer

$$P_{CV} = P_{CE} \quad (4-10)$$

(ii) It is now shown that equation (4-10) is a good approximation, provided the processed emulsions have the same "background" density in the neighbourhood of the last ring to disappear, even if the emulsions themselves and their processing are not similar, and the exposures do not (necessarily) satisfy equation (4-8):

Suppose that the scattering angle corresponding to a point on the centre of the last sharp ring to disappear is θ_R , and that the scattering angle corresponding to a neighbouring point on the "background" close to this ring is θ_B . Then, from equation (4-5), the densities, D_R and D_B , of the processed emulsion at these two points will be related in case (a) by

$$(D_R - D_B)_a = (D_B)_a \frac{E_a(\theta_R) - E_a(\theta_B)}{E_a(\theta_B)}$$

and in case (b) by

$$(D_R - D_B)_b = (D_B)_b \frac{E_b(\theta_R) - E_b(\theta_B)}{E_b(\theta_B)}$$

Assuming that the ring will be only just detectable when

$$D_R - D_B = \Delta D$$

where ΔD is some critical density difference, we obtain in case (a)

$$\frac{E_a(\theta_R)}{E_a(\theta_B)} = 1 + \frac{\Delta D}{(D_B)_a} \quad (4-11)$$

and in case (b)

$$\frac{E_b(\theta_R)}{E_b(\theta_B)} = 1 + \frac{\Delta D}{(D_B)_b} \quad (4-12)$$

If the processed emulsions have the same background density in the neighbourhood of the last ring to disappear, i.e.

$$(D_B)_a = (D_B)_b$$

then

$$\frac{E_a(\theta_R)}{E_a(\theta_B)} = \frac{E_b(\theta_R)}{E_b(\theta_B)}$$

It may now be demonstrated, using equations (4-6) and (4-7), that

$$P_b = P_a$$

(since $\{F_C(\theta_R) - F_L(\theta_R)\}\{F_L(\theta_B) M + F_S(\theta_B) m\} \neq$

$$\{F_C(\theta_B) - F_L(\theta_B)\}\{F_L(\theta_R) M + F_S(\theta_R) m\} \quad)$$

and we may infer, using equations (4-9), that

$$P_{CV} = P_{CE}$$

(iii) One further approximate result will now be obtained, which will be made use of in the discussion of errors in § 5.2.8.

Provided that the functions $F_L(\theta)$ and $F_S(\theta)$ vary slowly with the scattering angle, θ , in the neighbourhood of the last crystalline ring to disappear, we may assume

$$F_L(\theta_R) \approx F_L(\theta_B) \quad \text{and} \quad F_S(\theta_R) \approx F_S(\theta_B)$$

and neglecting the scattering from the crystalline metal at the scattering angle θ_B , we have

$$F_C(\theta_B) \approx 0$$

so that equations (4-11) and (4-12) become, with reference to equations (4-6) and (4-7),

$$\frac{F_C(\theta_R) M p_a}{F_L(\theta_B) M(1 - p_a) + F_S(\theta_B) m} = \frac{\Delta D}{(D_B)_a} \quad (4-13)$$

and

$$\frac{F_C(\theta_R) M p_b}{F_L(\theta_B) M(1 - p_b) + F_S(\theta_B) m} = \frac{\Delta D}{(D_B)_b} \quad (4-14)$$

Suppose that the "background" densities of the two processed emulsions, in the neighbourhood of the last ring to disappear, differ by a factor of two: say

$$(D_B)_a = 2(D_B)_b$$

then, from equations (4-13) and (4-14),

$$p_b = 2p_a \frac{F_L(\theta_B) M(1 - p_b) + F_S(\theta_B) m}{F_L(\theta_B) M(1 - p_a) + F_S(\theta_B) m} \quad (4-15)$$

From equation (4-15), it is clear that the proportions p_a and p_b differ by a factor which is somewhat less than two.

We may conclude, with reference to equation (4-9), that if the "background" densities of the two processed emulsions, in the neighbourhood of the last ring to disappear, differ by a factor of two; then the limiting detectable volume, P_{CV} , and the limiting detectable exposure, P_{CE} , differ by a factor which is somewhat less than two.

CHAPTER 5

RESULTS DEDUCED FROM THE EXPERIMENTAL DATA

5.1 The results

Insofar as the crystallites situated on an area A of a substrate, and having a size distribution $n(R)$, approximate to a group of spherical caps having the same contact angle θ with the substrate, the actual volume distribution of these crystallites is represented by the histogram

$$V(R) = k v(R)$$

where

$$k = \frac{\pi}{3}(1 - \cos \theta)^2(2 + \cos \theta)$$

and

$$v(R) = R^3 n(R)$$

as indicated in § 4.1 - compare equations (4-1) to (4-3). The total volume of the crystallites is

$$\sum_{R=0}^{\infty} k v(R) = k \sum_{R=0}^{\infty} v(R)$$

The volume of all the crystallites having a radius greater than some particular value r is

$$k \sum_{R=r}^{\infty} v(R)$$

and this constitutes a percentage

$$P_V = \frac{\sum_{R=r}^{\infty} v(R)}{\sum_{R=0}^{\infty} v(R)} \times 100$$

of the total volume. Provided that the crystallites situated on the area A are representative of the deposit as a whole, it follows from the discussion in § 4.4 that the radius, R_m , of the crystallites which are just melting at the "melting temperature" of the deposit, is given by

$$P_{CE} = \frac{\sum_{R=R_m}^{\infty} v(R)}{\sum_{R=0}^{\infty} v(R)} \times 100 \quad (5-1)$$

where P_{CE} is the limiting detectable exposure.

For each deposit whose melting temperature was determined, the limiting detectable exposure, P_{CE} , was obtained from the nominal mean thickness of the deposit and the data of figure 31. The "melting radius", R_m , was then calculated from equation (5-1). Thus each melting experiment yielded a crystallite radius and its associated melting temperature - see tables 2, 3 and 4.

As mentioned in § 4.3 (pg. 76), no superposition experiments were attempted with indium deposits, so in order to interpret the melting experiments with indium on carbon, values of P_{CE} were obtained from the superposition data for lead on carbon. As the radii of the last rings to disappear on melting are similar for lead and indium, and therefore fall in the same region of the diffuse "halos" due to the substrate, it was considered to be more appropriate to employ the data for lead on carbon than for bismuth on carbon.

It was observed - compare § 4.2 - that when a molten deposit of lead or bismuth, consisting of droplets of varying radii, was cooled, the crystalline diffraction pattern did not appear suddenly at a definite temperature, but gradually over a finite interval of temperature. Further, the appearance of the first rings of the crystalline pattern occurred at a temperature which decreased as the sizes of the droplets composing the deposit decreased. These findings can be explained on the assumption that the solidification of a droplet occurs at a temperature which decreases with decreasing droplet size. The arguments of § 4.4 can be invoked to identify the "solidification temperature" of a deposit with the solidification of those droplets which solidify into crystallites of radius R_m . Thus each solidification experiment yields a crystallite radius and its associated solidification temperature - see tables 2 and 3.

It should be noted that the picture of a partially-molten or partially-solidified deposit, in which a definite radius divides the

Substrate	Substrate temperature on deposition	Partial pressure of hydrogen	z	P _{CE}	Radius R _m	Errors in radius*		Melting and solidification temperatures**		
						R _{lwr.}	R _{upr.}			
	(°C)	(x 10 ⁻⁵ torr)	(Å)	%	(Å)	(Å)	(Å)	(°C)		
C	22.0		2.20	5.4	29.2	21.8	36.6	133.5±11	I	
SiO	25.5		1.23	10.9	32.1	23.9	39.8	147.7±11	I	
SiO	21.6		2.15	7.3	34.3	27.3	41.2	161.5±11	I	
C	22.0		3.82	3.6	42.2	34.5	50.3	237.9±8	I	
SiO	21.3		3.40	5.2	45.2	36.9	53.1	233.6±5	I	
SiO	21.6		4.42	4.3	48.3	40.7	55.6	250.2±5	I	
SiO	22.3		3.41	5.2	48.7	41.2	56.0	243.8±5	I	
SiO	22.7		4.50	4.3	51.2	42.3	59.7	237.4±8	I	
SiO	21.6		3.38	5.3	52.5	44.1	60.3	273.4±5	I	
C	26.9		9.58	1.9	53.8	46.9	60.5	266.3±5	I	
SiO	21.6		2.28	7.0	55.4	45.4	65.3	271.7±5	I	
SiO	22.0		3.48	5.2	59.7	51.2	67.4	279.8±2.5	I	
SiO	178.8		3.46	5.2	62.2	51.2	72.2	258.2±5	I	
C	22.7		11.9	1.6	63.5	55.6	71.0	281.5±2.5	I	
SiO	25.1		7.77	2.9	63.7	54.4	72.7	273.4±7	I	
SiO	183.3		1.94	7.9	64.0	46.1	80.9	274.4±4	I	
C	21.6		13.6	1.4	64.1	56.2	71.5	290.6±2.4	I	
C	22.3		12.6	1.5	66.1	57.2	74.8	263.9±2.5	I	217.5-222.1 SI
SiO	22.7		8.67	2.7	73.2	65.1	81.6	291.8±2.4	I	
C	21.6	2.0	20.8	1.1	80.7	71.3	90.5	282.5±5	I	283.5±5 II 219.1-232.3 SII
C	22.0		22.7	0.99	81.6	73.5	89.5	299.8±2.4	I	
SiO	23.0		10.0	2.4	82.6	73.6	91.1	297.4±2.4	I	294.5±2.4 II
C	24.4		26.2	0.90	92.5	83.9	101.3	307.1±1.2	I	
SiO	178.2		12.8	2.0	102	92	112	306.1±1.2	I	222.6-235.4 SI
C	21.6	2.0	28.7	0.84	102	94	111	302.7±2.4	I	229.8-236.7 SI 300.3±2.4 II 228.5-236.7 SII

Table 2 - continued overpage

continued from previous page

SiO	178.1		11.4	2.2	110	99	124	309.0±1.2 I	222.6-235.4 SI		
SiO	178.2		13.5	1.9	112	98	130	306.1±2.4 I	222.6-235.4 SI		
SiO	179.6		17.7	1.6	113	100	122	307.1±2.4 I			
SiO	175.5		20.0	1.5	118	106	128	308.0±1.2 I			
SiO	177.9		14.5	1.8	121	104	145	307.8±2.4 I			
C	26.9		41.5	0.64	126	116	135	314.2±1.2 I			
SiO	176.8		24.5	1.3	127	111	140	309.7±1.2 I			
C	25.5		55.2	0.52	160	148	171	317.8±1.2 I			
C	24.8		68.9	0.45	224	186	257	321.4±1.2 I			
C	13.2		109	0.32	240	226	254	315.4±1.2 I	236.7*** SI	316.4±1.2 II	
									229.0-236.7 SII	314.9±1.2 III	
C	20.6	5.0	115	0.31	255	240	269	320.4±1.2 I	229.0-236.7 SI	319.2±2.4 II	
										229.0-236.7 SII	
SiO	178.2		92.2	0.48	260	240	279	322.8±1.2 I			
SiO	180.7		82.6	0.52	282	234	329	321.6±1.2 I			
SiO	180.4		129	0.38	313	291	333	327.0±1.2 I			
SiO	178.1		150	0.34	323	302	344	325.9±1.2 I	322.3±1.2 II	235.4*** SII	
C	20.6		173	0.23	436	409	462	323.7±1.2 I			
C	20.9		181	0.22	489	443	534	324.4±1.2 I	234.1*** SI	322.5±1.2 II	
C	23.4		325	0.15	1089	995	1183	328.5±1.2 I	327.3±1.2 II		

* $R_{lwr.}$ and $R_{upr.}$ are, respectively, the "probable lower limit of R_m " and the "probable upper limit of R_m " - see § 5.2.7

** The first-, second- and third-melting temperatures are indicated by the Roman numerals I, II and III; the first-, second- and third-solidification temperatures (where observed) by SI, SII and SIII - see § 4.2 (pg. 73)

*** The crystalline pattern could only just be detected on this exposure - see § 4.2 (pg. 73)

Table 2. The results for lead

Substrate	Substrate temperature on deposition (°C)	Partial pressure of hydrogen ($\times 10^{-5}$ torr)	z (Å)	P _{CE} %	Radius R _m (Å)	Errors in radius*			Melting and solidification temperatures**			
						R _{lwr.} (Å)	R _{upr.} (Å)		(°C)			
C	22.0		0.86	3.0	22.1	15.7	28.4	90.0±15	I	126.9±6	II	81.6-96.9 SII
C	25.1		0.95	2.7	22.3	15.0	29.5	113.2±9	I	121.9±6	II	82.5-106.1 SII
C	21.3		0.47	5.2	26.3	18.7	33.7	134.4±6	I	124.0±6	II	119.0±6 III
C	24.8	1.0	1.61	1.7	29.3	22.7	35.8	147.1±8	I	100.1±9***	SI	131.5±6 II
C	23.7		0.89	2.9	31.1	24.6	37.5	137.8±6	I	156.0±14	II	
C	25.5		1.48	1.8	33.3	26.0	40.7	204.4±2.6	I			
C	24.8		1.83	1.5	38.8	32.2	45.3	222.7±5	I			
SiO	21.3		3.68	6.7	39.1	32.4	45.8	230.1±2.5	I	201.8±2.6	II	
SiO	152.9		2.44	10.6	44.2	36.4	51.8	221.1±5	I			
C	24.8	2.0	3.32	0.86	47.5	39.9	55.0	242.0±2.5	I	112.0-120.8	SI	215.2±5 II
C	24.4	2.0	6.00	0.50	53.6	44.9	62.0	243.0±1.3	I	114.6-117.6	SI	221.9±2.6 II 117.6±6*** SII
C	22.0		5.12	0.58	54.6	46.8	63.3	243.0±2.5	I			
C	22.0		6.47	0.46	55.4	48.7	62.2	243.8±2.5	I			
C	21.3		6.61	0.46	56.6	47.7	66.4	253.2±2.5	I	234.1±2.5	II	127.8-142.1 SII
C	17.8		7.71	0.40	60.5	53.2	67.7	260.7±5	I	240.2±5	II	231.6±8 III
SiO	25.5		8.73	2.6	66.4	58.6	73.8	264.6±1.2	I	112.3-130.1	SI	246.1±2.5 II 135.5±2.9***SII
C	19.9		9.74	0.32	69.1	60.7	77.5	260.7±1.2	I	241.8±2.5	II	140.7-154.6 SII
C	24.4	1.0	15.8	0.20	84.2	76.0	92.1	272.9±1.2	I	129.2-132.1	SI	258.2±2.5 II 140.7-154.6 SII
C	21.3		15.9	0.20	91.6	84.1	99.1	273.9±1.2	I	256.4±1.3	II	154.6-168.3 SII
C	19.5		19.5	0.17	102	91	113	271.2±1.2	I	142.1-156.0	SI	

Table 3 - continued overpage

continued from previous page											
SiO	25.8	27.0	0.74	148	128	168	284.5±1.2 I	171.1-173.8 SI	271.0±2.5 II	168.3-182.0 SII	
C	24.1	29.3	0.12	167	150	184	275.4±1.2 I	265.3±1.2 II			
SiO	154.7	50.4	0.37	175	163	187	276.6±1.2 I	270.7±5 II			
C	26.2	29.0	0.12	176	164	189	280.3±1.2 I	269.5±1.2 II	168.3-182.0 SII		
C	156.0	46.4	0.076	177	160	194	275.4±1.2 I				
C	156.0	50.4	0.070	197	184	211	278.1±1.2 I				
C	23.4	34.0	0.10	219	199	240	280.3±1.2 I	270.7±1.2 II	182.0-195.2 SII		
C	23.0	36.1	0.096	232	217	248	280.3±1.2 I	272.0±1.2 II	260.7±2.5 III	182.0-195.2 SIII	
C	21.3	75.6	0.048	717	673	761	275.9±1.2 I	270.5±2.4 II	182.0-195.2 SII		

* $R_{lwr.}$ and $R_{upr.}$ are, respectively, the "probable lower limit of R_m " and the "probable upper limit of R_m " - see § 5.2.7

** The first-, second- and third-melting temperatures are indicated by the Roman numerals I, II and III; the first-, second- and third-solidification temperatures (where observed) by SI, SII and SIII - see § 4.2 (pg. 73)

*** The crystalline pattern could only just be detected on these exposures - see § 4.2 (pg. 73)

Table 3. The results for bismuth

Substrate	Substrate temperature on deposition	Partial pressure of hydrogen	z	P _{CE}	Radius			Errors in radius*	Melting temperature**
					R _m	R _{lwr.}	R _{upr.}		
	(°C)	(x 10 ⁻⁵ torr)	(Å)	%	(Å)	(Å)	(Å)		(°C)
C	-42.1		1.13	8.7	19.5	13.1	25.7	-4.4 ± 7	I
C	-46.2		1.21	8.3	20.7	13.9	27.3	7.2 ± 7	I
C	25.5	1.3	1.69	6.5	23.3	17.0	29.6	38.4 ± 7	I
C	0.0	1.2	1.75	6.3	23.3	17.0	29.9	36.0 ± 7	I
C	1.1	1.3	3.95	3.5	34.4	27.9	40.7	54.5 ± 6	I
C	-1.8		3.46	3.9	37.1	29.2	45.3	74.4 ± 6	I
C	-7.4		4.06	3.5	37.2	30.5	43.7	71.3 ± 6	I
C	-14.9	1.1	3.82	3.6	37.9	31.1	44.5	64.4 ± 6	I

* R_{lwr.} and R_{upr.} are, respectively, the "probable lower limit of R_m" and the "probable upper limit of R_m" - see § 5.2.7

** The melting temperature shown is, in each case, the first-melting temperature (indicated by I)

Table 4. The results for indium

crystallites from the molten droplets, can only be justified approximately on statistical grounds. Moreover, statistical considerations are all important in the theoretical interpretation of the results of experiments on the solidification of metallic droplets - see § 6.4.

Plots of the melting and solidification temperatures against the radius R_m are shown for lead, bismuth and indium in figures 32-34. The continuous curves represent theoretical fits to the data - see chapter 7.

Notes to figure 32:

In cases where more than one melting or solidification temperature were determined for a particular lead deposit, only the first temperature determined is plotted.

Key:

	carbon	silicon monoxide
melting temperature		
first-solidification temperature	or	or
second-solidification temperature	or	or

Notes to figure 33:

Four of the bismuth deposits examined were prepared by condensation on to a substrate at a temperature $\sim 150^{\circ}\text{C}$ - see table 3. The results for these four deposits are not plotted.

Key:

	carbon	silicon monoxide
first-melting temperature		
second-melting temperature		
third-melting temperature		
first-solidification temperature	or	or
second-solidification temperature	or or	or
third-solidification temperature	or	or

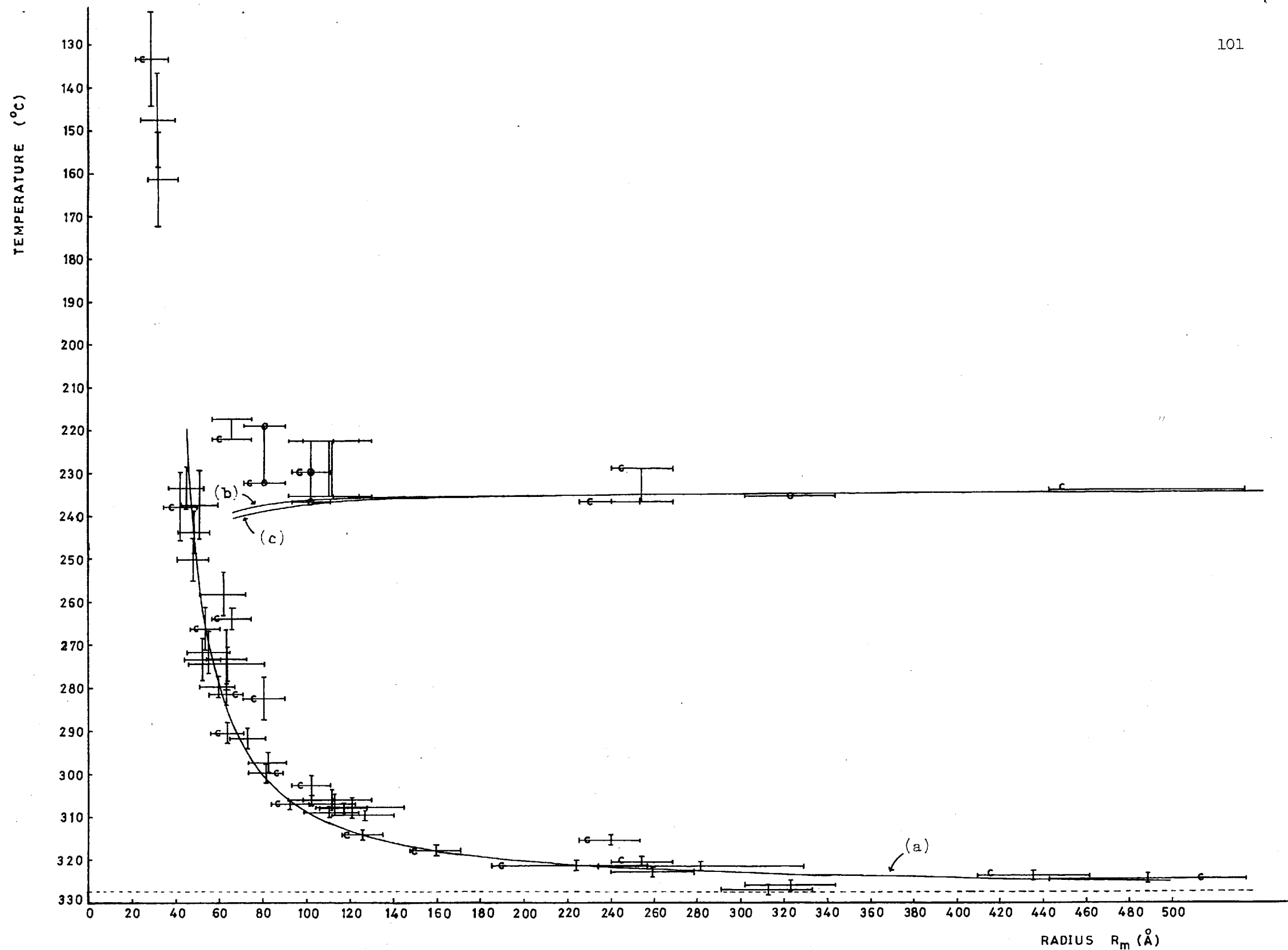


Figure 32. The results for lead

- (a) melting temperature according to equation (7-1)
- (b) solidification temperature deduced from equation (7-13) (homogeneous nucleation)
- (c) solidification temperature deduced from equation (7-15) (heterogeneous nucleation)

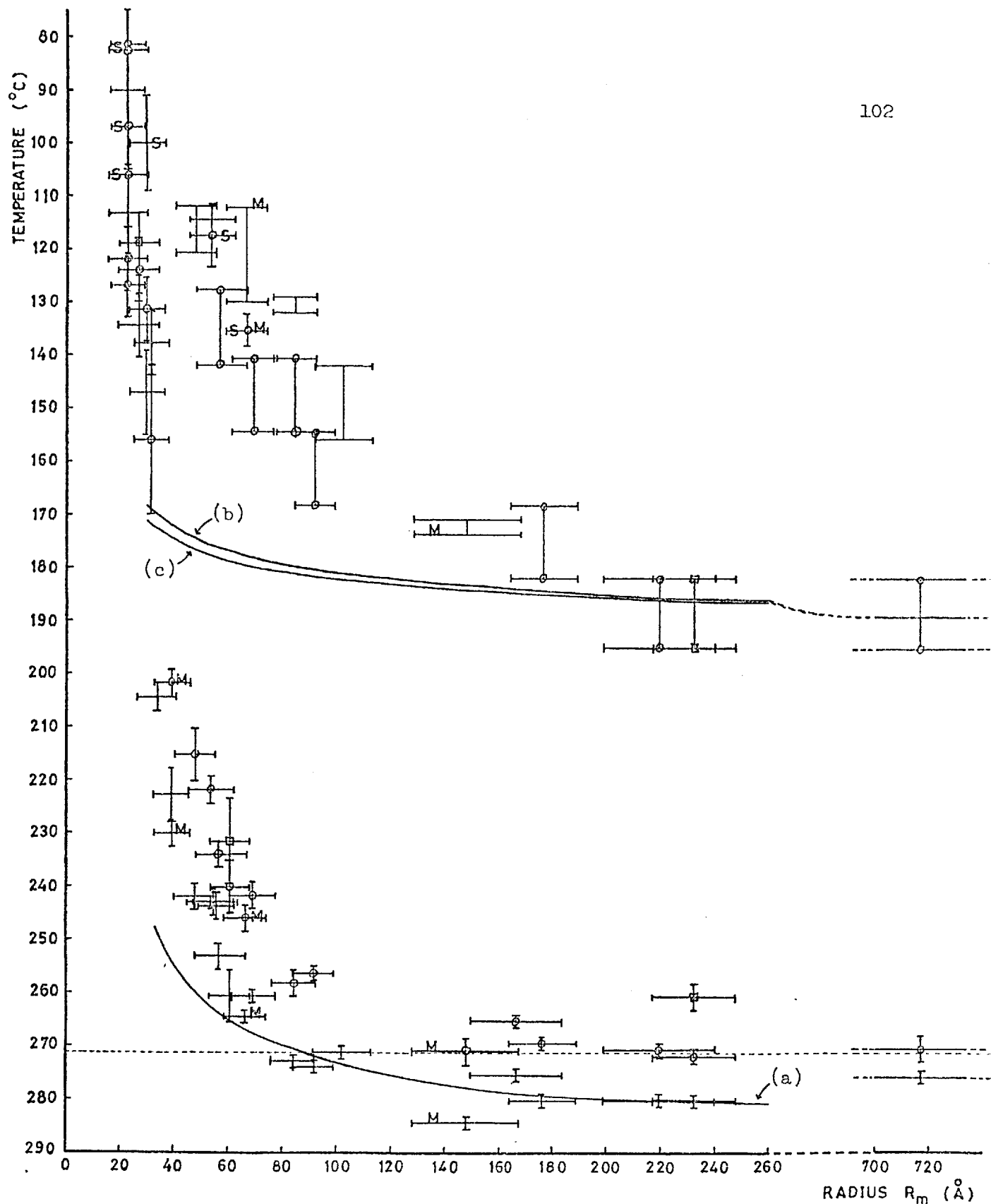


Figure 33. The results for bismuth

- (a) melting temperature according to equation (7-3)
- (b) solidification temperature from equation (7-18) (homogeneous nucleation)
- (c) solidification temperature from equation (7-20) (heterogeneous nucleation)

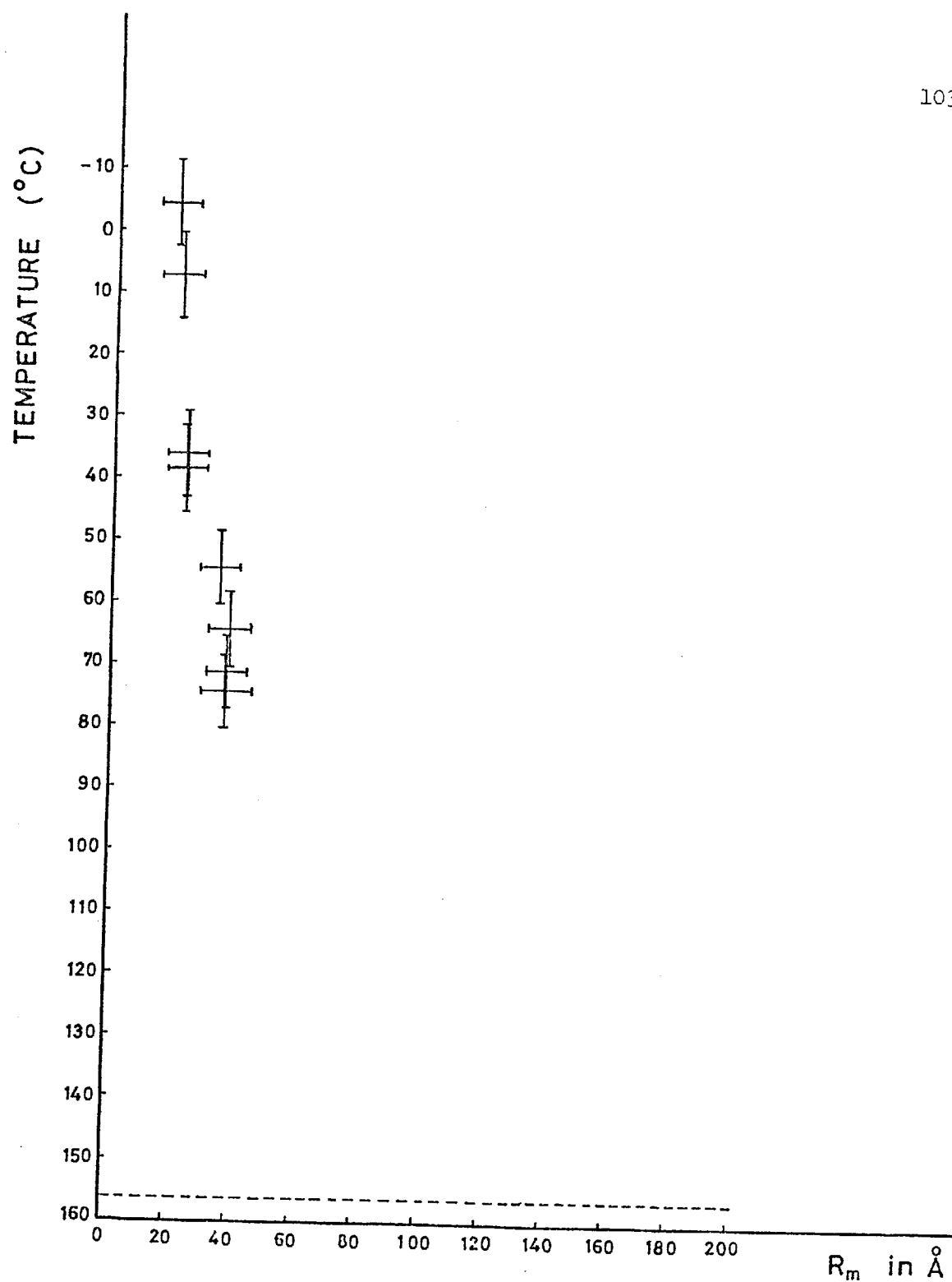


Figure 34. The results for indium

5.2 Estimation of errors

Sources of error are considered, broadly, in terms of errors in the melting temperature - § 5.2.1 to § 5.2.3 - and errors in the melting radius, R_m , associated with it - § 5.2.4 to § 5.2.7.

5.2.1 The temperature of the furnace

After the completion of the experiments, thermocouple I was calibrated by filling the cylindrical cavity of the furnace with lead, bismuth and tin, in turn, and noting the melting point of each as recorded on the Unipivot microammeter. This was achieved either by observing the arrest point on heating, or (with the cylinder of the furnace horizontal) by observing the dropping of a horizontal steel pin whose point was embedded some 1 mm. into the surface of the metal. The furnace was carefully cleaned between each melting point determination.

The results were found to be consistent with the copper-constantan thermocouple calibration of Roeser and Wensel (National Bureau of Standards) given on page 2631 of the "Handbook of Chemistry and Physics" (1959-60). Intermediate temperatures were therefore interpolated on the basis of their more detailed calibration. The temperature of the furnace, as estimated from the current registered by the Unipivot microammeter, should not be in error by more than 2°K .

5.2.2 The temperature difference between a deposit and the furnace

As indicated in § 2.9.2 (pg. 40), any temperature difference between a deposit and the furnace should not exceed 1°K in the absence of electron-beam heating.

It was ascertained - see § 4.2(i) (pg. 74) - that the melting temperature of a deposit of lead was reproducible on a second melting to within 3°K . The possibility of substantial heating of a deposit by the electron beam was investigated by melting a deposit of lead, consisting of crystallites of some $200 \text{ \AA}$ radius, twice; the beam current being increased for the second melting temperature determination to some three times the value usually employed. Appreciable beam heating would be expected to manifest itself in an apparent lowering of the melting temperature (as registered by thermocouple I) on the second melting:

however, the melting temperatures were found to coincide within the degree of reproducibility indicated. It is therefore concluded that any temperature difference between a deposit and the furnace arising from beam heating did not exceed some $1\frac{1}{2}^{\circ}\text{K}$ at the beam currents employed.

5.2.3 The photographic record

In determining the melting and solidification temperatures of a deposit, the diffraction pattern was recorded at temperature intervals of either 2.4°K or 1.2°K on heating, and of some 13°K on cooling - see § 3.2.

Three separate examinations (which were spaced over a period of some months) made of each photographic record, yielded three melting temperatures, each one inferred from the photographic record in the manner described in § 4.2. The mean of these was taken to be the melting temperature of the deposit. For the thinner deposits investigated, the three melting temperatures often exhibited a spread considerably larger than the temperature interval between successive diffraction patterns. This was a consequence of the low intensity and diffuse nature of the rings of the crystalline diffraction pattern, and of the slow variation of the pattern with temperature.

An error was estimated in each melting temperature based on the clarity of the diffraction record and the spread of the three melting temperatures. This error which was, of course, never less than the temperature interval between successive diffraction patterns, is that shown against the melting temperatures in tables 2-4 and shown in figures 32-34. It may be emphasised that this error does not include the possible systematic errors discussed in § 5.2.1 and § 5.2.2.

On examining the photographic record of solidification there was, in almost every instance, little doubt between which two successive diffraction patterns solidification had begun, and a smaller temperature interval between successive diffraction patterns would undoubtedly have made possible a better estimate of the solidification temperature. The uncertainty in the solidification temperature of a deposit is therefore represented in tables 2-4 and figures 32-34 by indicating the temperature interval within which solidification began - c.f. § 4.2 (p. 73).

5.2.4 Two sources of error in the radius R_m

In this section it is assumed that the limiting detectable volume, P_{CV} , is known accurately as a function of the nominal mean thickness of a deposit, z , and two possible sources of error in the radius, R_m , which is associated with the melting temperature of a deposit, are discussed. For convenience it is assumed that the limiting detectable volume is identical to the limiting detectable exposure, P_{CE} , and that its dependence on the deposit thickness is given exactly by the four straight lines in figure 31.

The limiting detectable exposure, P_{CE} , determined from the superposition experiments was surprisingly small for the thicker deposits: as a consequence the melting radius, R_m , evaluated from equation (5-1), was located extremely close to the upper limit of the size-distribution histogram. Even when the total number of crystallites of such a deposit measured was several hundred, the statistical significance of R_m seemed in doubt, because of the relatively small number of crystallites having radii greater than R_m .

Little evidence of contamination of the substrate was observed, either on the diffraction patterns taken of the substrate prior to evaporation - see § 3.2(iv) - or in the formation of the deposits examined in the electron microscope, which appeared very uniform. However, even if the surface of a substrate film was clean, any departure of the suspended film from perfect flatness would result in a spatial variation in the size distribution of the crystallites formed on evaporation onto the substrate, since the mass of metal impinging on unit area of the substrate is dependent on the angle of incidence of the metallic vapour on the substrate. As was remarked in § 4.1 (pg. 52), the histograms obtained from different areas of the same specimen were, in general, very similar: however, the more discriminating test of the uniformity of the deposit provided by comparing the figures for the nominal mean thickness of the deposit evaluated for different areas of the same deposit, indicated some lack of uniformity.

In order to obtain a quantitative impression of the uncertainty in R_m resulting from variation in the size distribution of the crystallites over the deposit, and also an idea of the statistical significance of R_m

particularly for the thicker deposits, the following procedure was adopted:

For each deposit, n histograms were constructed (where $n = 2, 3$ or 4 - see § 4.1 (pg. 52)), representing the size distribution of the crystallites on n equal, but widely separated, areas of the deposit. The volume-distribution histogram $v(R)$ - see equation (4-3) - and the nominal mean thickness were computed for each of the n areas (taken separately). The percentage, P_{CE} , for each of the n areas was then obtained from the data of figure 31. The values of the "melting radius" for the n areas (taken separately) - $R_m^1, \dots, R_m^n$ say - were calculated. The deviations of the radii $R_m^1, \dots, R_m^n$ from the value R_m computed for the data as a whole, were then evaluated as percentages of R_m , and the root-mean-square percentage deviation, p_s , calculated:

$$p_s = \frac{100}{R_m} \left(\frac{(R_m^1 - R_m)^2 + \dots + (R_m^n - R_m)^2}{n} \right)^{\frac{1}{2}}$$

Of 42 deposits of lead whose melting temperatures were investigated, only one showed a deviation p_s greater than 20 %, four showed a deviation p_s between 10 % and 20 %, eight between 5 % and 10 %, and the remaining 29 less than 5 %. Comparable results were obtained for bismuth and indium.

The lack of any apparent correlation between the percentage deviation, p_s , and the melting radius, R_m (in particular there was no apparent tendency for p_s to increase for the thicker deposits), allayed the fears indicated above concerning the statistical significance of R_m for the thicker deposits. It is felt that the numbers of crystallites measured constituted adequate samples for the statistical calculations.

There was, not surprisingly, a marked correlation between the percentage deviation, p_s , and the variation of the nominal mean thickness from area to area of a deposit: p_s being larger for the less uniform deposits. In order to weight the results in favour of those deposits which were seemingly (from the areas examined) more uniform, the percentage deviation, p_s , was incorporated into the estimation of the overall percentage error in each individual melting radius, R_m - see § 5.2.7.

5.2.5 The uncertainty in R_m consequent upon an imperfect knowledge of the limiting detectable volume, P_{CV}

In this section it is assumed that the limiting detectable volume may be identified with the limiting detectable exposure, P_{CE} .

Any error in the empirical relationship between P_{CE} and the deposit thickness, z , will result in an error in the radius, R_m , associated with the melting temperature of a deposit. To obtain a quantitative impression of the uncertainty in R_m , it is necessary to examine the experimental results shown in figure 31:

For deposits of lead on carbon, the scatter of the experimental points about the straight line fitted to the plot of $\log P_{CE}$ against $\log z$ suggests that the percentage P_{CE} corresponding to any particular film thickness z is probably in error by less than a factor of 2. (The portion of the plot corresponding to the range of film thicknesses over which melting temperatures were investigated is indicated by a continuous line.)

The superposition results for bismuth on carbon are less satisfactory, though only one of the experimental points shows a scatter from the straight line fitted, representing more than a factor of two in the percentage P_{CE} .

The results for lead on silicon monoxide and bismuth on silicon monoxide are not conclusive. The single result for lead on silicon monoxide is close to the plot for lead on carbon, which is to be expected if the diffuse scattering of electrons from a silicon monoxide substrate in the directions of the last rings to disappear (the $\sqrt{8}$ and $\sqrt{11}$ rings in the case of lead) does not differ much from the scattering of a carbon substrate in these directions. The scattering of both substrates in these directions is indeed comparatively weak and not marked by any dense halos.

The two results for bismuth on silicon monoxide are both displaced appreciably from the plot for bismuth on carbon. This is probably a consequence of the markedly higher scattering of the silicon monoxide substrates over that of the carbons, at the much smaller angle corresponding to the direction of the last bismuth ring to disappear.

It is felt that the straight lines in figure 31, fitted to the superposition results, probably represent the limiting detectable

exposure, P_{CE} , for any particular deposit thickness, z , to the degree of accuracy represented by a factor of 2 in the limiting detectable exposure, P_{CE} . The uncertainty in R_m resulting from this uncertainty in the limiting detectable exposure, was estimated in the following way:

Suppose z is the nominal mean thickness of a deposit, P_{CE} the corresponding limiting detectable exposure read from the appropriate plot in figure 31, and R_m the melting radius evaluated from equation (5-1). The radii R_{m2} (less than R_m) and R_{m1} (greater than R_m), obtained from equation (5-1) by taking the limiting detectable exposure to be $2P_{CE}$ and $\frac{1}{2}P_{CE}$ respectively, were computed. The deviations of the radii R_{m2} and R_{m1} from R_m were expressed as percentages p_2 and p_1 of R_m .

The values of p_2 and p_1 for a particular deposit were in most cases similar, and together they showed an increasing trend as the deposit thickness decreased (from some 1 % to some 6 % over the range of deposit thicknesses investigated for lead and bismuth). They were incorporated into the estimate of the overall percentage error in each individual melting radius - see § 5.2.7.

5.2.6 Electron microscopy and errors in R_m

The radius of a crystallite, calculated from a measurement made of the diameter of its image on an enlarged print of an electron-micrograph, may be in error both because the overall magnification of the print is not known accurately, and because the quality of the image of the crystallite is limited by the resolution of the electron microscope. Poor adjustment of the instrument, resulting in astigmatism or improper focusing, may further impair the quality of the image. (Errors in the diameters of the images of the crystallites arising from the build up of hydrocarbons on the deposits should have been small, as the time for which the electron beam was incident on a specimen, prior to the exposure of the micrographs, was reduced to a minimum.)

A ray diagram illustrating image formation in the electron microscope at high magnification is shown in figure 6 (pg. 28). In the present experiments, the intermediate and projector lens currents had fixed values, so that the image distance, v , for the objective lens was constant. Focusing was achieved by varying the focal length of the

objective lens, by adjustment of the objective lens current. Under these circumstances, a variation of 5 % in the distance, u , of the specimen from the objective lens results in a variation of 5 % in the magnification v/u of the objective lens, and thus in a variation of 5 % in the magnification of the final image on the photographic plate. The object distance, u , for the objective lens was approximately 5 mm., so that a change in the position of the specimen of some $\frac{1}{4}$ mm. corresponded to a variation of 5 % in the overall magnification of the instrument. The construction of the specimen holder and its mounting was such, that an uncertainty of this order in the positioning of the specimen on its insertion into the electron microscope was possible.

Accurate determinations of the magnification of the electron microscope - see § 3.5 - exhibited a spread of somewhat less than 5 % about the mean; presumably attributable to variations in the positioning of the specimen, since the accuracy of each individual determination should have been rather better than 2 %. The magnification of the optical enlarger employed to print the micrographs was determined by conventional methods, and should be in error by less than 1 %. It is concluded that the overall magnification of the final prints should not be in error by more than 5 %, and an error from this source of 5 % was associated with the calculated radius of every crystallite measured.

The astigmatism of the electron microscope was checked, and if necessary corrected, before almost every set of micrographs taken; by observing the images of circular holes in a specially prepared thick carbon film. Before taking each micrograph, the image was focused carefully: the optical microscope attached to the instrument enabled the image on the fluorescent screen to be observed in detail. However, in some cases, the quality of the final prints suggested that the limit of resolution of the electron microscope - some $12 \text{ \AA}^{\circ}$ - had not been attained. An error of from $12 \text{ \AA}^{\circ}$ to $16 \text{ \AA}^{\circ}$ was associated with the calculated diameters of the crystallites, depending upon the quality of the final enlarged prints.

The uncertainty in the melting radius, R_m , which results from the sources indicated above, was taken to be 5 % from the uncertainty in the overall magnification and from $6 \text{ \AA}^{\circ}$ to $8 \text{ \AA}^{\circ}$ consequent upon the limitations

of the image. This latter error was evaluated as a percentage p_r of R_m .

It was considered unnecessary to postulate any uncertainty in R_m arising from the measurement of the diameters of the images of the crystallites in 1 mm. or $\frac{1}{2}$ mm. increments - see § 3.6. These increments are somewhat smaller than the uncertainty in any particular crystallite diameter resulting from the limitations of the image (with the print at an overall magnification of 800,000).

5.2.7 Overall error in R_m

Referring to § 5.2.4 to § 5.2.6, the overall percentage error, $p_{lwr.}$ or $p_{upr.}$, in each individual melting radius, R_m , was taken to be the root of the sum of the squares of the percentage errors p_s , p_2 , 5 and p_r ; or p_s , p_1 , 5 and p_r ; respectively: the former representing the probable lower limit of R_m and the latter the probable upper limit. These two percentages were used to calculate the probable lower limit, $R_{lwr.}$, and probable upper limit, $R_{upr.}$, of R_m shown in figures 32-34 and tables 2-4.

5.2.8 Other sources of error

Although the processing of the photographic emulsions was not *strictly* standardised in the present experiments, the densities of the processed emulsions in the neighbourhood of the last ring to disappear (for a particular metal and substrate), did not vary by a factor as great as two. We may therefore conclude from the approximate result obtained in § 4.4(iii) (pgs. 90-91), that any errors in the melting radii resulting from this lack of standardisation were less than those corresponding to a change in the limiting detectable exposure of a factor of two. The errors were therefore less than the percentage errors p_2 or p_1 estimated in § 5.2.5.

One further possible source of error arose from the occasional use of Farmer's solution to reduce negatives that had been accidentally overdeveloped and were too dense to be examined conveniently. Concerning the action of this reducer, the Ilford Manual of Photography (1958) may be quoted (pg. 459):

"In theory a reducer of this kind does not affect the contrast of a negative except that the faintest densities may be entirely removed, ..."

The affect of reduction by Farmer's solution on the melting temperature ascribed to a particular photographic record was tested by comparing the melting temperatures ascribed before and after reduction. It was concluded that errors from this source could be neglected.

The detectability of a ring is not dependent on the exposure as such, but only on the final processed density of the emulsion (c.f. equations (4-13) and (4-14)). Slight breakage of the substrate film will therefore not affect the results of the melting temperature experiments, provided that the final densities of the negatives do not vary appreciably. Similarly, it will not affect the results of the superposition experiments, unless breakage occurs between the making of the two exposures. Some damage to the substrate film in the form of tears was often observed when a deposit was examined in the electron microscope, but it was not in general extensive enough to have materially influenced the results.

It will be noted that the conclusion

$$P_{CV} = P_{CE}$$

arrived at in § 4.4 is a fundamental link in the association of a particular radius, R_m , with the melting temperature of a metallic deposit. The validity of this conclusion rests, amongst other things, upon the assumption that " $F_C(\theta, T)$ is ... largely independent of the distribution and sizes of the crystallites provided they are small enough for the kinematic approximation to hold" (see pg. 87). Whilst the experimental evidence adduced below does not constitute a proof of the validity of the kinematic approximation over the range of crystallite radii investigated in the present experiments; it does show that the complete breakdown of the kinematic approximation represented by opacity of a crystallite to the electron beam, does not occur even for the largest crystallites investigated in the present experiments.

A portion of the next-to-thickest deposit of lead investigated, is shown in figure 35. The penetration of the crystallites by the 80 kV

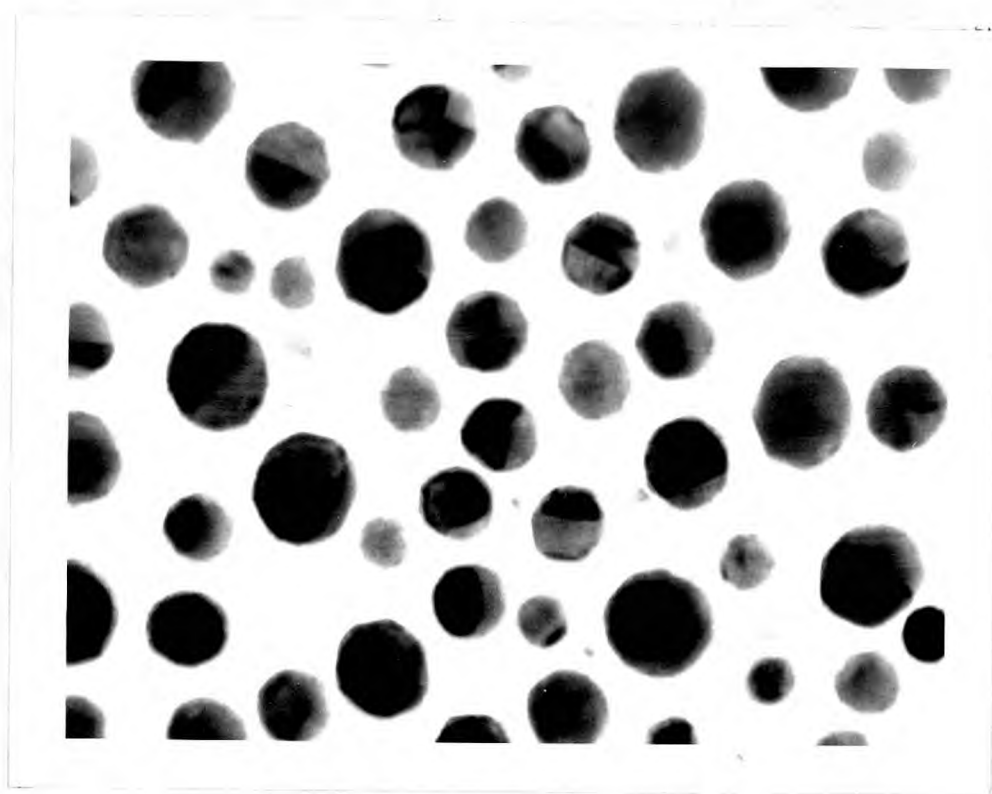


Figure 35. Electron micrograph ($\times 200,000$) of a lead deposit (on carbon) of nominal mean thickness $181 \text{ \AA}$. The print has been lightly exposed to illustrate the faults in the interiors of the lead crystallites.

electron beam is evident from the faults visible in the interiors of even the larger crystallites (some 350 Å radius). Similar effects were observed on the micrographs of all but the thinnest deposits (they are not visible on the prints in figures 11-19 because of the relatively longer exposures of these prints and the high contrast paper used). Further evidence of penetration of the larger crystallites by the 80 kV beam of the electron microscope was obtained by selected area diffraction, though the results were less conclusive because of the possibility that the diffraction arose only from the edges of the crystallites.

Although the accelerating voltage in the electron diffraction camera was only half that employed in the electron microscope, it is felt that over most of the range of crystallite radii investigated, the kinematic approximation of § 4.4 is probably good.

5.3 Observations of the profiles of crystallites viewed parallel to the substrate

By scratching a specimen with the point of a pin before its insertion into the electron microscope, tears may be produced in the substrate film, the edges of which have a tendency to curl under the influence of the electron beam. The profiles of the crystallites, as viewed parallel to the substrate, may be examined on these edges - see figure 36. At some distance from an edge the crystallites have approximately circular images, but as the curved edge is approached the profiles of the crystallites show a cap-like structure similar to figure 20 (b) or (a) (pg. 65).

Let h be the height of such a crystallite, R its radius, and $D (= 2R)$ its diameter; where D is the diameter which would be observed on viewing the crystallite perpendicular to the substrate - see figure 20. If the crystallite has the form of a segment of a sphere, the volume of the crystallite is

$$\pi h^2 \left(\frac{D}{2} - \frac{h}{3} \right)$$

The "equivalent radius", R_E , of the complete sphere whose volume is equal

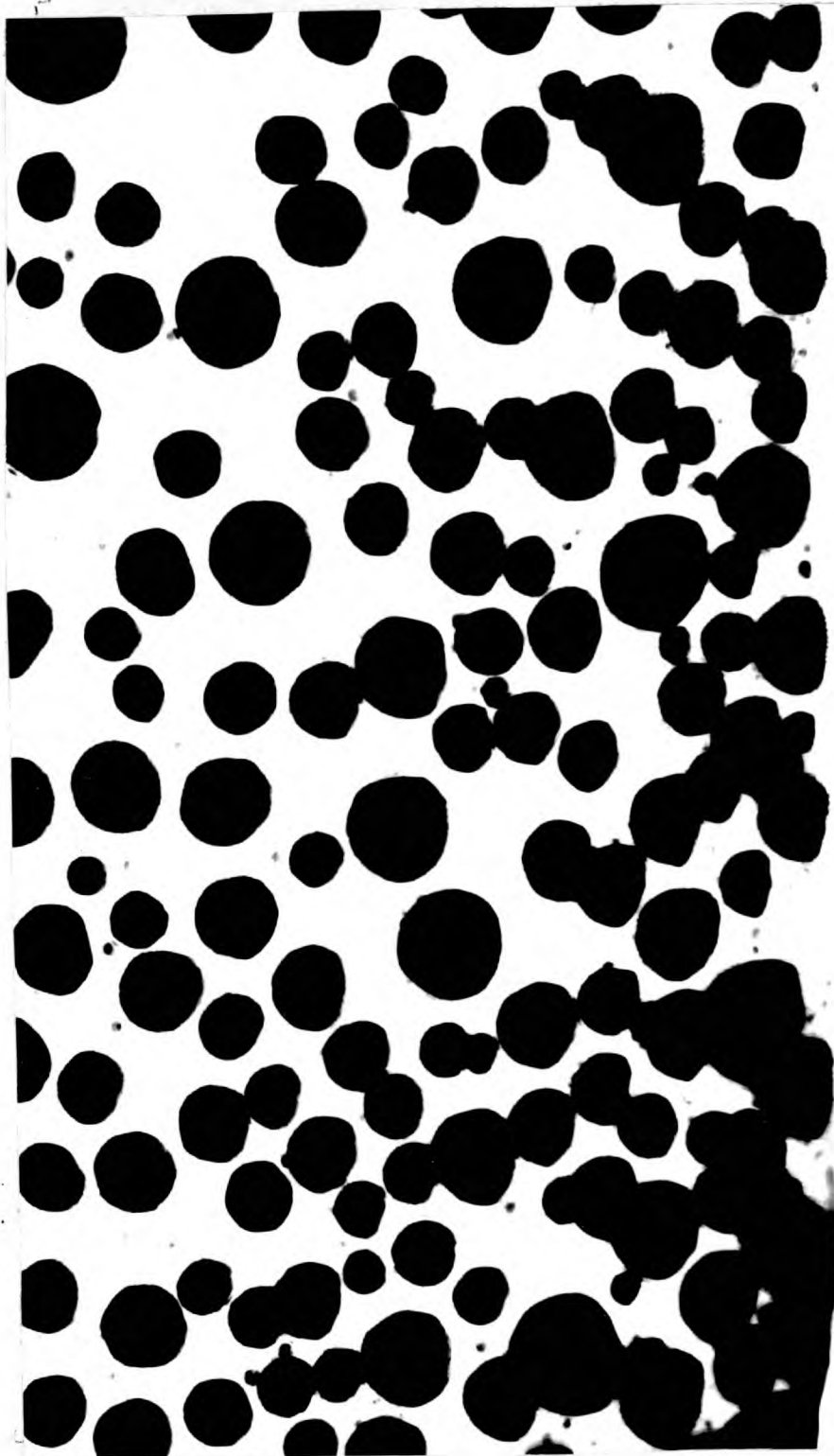


Figure 36. Electron micrograph ($\times 100,000$) of the lead deposit of nominal mean thickness $325 \text{ \AA}$ shown in figure 13, illustrating the change in the profiles of the lead crystallites as a curved edge of the carbon substrate is approached (on right-hand side of print).

to that of the crystallite is therefore

$$R_E = KR$$

where

$$K = \frac{h}{D} \left(3 \frac{D}{h} - 2 \right)^{1/3} \quad (5-2)$$

As here defined, K is the factor by which the observed crystallite radius must be multiplied in order to get the radius of a (hypothetical) spherical crystallite having the same volume as the actual crystallite.

For crystallites having the form of spherical caps, we may calculate the contact angle, θ , for a particular value of the ratio h/d using the formula

$$\sin (\theta - 90^\circ) = \frac{h - \frac{D}{2}}{\frac{D}{2}} = 2 \frac{h}{D} - 1 \quad (5-3)$$

For deposits of lead on carbon, bismuth on carbon and bismuth on silicon monoxide, micrographs were obtained showing the profiles of the crystallites viewed parallel to the substrate. Measurements were made of the diameters, D, and heights, h, of a number of crystallites: in the case of the thicker deposits, enlargements of the micrographs were printed and the measurements taken with a ruler from the prints, though for the thinner deposits the measurements were taken directly from the micrographs using a travelling microscope.

Measurements were made on 31 comparatively large ($\sim 440 \text{ \AA}$ radius) crystallites of lead on carbon, and the ratio h/d was computed for each. The average value of h/d was found to be 0.73, with 22 values lying within 10 % of the mean (i.e. between 0.66 and 0.80). The values of θ and K, calculated from the mean value of h/d and equations (5-3) and (5-2), were 117.4° and 0.93 respectively. These results are summarised, together with the other results obtained, in table 5.

Metal	Substrate	Number of crystallites measured	Mean radius of crystallites ($\text{\AA}$)	Average value of h/d	Number of crystallites having h/d within 10 % of average value	Contact * angle, θ ($^{\circ}$)	K **
Lead	Carbon	31	439	0.73	22	117.4	0.93
Lead	Carbon	5	117	0.77	5	122.7	0.95
Bismuth	Carbon	28	379	0.64	15	106.3	0.89
Bismuth	Carbon	6	134	0.81	4	128.3	0.97
Bismuth	Silicon monoxide	10	109	0.78	9	124.1	0.96

* Calculated from the average value of h/d and equation (5-3)

** Calculated from the average value of h/d and equation (5-2)

Table 5. Data from measurements of the profiles of crystallites viewed parallel to the substrate.

5.4 Discussion of the factors which may influence the melting temperature of a crystallite

5.4.1 The form of the crystallite, the nature of the substrate, and crystal defects

It is to be expected that the substrate will exert an influence on the melting of a crystallite which has a comparatively large area of contact with the substrate. The free energy of the crystal-substrate interface will be an important contribution to the free energies involved in the melting of the crystallite. The free energy per unit area of this interface will depend, in the absence of contamination, on the particular metal and substrate: for a given metal, the nature of the substrate should therefore effect the melting temperature of a small crystallite.

The melting and solidification of metallic deposits of lead and bismuth were investigated on two different substrates - carbon and silicon monoxide. Observations of the profiles of crystallites viewed parallel to the substrate (see § 5.3) were made at room temperature, after the completion of melting and solidification experiments. They showed that, on both substrates, each crystallite has an area of contact with the substrate comparable with the overall area of the crystallite. However, the plots of the results of the melting and solidification experiments on the respective substrates (see figures 32 and 33) suggest that there is no significant difference either between the melting temperatures of crystallites (of equal radius) on the two substrates, or between the solidification temperatures. These findings do not constitute a proof that the substrate has a negligible influence on the melting and solidification of the crystallites - the problem is discussed in § 6.3.1(v) with reference to specific models of melting - they may be a consequence of the similar natures of the two amorphous substrates. It would be interesting to examine the melting and solidification of crystallites on a crystalline substrate on which the crystals could be grown epitaxially.

The shape of a crystallite which minimises the free energy of the system "crystallite plus local substrate" is referred to as its "equilibrium form" - see § 6.3.1(i). After the condensation of a metallic

vapour onto a substrate at room temperature, the forms of the crystallites may well depart appreciably from their equilibrium forms - for example, they may have a larger area of contact with the substrate than the equilibrium forms. Once a crystallite has been melted, however, its form after solidification may be expected to reflect its equilibrium form at the temperature of solidification or possibly the equilibrium form of the liquid droplet from which it crystallised. Thus there may well be a difference between the morphology of a deposit after its condensation, and that after it has been melted and resolidified: this difference could result in a difference between the melting temperature ascribed to the deposit on its first melting and on subsequent meltings.

On raising the temperature of a crystallite, a change in the form of the crystallite might occur by volume or surface diffusion prior to the actual melting of the crystallite. A motivation for this process would only exist, however, insofar as the final form of the crystallite approximated more closely to its "equilibrium form" at the temperature in question. Such diffusional mechanisms would tend to reduce any difference between the first- and second-melting temperatures of a deposit, arising from structural changes in the deposit during the first melting. An observation of pre-melting structural changes in the deposits, made by heating deposits in the electron microscope, would raise the problem of the influence of the relatively much higher level of carbonaceous contamination in the electron microscope, on the diffusional mechanisms involved.

It was observed that the appearance of a lead deposit after melting and resolidification was very similar to that of the initial deposit produced by condensation onto a substrate at room temperature; moreover, the melting temperature of a resolidified deposit was found to be extremely close to that of the initially condensed deposit. In the case of bismuth, however, the appearance of the initially condensed deposit was markedly altered on melting and resolidification, the changes being similar to those reported by Hanszen (1966).

A theory of melting based on the contention that melting occurs when the free energy of formation of glide dislocation cores becomes

negative, has been developed by Kuhlmann-Wilsdorf (1965) - see also § 6.1. Such theories focus attention on the role of crystal defects in the melting process. The present experiments suggest certain interesting developments, whereby the dependence of the melting temperature of a crystallite on the presence of dislocations in the crystallite might be investigated:

As was mentioned in § 5.2.8, the resolidified crystallites photographed in the electron microscope showed an appreciable density of dislocations. Dislocations were also observed in vacuum condensed deposits which had not been melted, though no systematic attempt was made to compare the densities of dislocations in the two cases. The first-melting temperature of a vacuum condensed deposit of lead was found to be closely reproducible on further meltings, so that any marked difference in the density of dislocations in an unmelted deposit of lead and in a resolidified deposit would be interesting. It is possible that on heating a metallic deposit there would be a tendency for the dislocations to migrate out of the crystallites, so that repeated heating and cooling over a temperature interval below the melting temperature of the crystallites might well produce an aggregate of crystallites relatively free from dislocations. The melting temperature of such a deposit might differ appreciably from that of an untempered deposit.

5.4.2 Oxidation

The partial pressure of oxygen which will exist in equilibrium with a mixture of crystalline lead and red lead oxide (PbO) at any particular temperature, may be calculated from available thermodynamic data - see appendix 2. It is approximately 10^{-25} torr at the melting temperature of bulk lead (327.4°C). The corresponding figures for the partial pressure of oxygen in equilibrium with a mixture of crystalline bismuth and bismuth sesquioxide (Bi_2O_3) at 15°C , and with a mixture of indium and indium sesquioxide (In_2O_3) at the melting point of bulk indium, are both appreciably smaller than this. Since, in the present experiments, the partial pressure of oxygen in the diffraction camera was some 10^{-6} torr, all of the metallic deposits investigated would have a tendency to oxidise, both during the vacuum deposition and during the observation of

the melting and solidification. The rate at which oxidation occurred would be likely to increase as the temperature of the deposit increased. The extent of oxidation can only be assessed from experimental evidence.

The oxidation of indium has already been described - see § 4.2(iii) (pgs 75-76).

No evidence of oxidation was found on the photographic records of the melting and solidification of bismuth deposits. The bismuth deposits would be expected to oxidise to bismuth sesquioxide - see Hapase, Tare and Biswas (1967). The oxidation of bismuth has been observed, using electron-diffraction techniques, by Zar'yalova, Imamov and Pinsker (1965).

Faint, unidentified rings were observed on the photographic records of the melting and solidification of a few (at most 7) of the thicker deposits of lead. On three of the records - the three on which unidentified rings were most clearly visible - the same three rings could be seen. The rings were not visible on the diffraction patterns of the substrates before deposition, nor on the patterns of the deposits immediately after deposition; they became visible only after heating the deposits. The diameters of the rings corresponded to reflections from crystal planes having reciprocal plane spacings, $1/d$, of 0.420, 0.552 and $0.587 \text{ \AA}^{-1}$. These rings cannot be satisfactorily identified as belonging to any of the common oxides of lead, or to crystalline copper - compare the reciprocal plane spacings of the common oxides of lead and of crystalline copper given in appendix 1.

It is possible that the crystallites might first oxidise at their surfaces, and that the resulting thin layer of oxide might then protect the crystallites from further oxidation. If this happened, little or no evidence of this oxidation might result from the diffraction of electrons. It was therefore decided to investigate whether the presence of a small partial pressure of hydrogen, which might reduce such a layer, had any influence on the melting temperature of the deposits - see § 3.3.

The ratio of the partial pressure of hydrogen, p_{H_2} , to that of water vapour, $p_{\text{H}_2\text{O}}$, which can exist in equilibrium with a mixture of lead

and lead monoxide, may be calculated from available thermodynamic data - see appendix 2. At the melting point of bulk lead (327 °C), we find

$$p_{H_2}/p_{H_2O} \sim 10^{-5}$$

and the ratio varies by a factor of only 100 or so over the temperature range 15 °C to 327 °C. The corresponding ratio for equilibrium with a mixture of bismuth and bismuth sesquioxide at 15 °C (suitable figures were not readily available for a calculation at the melting point of bulk bismuth) is

$$p_{H_2}/p_{H_2O} \sim 10^{-11}$$

and for a mixture of indium and indium sesquioxide at the melting point of bulk indium (157 °C)

$$p_{H_2}/p_{H_2O} \sim 10^4$$

The partial pressure of water vapour in the residual gases in the electron diffraction camera was probably some 10^{-6} torr. The partial pressures of hydrogen - some 10^{-5} torr, see tables 2-4 - maintained during the deposition and melting of the deposits would therefore have had a tendency to reduce any lead or bismuth oxide formed on the metallic deposits, though reduction of indium sesquioxide was not to be expected. Experimentally it was found that the admission of hydrogen had no apparent influence on the melting temperature of deposits of lead, bismuth or indium. It was also found that it did not exert any inhibiting influence on the oxidation of indium deposits at temperatures above some 100 °C.

5.4.3 Adsorption and alloying

During the experiments described here, the pressure of the residual gases in the electron diffraction camera was measured by a Penning gauge which was situated immediately above the large vapour trap - see § 2.1 (pg. 17). At the completion of these experiments, the camera was pumped down to simulate the conditions during an actual experiment, but with the Penning gauge attached directly to the specimen chamber: the pressure registered by the gauge - 5×10^{-6} torr - suggested that the pressures measured during the actual experiments should not differ greatly from the pressures in the specimen chamber itself.

The effect of varying the residual gas pressure upon the melting temperature of metallic deposits was not investigated: this could provide a basis for further experimentation. However, it is quite possible that the partial pressures of the residual gases present (say $\sim 10^{-6}$ torr for oxygen and $\sim 4 \times 10^{-6}$ torr for nitrogen) might have an appreciable influence on the melting temperatures. Aside from actual oxidation, the adsorption of these gases at the surfaces of the crystallites would have the effect of lowering the specific surface free energy. This problem can be approached via the Gibbs adsorption equation - see § 6.3.1(vi). Interesting work on the effect of the residual gases present during condensation on the electrical properties of indium deposits has been done by Caswell (1961).

The possibility that the metallic deposits investigated might alloy with foreign materials requires investigation:

The "spectroscopically-pure" metals used, were supplied by Johnson Matthey Chemicals Ltd. with the following specifications:

	total metallic impurity (parts per million) not exceeding
Lead	10
Bismuth	10
Indium	5

On the basis of these figures, for lead crystallites of radius $100 \text{ \AA}$, one

would expect not more than 1.3 metallic impurity atoms per crystallite. Clearly this level of impurity would not materially affect the results.

We may consider whether copper atoms might diffuse across the substrate and either be adsorbed at the surfaces of the crystallites, lowering the specific surface free energy, or alloy with the material of the crystallites. The solid-solubilities of copper in lead, bismuth and indium are, nevertheless, very small; moreover, the eutectic temperatures lie only 1 °C, 1 °C and 2.4 °C, respectively, below the melting points of the pure metals - see Hansen and Anderko (1958), pgs. 609, 308 and 590. Thus the alloying of copper with the material of the crystallites should not affect their melting temperatures greatly. No evidence of the electron diffraction pattern of crystalline copper was found on any of the photographic records - the reciprocal plane spacings of crystalline copper are given in appendix 1.

Another possibility is that the metallic crystallites might alloy by dissolving the residual gases in the vacuum. However, the solubility of oxygen in liquid lead at 350 °C is small (0.0017-0.0078 atomic % oxygen), and nitrogen and hydrogen are insoluble - see Hansen and Anderko (1958), pgs. 1064, 985 and 789. The solubility of oxygen in liquid bismuth at 400 °C is 0.00034 weight % oxygen, and nitrogen and hydrogen are insoluble - see Hansen and Anderko (1958), pgs. 324, 321 and 312. Indium forms a nitride, InN, having a structure of the wurtzite type - see Hansen and Anderko (1958), pg. 852 - no evidence of this was found.

CHAPTER 6

THEORETICAL CONSIDERATIONS ON THE MELTING AND SOLIDIFICATION OF METALLIC CRYSTALLITES

6.1 Discussion

The experiments described concern the influence of the size of a metallic crystallite on the temperature at which it melts and solidifies.

The structures of liquids are at present still very imperfectly understood, and the problems of relating their properties to their interatomic or intermolecular forces are formidable. Various models have contributed to a valuable physical insight into the structure of liquids and liquid surfaces, and among these may be mentioned the "hole" model, the "cell" model, and the "significant structure" or "cybotactic" model - see, for example, Hill (1956), Green (1960), Levelt and Cohen (1964), Pryde (1966), Symposium (1963), and Symposium (1967).

Since the concept of the radial distribution function of the molecules of a liquid came into being as a result of X-ray studies of liquids in the nineteen twenties, considerable progress has been made in relating this to intermolecular forces, at least for a "simple" liquid like argon whose molecules can be considered to be spheres interacting with central forces. Very wide use is being made of radial distribution functions, obtained from data on X-ray and neutron scattering, in studying the intermolecular forces, equations of state, and properties of liquids. Machine calculations have made available the equations of state of assemblies of particles interacting with chosen pair potentials: these assemblies resemble real liquids and provide a check on the theoretical methods being employed.

In the case of liquid metals the problems are further complicated by the presence of conduction electrons. Parallel to the current work - see, e.g., Harrison (1966) - on crystalline metals using screened-ion model potentials, extensions of this method to liquid metals are being made - see, e.g., Ballentine (1966). Although the interactions between ions in a liquid metal have usually been assumed to be of the "many-body" type, recent work by March and his colleagues - see Johnson and

March (1963) and Johnson, Hutchinson and March (1964) - has made use of pair potentials. In this work, pair potentials between the ions in liquid metals, derived on the basis of the Born-Green or Percus-Yevick theories from radial distribution functions, were used to calculate viscosities and surface tensions: the results obtained were in good agreement with experiment. The approximate validity of such methods has opened up important new avenues in the study of the melting and crystallisation of metals.

Because of the difficulties associated with the structures of liquids, there are inevitably difficulties in understanding the mechanisms of melting. Excellent reviews of the various theories of fusion have been written by Temperley (1956), pg. 97, and Ubbelohde (1965), pg. 43.

Many of the models employed for studying fusion have not involved a detailed characterisation of the liquid structure, but have pivoted on the consideration that a crystalline structure becomes mechanically unstable at a certain temperature. An early example of such an idea is due to Lindemann (1910). Using the Einstein model of a vibrating solid, Lindemann proposed that as the temperature rose, and the vibrations of the atoms about their equilibrium positions in the lattice increased progressively in amplitude, a temperature would be reached at which the atomic vibrations interfered mutually to such an extent that the crystal became mechanically unstable. He supposed that this would occur, when the amplitude of movement of an atom attained a critical fraction of the distance between the equilibrium positions of neighbours. From this he deduced the melting point formula

$$T_m = C v_E^2 V_S^{2/3} M$$

where v_E is the characteristic frequency of the Einstein solid

V_S is the molar volume

M is the atomic weight

and C is a constant depending on the crystal structure

Later attempts to demonstrate that a crystal structure will become unstable at a certain temperature have been made by Herzfeld and

Geopfert-Mayer (1934), who considered the temperature at which the bulk modulus of a Debye lattice would vanish; by Born (1939), who investigated the temperature at which the shear modulus of a crystal would become zero; by Bonfiglioli, Ferro and Montalenti (1952) and McLachlan and Chamberlain (1964), in both cases returning to a criterion of vibrational instability; and by Brout (1965) using molecular field theory.

It should be mentioned that the above models, which have often been termed one-phase models, apply to ideal crystal structures. Moreover, they represent an upper limit to the melting temperature, as they do not involve the evaluation of the partition functions of both the solid and the liquid state, and so cannot take account of the possibility that the liquid phase might become competitive at a lower temperature. The importance of crystal defects, both point defects and dislocations, in the melting process has also been discussed: a theory of melting due to Kuhlmann-Wilsdorf (1965) is based on the contention that melting occurs when the free energy of formation of glide dislocation cores becomes negative, and Gibbs (1964) has investigated the assumption that the solid-liquid phase change occurs when a certain fraction of lattice sites are vacant.

We may now turn our attention to the theories of fusion which attempt to describe both the solid and the liquid phases. Among these is that due to Fowler and Guggenheim (1939), who employed the Einstein model of a crystalline solid and the related simple-harmonic-oscillator model of a liquid. Another such theory, which characterises the solid and the liquid phases by two distinct but closely related models, is the "cybotactic" theory of melting. Very considerable interest has centred around the work of Lennard-Jones and Devonshire (1939a, 1939b) - see also Lennard-Jones (1940), Rowlinson and Curtiss (1951), de Boer (1952) and Barker (1956). In this, both phases are represented by a single model, and the solid is pictured as melting into a quasi-crystalline liquid by a (positional) order-disorder transition.

The model of melting of Lennard-Jones and Devonshire has lately been discussed by Ubbelohde (1965), pp. 199-213. The characterisation of the liquid state in the work of Lennard-Jones and Devonshire is usually referred to as the "cell" model. This model was early extended to a

consideration of the properties of liquid surfaces - see Lennard-Jones and Corner (1940), Corner (1948), the appendix to the paper by Hill (1952), and Prigogine and Saraga (1952) - for a recent commentary see Defay, Prigogine, Bellemans and Everett (1966), pgs. 145-153. With so much work already done, there should be no real difficulty in obtaining an expression for the size dependence of the melting temperature of a small, inert-gas crystallite, on the basis of the Lennard-Jones and Devonshire approach. The application of these ideas to the melting of a small metallic crystallite is dependent upon the possibility of representing the interactions between metallic ions by pair-central potentials. The work of March et al. (op. cit.) suggests that this can be done, though the influence of surface on the pair potential between metallic ions is still under investigation - March (private communication).

A formulation of the melting mechanism of metals in terms of order-disorder processes is likely to evolve in the near future. Work on the melting of close-packed metals by Enderby and March (1966a, 1966b, 1967) - see also March (1966, 1968) - has yielded an expression for the constant (the constant C above) in the Lindemann melting relationship, so that we already have a semi-quantitative understanding of this law for metals. However, at the present time, a thermodynamic interpretation of the results of the present experiments on the melting of small metallic crystallites is felt to be the most pertinent: the remainder of this chapter is therefore devoted to such an approach.

6.2 Capillarity theory

The branch of thermodynamics which deals with interfaces between phases and their role in determining equilibrium in a system, is known as capillarity theory. Because of its importance in such fields as nucleation theory, adsorption, sintering, and the behaviour of small droplets, there has been considerable interest in capillarity theory in recent years particularly in its application to crystalline surfaces: this has resulted both in a deeper understanding of the significance of the various superficial thermodynamic quantities in terms of the detailed atomic structure of surfaces, and in a derivation of new results. Nevertheless, the methods which will be used here are essentially those established by Gibbs (1876-1878), which are still found to be of sufficient rigour and generality.

Before discussing specific thermodynamic models resembling the melting of a small metallic crystallite, it will be convenient to derive some general results appertaining to interfaces separating homogeneous phases. In doing this, the framework constructed by Gibbs for the treatment of fluid-fluid interfaces (its suitability has been discussed by Tolman (1948)) will be outlined; the points at which it becomes unsatisfactory for the treatment of crystalline-fluid interfaces noted, and an approach largely due to Gibbs appropriate to crystalline-fluid interfaces will be indicated.

6.2.1 Designation of superficial quantities

The term "surface of discontinuity" was coined by Gibbs to denote the non-homogeneous film which separates homogeneous or nearly-homogeneous masses, for which the more recent term "capillary layer" due to P.S. Epstein is now in common use. Gibbs also introduced the term "dividing surface": by this he understood a geometrical surface, in or very near to the physical surface of discontinuity, passing through all points "similarly situated with respect to the condition of the adjacent matter". There are clearly an infinite number of such dividing surfaces (for a particular surface of discontinuity), all parallel to one another and sensibly coincident with the physical surface of discontinuity. It will be assumed here that there is no difficulty in constructing such a

surface for a crystalline-fluid interface.

Consider a closed surface which contains a portion $\underline{s}$ of area s of a particular dividing surface, and extends on either side of it into the regions of homogeneity of the two phases; that portion of the closed surface which lies in the inhomogeneous film being everywhere normal to the dividing surface. The dimensions of $\underline{s}$ are considered to be small compared with the local radii of curvature of $\underline{s}$. Suppose that the closed surface contains a total mass M having an energy ϵ (now referred to as the "internal energy") and entropy η : Gibbs argues with delicacy the question of the apportionment of energy between the material on either side of the imaginary closed surface - see Gibbs (1928), pg. 220.

Consider the hypothetical situation in which the two phases extend homogeneously right up to the dividing surface (in the case of a crystalline phase, the shear strain is regarded as extending unchanged up to the dividing surface). Suppose that in this hypothetical system, the two volumes v' and v'' , into which the volume within our closed surface is separated by the dividing surface, contain masses M' and M'' having energies ϵ' and ϵ'' and entropies η' and η'' - see figure 37(a). In order to make the total mass, energy and entropy within the closed surface identical in this hypothetical system and in the actual system, we ascribe a mass M^s , energy ϵ^s and entropy η^s to the dividing surface (in the hypothetical system) such that

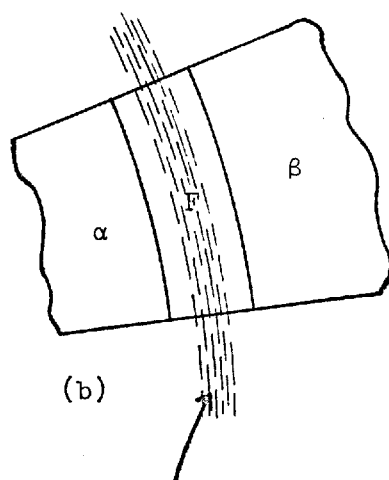
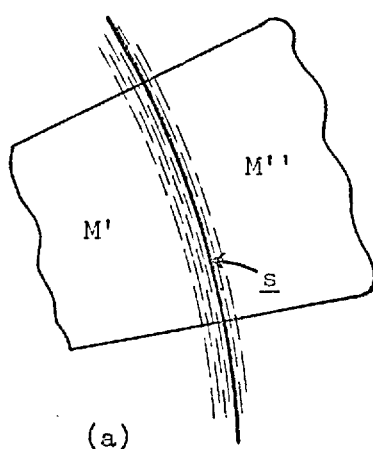
$$M = M' + M'' + M^s \quad (6-1)$$

$$\epsilon = \epsilon' + \epsilon'' + \epsilon^s \quad (6-2)$$

$$\text{and } \eta = \eta' + \eta'' + \eta^s \quad (6-3)$$

Suppose that the mass M is made up of masses $m_1, m_2, \dots$ etc. of the various components contained within the system of which we are considering a part, and that the masses M' and M'' are composed of masses $m_1', m_2', \dots$ and $m_1'', m_2'', \dots$. Then we ascribe masses $m_1^s, m_2^s, \dots$ etc. to the dividing surface such that

$$\begin{aligned} m_1 &= m_1' + m_1'' + m_1^s \\ m_2 &= m_2' + m_2'' + m_2^s \\ &\text{etc.} \end{aligned} \quad (6-4)$$



inhomogeneous region
("surface of discontinuity")

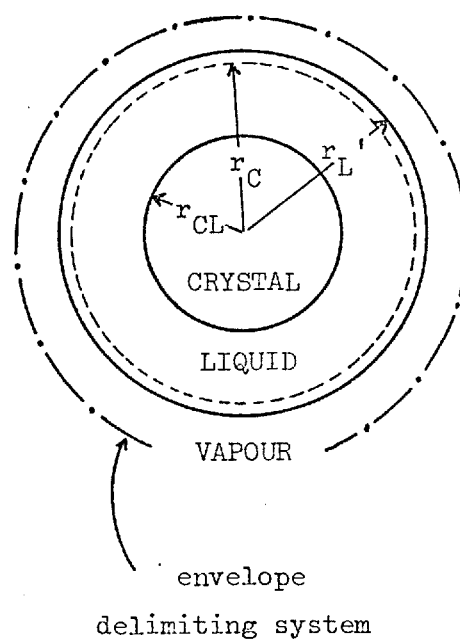


Figure 38. The
"liquid-shell" model

Figure 37 (a) and (b).

Interface between two phases

It is clear that the quantities M^S , m_1^S , m_2^S , ..., ϵ^S , and η^S , which are referred to as the superficial masses, energy and entropy, are dependent on the particular dividing surface chosen.

We may further define the quantities Γ , Γ_1 , Γ_2 , ..., ϵ_s , and η_s , which are termed the superficial densities of mass, energy and entropy, by the equations

$$\Gamma = \frac{M^S}{s}, \quad \Gamma_1 = \frac{m_1^S}{s}, \quad \text{etc.}, \quad \epsilon_s = \frac{\epsilon^S}{s}, \quad \text{and} \quad \eta_s = \frac{\eta^S}{s} \quad (6-5)$$

6.2.2 Conditions of local equilibrium of an interface derivable from consideration of local mass and entropy variations (c.f. § 6.2.3)

Certain relationships involving the superficial quantities defined above may be obtained as criteria of the local equilibrium of a portion of an interface. The infinitesimal reversible variations, by a consideration of which the relationships are obtained, involve entropy, mass of the various components, and form of the dividing surface - this last is discussed in § 6.2.3.

For a crystalline-fluid interface, if the crystalline material is regarded as dislocation free, such variations must be consistent with the maintenance of the continuity of the lattice. The entropy variations may be regarded as unaffected by this constraint, and lead, both for a fluid-fluid and for a crystalline-fluid interface, to the local uniformity of the temperature in equilibrium. The significance of this constraint when considering mass variations, depends upon whether the crystalline material is regarded as ideal or quasi-ideal (where the latter term admits of the existence of point defects in the material). Whereas in the case of a fluid-fluid interface, the mass variations imply the local uniformity of the chemical potentials of the various components; for a crystalline-fluid interface the chemical potential (as most conveniently defined) of the substance of the solid is, in general, not uniform in equilibrium (for a full understanding of the intention of this remark, please read to the end of § 6.2.3).

The local uniformity of the chemical potentials for a fluid-fluid interface in equilibrium is demonstrated (see below for details) by

considering a small envelope which embraces a portion of the interface, and is itself divided into a number of (contiguous) regions. Variations in the masses contained in these several regions are supposed to be constrained only by the condition that the total mass (of each component) within the envelope shall be constant. However, for a crystalline-fluid interface, any mass variation in such a wholly- or partially-crystalline region which altered the associated lattice parameter, would, because of the long-range order, imply dependent mass variations in adjacent crystalline regions. The demonstration of the local uniformity of the chemical potentials revolves around the independence of the mass variations. Such independence can only be achieved for a crystalline region, for variations in the mass of the substance of the solid which do not alter the associated lattice parameter, and this means in the case of a quasi-ideal crystalline region, variations in the mass resulting from the movement of point defects (interstitials or vacancies) across its surfaces. A chemical potential may be associated with such mass variations - see Herring (1952), pg. 37 - and its value will be equal to the chemical potential of the substance of the solid in the fluid phase - see Herring (1952), pg. 40, and Herring (1949), pg. 150.

For the purpose of investigating the local equilibrium of a fluid-fluid interface in detail, it is convenient to examine the internal equilibrium of the mass M - see § 6.2.1 - within the closed surface. Consider the volume within our closed surface to be divided into three regions α , F and β - see figure 37(b) - having volumes v^α , v^F and v^β , by two surfaces close to the dividing surface (and on either side of it) lying within the regions of homogeneity of the two phases. We suppose that the mobility of the components within the closed surface is not limited, and that no one component can be formed out of the others. Suppose that the masses contained within the three regions α , F and β are M^α , M^F and M^β having energies ϵ^α , ϵ^F and ϵ^β and entropies η^α , η^F and η^β . Suppose that the masses M^α , M^F and M^β are composed of masses $m_1^\alpha, m_2^\alpha, \dots$; $m_1^F, m_2^F, \dots$; and $m_1^\beta, m_2^\beta, \dots$ (respectively) of the different components.

The internal equilibrium of the mass M^α (constrained within the fixed volume v^α) necessitates for reversible variations

$$\delta \epsilon^\alpha = t^\alpha \delta \eta^\alpha + \sum_i \mu_i^\alpha \delta m_i^\alpha \quad (6-6)$$

where t^α is the absolute temperature of the mass M^α

i refers to the i^{th} component

and the equation is regarded as defining the quantities μ_i^α which are termed the chemical potentials of the various components in the mass M^α .

Referring to equation (6-6), it may be noted that the energy of the mass M^α after the variation, $\epsilon^\alpha + \delta \epsilon^\alpha$, is specified as being that which would pertain to the mass M^α , if there were no discontinuity at the surface bounding M^α after the variation. As has been indicated by Gibbs (1928), pg. 220, the apportionment of energy on this basis does not affect the total amount of energy, and the mass M^α may be regarded as isolated.

An equation exactly analogous to equation (6-6) pertains to the mass M^β :

$$\delta \epsilon^\beta = t^\beta \delta \eta^\beta + \sum_i \mu_i^\beta \delta m_i^\beta \quad (6-7)$$

Furthermore, the internal equilibrium of the lamelliform mass M^F , when its boundaries are fixed, necessitates for infinitesimal reversible variations

$$\delta \epsilon^F = t^F \delta \eta^F + \sum_i \mu_i^F \delta m_i^F \quad (6-8)$$

where t^F is the absolute temperature of the mass M^F

and the equation defines the quantities μ_i^F which are termed, by an extension of the terminology for homogeneous phases, the chemical potentials of the various components in the mass M^F .

It is necessary for the internal equilibrium of the whole mass M , when the various surfaces are considered to be fixed, that

$$t^\alpha \delta \eta^\alpha + \sum_i \mu_i^\alpha \delta m_i^\alpha + t^\beta \delta \eta^\beta + \sum_i \mu_i^\beta \delta m_i^\beta + t^F \delta \eta^F + \sum_i \mu_i^F \delta m_i^F = 0 \quad (6-9)$$

for all reversible variations subject (only) to the equations of condition

$$\delta \eta^\alpha + \delta \eta^\beta + \delta \eta^F = 0 \quad (6-10)$$

and for each component i

$$\delta m_i^\alpha + \delta m_i^\beta + \delta m_i^F = 0 \quad (6-11)$$

To satisfy the above condition, it is necessary and sufficient that: the temperatures of the two homogeneous regions α and β and of the inhomogeneous film F be the same - t say; and that insofar as any component i may be found in the three regions and its chemical potentials μ_i^α , μ_i^β and μ_i^F in these regions may thus be defined, they are subject to the condition

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^F = \mu_i \text{ say} \quad (6-12)$$

Following from the above, the definition of the chemical potential of the component i in the mass M^α may be written

$$\mu_i^\alpha = \left. \frac{\partial (E^\alpha - t \eta^\alpha)}{\partial m_i^\alpha} \right|_{t, m_j^\alpha \neq i, v^\alpha} \quad (6-13)$$

We may extend these results for a fluid-fluid interface to the case of a crystalline-fluid interface in the following way:

When the region α is part of a quasi-ideal crystal and the region β is fluid, equations (6-6) and (6-8) will only represent the (internal) energy variations adequately if the shear strain of the crystalline material is specified. In addition, it is necessary to stipulate that the mass variations δm_i^α and δm_i^F in equation (6-9) do not alter the lattice parameter associated with the crystalline material, otherwise equation(s)

(6-11) is not the only constraint on the mass variations.

For the crystalline-fluid interface, equation (6-12) may be replaced by

$$\mu_i^\alpha(c) = \mu_i^\beta = \mu_i^F(c) = \mu_i \text{ say} \quad (6-14)$$

where the chemical potential $\mu_i^\alpha(c)$ is defined subject to the constraints that the number of unit cells in the crystalline region α , N_c^α , shall remain constant and the shear strain unchanged:

$$\mu_i^\alpha(c) = \left. \frac{\partial(\epsilon^\alpha - t\eta^\alpha)}{\partial m_i^\alpha} \right|_{t, m_j^\alpha \neq i, N_c^\alpha, v^\alpha, \text{ shear strain}} \quad (6-15)$$

and $\mu_i^F(c)$ is similarly defined, insofar as the film F containing the inhomogeneous layer may be regarded as partially crystalline in nature. Compare Herrings (1952), pgs. 37 and 40, and Herring (1949), pg. 150.

For a reversible variation of the mass M, when

- 1) the surface enclosing M is regarded as fixed, and
- 2) the variation does not alter the lattice (either its parameter or its shear) associated with any crystalline material,

we may now write

$$\delta\epsilon = t\delta\eta + \sum_i \mu_i \delta m_i \quad (6-16)$$

If, in addition,

- 3) this variation does not change the form $\underline{s}$ of the dividing surface ("similarly situated with respect to the condition of the adjacent matter" in accordance with some previously-chosen criterion),

we have for the (homogeneous) masses M' and M'' in our hypothetical system (whose volumes are unchanged by the variation)

$$\delta\epsilon' = t\delta\eta' + \sum_i \mu_i \delta m_i' \quad (6-17)$$

$$\text{and } \delta\epsilon'' = t\delta\eta'' + \sum_i \mu_i \delta m_i'' \quad (6-18)$$

Subtracting equations (6-17) and (6-18) from (6-16), we have

$$\delta\epsilon - \delta\epsilon' - \delta\epsilon'' = t(\delta\eta - \delta\eta' - \delta\eta'') + \sum_i \mu_i(\delta m_i - \delta m_i' - \delta m_i'')$$

and hence, with reference to equations (6-2) to (6-4), we obtain

$$\delta\epsilon^s = t\delta\eta^s + \sum_i \mu_i \delta m_i^s \quad (6-19)$$

Equation (6-19) is valid for any reversible variation of the mass M (initially in equilibrium) subject to the constraints 1) to 3) enumerated above.

At this juncture it is convenient to define a new quantity, σ , by the equation

$$\sigma = \epsilon_s - t\eta_s - \sum_i \mu_i \Gamma_i \quad (6-20)$$

The quantity σ will be termed, after a suggestion by Mullins - see Mullins (1963), pg. 18, the "specific surface work".

It is, perhaps, helpful to observe that equations (6-16) to (6-20) are applicable both to a fluid-fluid interface and to a crystalline-fluid interface, and that μ_i is considered to be defined by equation (6-12) or (6-14), whichever is appropriate.

The quantity σ (which clearly depends upon the particular dividing surface chosen) becomes, in the case of a single-component system in which the dividing surface is chosen to make the superficial density of mass vanish, the specific surface Helmholtz free energy; and in the case of a fluid-fluid interface when the dividing surface chosen is the "surface of tension" (see § 6.2.3), the surface tension. On account of this latter property σ is still most commonly referred to as the surface tension.

Referring to equation (6-19), we may distinguish the case when both the initial and the final states of the mass M are equilibrium states by writing

$$d\epsilon^S = t d\eta^S + \sum_i \mu_i dm_i^S \quad (6-21)$$

from which, with reference to equations (6-5), we obtain

$$d\epsilon_s = t d\eta_s + \sum_i \mu_i d\Gamma_i \quad (6-22)$$

Differentiation of equation (6-20) yields

$$d\sigma = d\epsilon_s - t d\eta_s - \eta_s dt - \sum_i \mu_i d\Gamma_i - \sum_i \Gamma_i d\mu_i \quad (6-23)$$

From equations (6-22) and (6-23) we find

$$d\sigma = - \eta_s dt - \sum_i \Gamma_i d\mu_i \quad (6-24)$$

This equation is the Gibbs adsorption equation, and is valid for any variation in the mass M from an initial to a final equilibrium state, which satisfies the conditions 2) and 3) enumerated above. In the case of a fluid-fluid interface, it can be shown that the equation remains valid for a variation in which the orientation and area s of the surface $\underline{s}$ change, provided the curvature is unaltered: correction terms must be added if the curvature of the surface changes - see Buff (1951) - unless the dividing surface chosen is the surface of tension. For a crystalline-fluid interface, the Gibbs adsorption equation remains valid for a variation which changes the area s of the surface $\underline{s}$ without altering the orientation or curvature of $\underline{s}$.

6.2.3 Conditions of local equilibrium of an interface derivable from consideration of local variations in the form of the interface

(c.f. § 6.2.2)

We now consider terms which shall represent the variation, under the constraints of constant temperature and chemical potentials in our mass M , of the quantity

$$\delta \epsilon^s - t \delta \eta^s - \sum_i \mu_i \delta m_i^s \quad \text{c.f. equation (6-19).}$$

due to variation in the form of $\underline{s}$: under these constraints we may write

$$\begin{aligned} \delta \epsilon^s - t \delta \eta^s - \sum_i \mu_i \delta m_i^s &= \delta (\epsilon^s - t \eta^s - \sum_i \mu_i m_i^s) \\ &= \delta (s\sigma) \end{aligned} \quad (6-25)$$

When the interface is between two fluid phases, we may represent $\delta(s\sigma)$ quite generally by an expression of the form - see Gibbs (1928), pg. 225

$$\delta(s\sigma) = \gamma \delta s + C_1 \delta c_1 + C_2 \delta c_2$$

where γ , C_1 and C_2 denote quantities which are determined by the initial state of the system

and c_1 and c_2 denote the principle curvatures of the surface $\underline{s}$

When the thickness of the inhomogeneous film is small compared with the radii of curvature of the surface $\underline{s}$, the dividing surface may be chosen such that $C_1 + C_2 = 0$ - this dividing surface is termed the "surface of tension". If we assume, with Gibbs, that terms in $C_1 - C_2$ may be neglected for the surface of tension, we obtain

$$\delta(s\sigma) = \gamma \delta s$$

so that the explicit dependence of σ on curvature disappears, and

$$\delta(s\sigma) = \sigma \delta s \quad (\sigma = \gamma) \quad (6-26)$$

The result (6-26) is an approximation in the general case when $c_1 \neq c_2$ - see Buff (1951) - but is exactly true for a spherical interface.

For a crystalline-fluid interface, no such simple expression may be obtained for the variation of $s\sigma$ with the form of $\underline{s}$, and it is convenient to consider possible variations in the form of $\underline{s}$ under two distinct sets of constraints. These two sets of constraints correspond to the distinction made by Gibbs between "forming" a new surface which is identical in nature with the original, and "stretching" the existing surface and thereby altering its state of strain: compare Benson and Yun (1967), pg. 207.

We therefore consider firstly variations at constant temperature and chemical potentials in the mass M , which do not alter the state of strain (dilation and shear) of the crystalline material. We assume that the variation $\delta(s\sigma)$ due to a variation in the form of $\underline{s}$ may be completely characterised, for a spherical interface of curvature c , in terms of δs , δc and $\delta \underline{n}^\alpha$, where $\underline{n}^\alpha$ is a unit vector (having components n_μ where $\mu = 1, 2, 3$) specifying (in any convenient way) the orientation of $\underline{s}$ relative to the underlying crystal lattice in the region α . (The present treatment is valid, with slight modifications, for a faceted interface. That smoothly-curved surface regions, such as the one considered here, actually exist on crystalline masses in equilibrium, has been argued theoretically by Herring - see Herring (1949), pg. 152, and Herring (1951) - and reported by Sundquist (1964a, 1964b).) We may write

$$\begin{aligned} \delta(s\sigma) &= A\delta s + B\delta c + \sum_{\mu} C_{\mu} \delta n_{\mu}^{\alpha} \quad \mu = 1, 2, 3 \\ &= \sigma(\underline{n}^{\alpha}, c) \delta s + s \frac{\partial \sigma(\underline{n}^{\alpha}, c)}{\partial c} \delta c + s \sum_{\mu} \frac{\partial \sigma(\underline{n}^{\alpha}, c)}{\partial n_{\mu}^{\alpha}} \delta n_{\mu}^{\alpha} \quad (6-27) \end{aligned}$$

or for a variation in which $\delta c = 0$ and $\delta \underline{n}^{\alpha} = 0$

$$\delta(s\sigma) = \sigma(\underline{n}^{\alpha}, c) \delta s \quad (6-28)$$

Equation (6-28) represents a variation of the type "forming" a new

surface which is identical in nature with the original, and the equation shows that σ is a measure of the work required per unit area to form new surface in this way (hence the term "specific surface work").

The dependence of σ on the curvature may be expected to be small, when the radii of curvature of the surface are large compared with the thickness of the inhomogeneous layer, and (without reference to the choice of a dividing surface) we shall neglect it from here on, which brings this treatment into line with Herring (1952). With this approximation, equation (6-27) becomes, for a variation in the form of $\underline{s}$ in which its orientation is unchanged ($\delta \underline{n}^\alpha = 0$)

$$\delta(s\sigma) = \sigma(\underline{n}^\alpha) \delta s \quad (6-29)$$

Moreover, if we also neglect the dependence of σ on the orientation of the surface, equation (6-27) becomes

$$\delta(s\sigma) = \sigma \delta s \quad (6-30)$$

We consider secondly a variation at constant temperature and chemical potentials in the mass M , which does not alter the curvature or orientation of the surface $\underline{s}$. The state of strain (dilation and shear) of the crystalline material in the mass M is considered to vary, and any change in the area s is supposed to be entirely due to this strain. We may write

$$\begin{aligned} \delta(s\sigma) &= \sigma \delta s + s \delta \sigma \\ &= \sigma s \sum_{\mu} \delta u_{\mu\mu} + s \sum_{\mu, \nu} \frac{\partial \sigma}{\partial u_{\mu\nu}} \delta u_{\mu\nu} \end{aligned} \quad (6-31)$$

where $\delta u_{\mu\nu}$ ($\mu = 1, 2$; $\nu = 1, 2, 3$) is the strain tensor of the deformation

Compare Herring (1949), pg. 165, and Herring (1952), pg. 14.

For a crystal surface having a threefold (or greater) axis of rotational symmetry, or for any crystal surface for which the strain is

a uniform surface dilatation, equation (6-31) takes a simpler form, and we may write - see Shuttleworth (1950), pg. 449

$$\begin{aligned}\delta(s\sigma) &= \sigma\delta s + s \frac{\partial\sigma}{\partial s} \delta s \\ &= \left(\sigma + s \frac{\partial\sigma}{\partial s} \right) \delta s\end{aligned}\tag{6-32}$$

An investigation of the internal equilibrium of the mass M with respect to the variations in the form of s which we have been considering, leads to important relationships involving the superficial quantities. Of the three relationships obtained here, the first two have been discussed extensively in the literature. The third has, to this writer's knowledge, only been derived explicitly by C.R.M. Wronski (1963), though it is implicit in Gibbs' treatment of a solid-fluid interface.

Consider a spherical fluid-fluid interface of curvature c , when the dividing surface chosen is the surface of tension. If we consider a variation such as is represented by equation (6-26), the internal equilibrium of the mass M requires

$$p' - p'' = 2\sigma c\tag{6-33}$$

where p' and p'' are the pressures in the regions α and β .

Equation (6-33) is the Gibbs-Kelvin equation: the quantity σ here behaves as a "surface tension".

For a spherical crystalline-fluid interface of curvature c , on considering a variation for which equation (6-32) is valid, the internal equilibrium of the mass M necessitates

$$p' - p'' = 2 \left(\sigma + s \frac{\partial\sigma}{\partial s} \right) c\tag{6-34}$$

where p' and p'' are the pressures in the regions α and β .

Equation (6-34) was first derived by Shuttleworth - see Shuttleworth (1950), pg. 450, equation (4) - who identified the quantity $\sigma + s \frac{\partial\sigma}{\partial s}$

as the "surface stress". The surface stress is here denoted by g , so that

$$g = \sigma + s \frac{\partial \sigma}{\partial s} \quad (6-35)$$

A more generalised formulation of the relationship (6-35) was obtained independently by Herring (1949) - see also the interesting treatment by Benson and Yun (1967).

The similarity of equations (6-26) and (6-30) makes it appear that an equation identical to equation (6-33) must hold for a crystalline-fluid interface, and indeed extensive use has been made of such an equation (as applied to a crystalline-fluid interface) in the literature. However, as can be seen from equation (6-34), the use of such an equation implies the identity of the specific surface work σ and the surface stress g . The equation which is properly derived from equation (6-30), as a condition of the local equilibrium of a crystalline-fluid interface, is equation (6-42) (derived here for a single-component system).

Consider our mass M , and suppose that the surface $\underline{s}$ is a spherical portion of curvature c of a crystalline-fluid interface in a single-component system, with the dividing surface located so as to make the superficial density of mass vanish. Consider an infinitesimal variation in the form of $\underline{s}$, for which equation (6-30) is valid. The variation may be considered to result in the formation of an infinitesimal hump, whose volume, $\delta v'$, is related to the increase, δs , in the dividing surface area by the equation

$$\delta s = 2c\delta v' \quad (6-36)$$

to first order - see Herring (1949), pg. 152, and pg. 175 equation (33). From equations (6-25) and (6-30), we have (since the dividing surface is chosen to make the superficial density of mass vanish)

$$\delta(\epsilon^s - t\eta^s) = \sigma\delta s \quad (6-37)$$

We may write for the crystalline mass M' (c.f. equation (6-17))

$$\delta(\epsilon' - t\eta') = \mu'\delta m' - p'\delta v' \quad (6-38)$$

For a variation for which equation (6-30) is valid, the mass variation, $\delta m'$, and the volume variation, $\delta v'$, in equation (6-38) are not independent: they are related by the equation

$$\delta m' = \rho' \delta v' \quad (6-39)$$

where ρ' is the density of the crystalline mass M' .

Moreover, the chemical potential μ' , which we may regard as being defined by equation (6-38), is not, in general, equal to the chemical potential $\mu'_{(c)}$, which may be defined after the manner of equation (6-15).

We may write for the fluid mass M'' (c.f. equation (6-18))

$$\delta(\epsilon'' - t\eta'') = \mu''\delta m'' - p''\delta v'' \quad (6-40)$$

where μ'' is the chemical potential in the fluid mass M'' ($\mu'' = \mu'_{(c)}$). From equations (6-37), (6-38) and (6-40), the variation in the Helmholtz free energy of the mass M may be written

$$\delta(\epsilon - t\eta) = \mu'\delta m' - p'\delta v' + \mu''\delta m'' - p''\delta v'' + \sigma\delta s \quad (6-41)$$

The internal equilibrium of the mass M requires for reversible variations

$$\delta(\epsilon - t\eta) = 0$$

subject to the equations of condition

$$\delta v' + \delta v'' = 0 \quad \text{and} \quad \delta m' + \delta m'' = 0$$

and to the constraints (6-36) and (6-39). We obtain as our condition of equilibrium

$$\mu'' - \mu' = -\frac{p'}{\rho'} + \frac{p''}{\rho'} + \frac{2c}{\rho'} \sigma \quad (6-42)$$

Equation (6-42) may be written, with reference to equations (6-34) and (6-35)

$$\mu'' - \mu' = \frac{2c}{\rho'} (\sigma - g) \quad (6-43)$$

Equation (6-43) has been derived explicitly by Wronski (1963), pg. 126, from consideration of the equilibrium of a particular thermodynamic model, though it clearly has a more general application. It may be deduced immediately from Gibbs (1928), pg. 317 equation (661), and pg. 318.

It may be noted that for a variation at a fluid-fluid interface to which equation (6-26) pertains, there is no constraint corresponding to equation (6-39): without this constraint, equation (6-33) is obtained as a condition of the local equilibrium of the interface.

6.2.4 A condition of equilibrium of a spherical, crystalline-liquid interface in a single-component system

The implications of equation (6-42) for the equilibrium of a (spherical) crystalline-liquid interface in a single-component system will now be investigated.

The chemical potential of the crystalline phase, $\mu_C(p_C, t)$, at the pressure p_C and temperature t may be written in terms of the chemical potential at a pressure, p_O , of one atmosphere and at the bulk melting temperature, t_O , by a Taylor's expansion about p_O, t_O : defining the operator D_C by

$$D_C = (p_C - p_O) \frac{\partial}{\partial p} + (t - t_O) \frac{\partial}{\partial t}$$

we may write to second order

$$\begin{aligned} \mu_C(p_C, t) &= \left| (1 + D_C + \frac{1}{2} D_C^2) \mu_C \right|_{p_O, t_O} \\ &= \mu_C(p_O, t_O) + (p_C - p_O) v_C^O - (t - t_O) \eta_C^O + \frac{1}{2} \left| -(p_C - p_O)^2 v_C^O K_C^O \right. \\ &\quad \left. + 2(p_C - p_O)(t - t_O) v_C^O \alpha_C^O - (t - t_O)^2 \frac{C_{p_C}^O}{t_O} \right| \quad (6-44) \end{aligned}$$

where v_C^O , η_C^O , K_C^O , α_C^O and $C_{p_C}^O$ are, respectively, the volume per gram,

entropy per gram, compressibility, coefficient of cubical expansion, and specific heat at constant pressure of the solid at p_o, t_o .

In a similar way we may write for the liquid phase

$$\begin{aligned} \mu_L(p_L, t) = \mu_L(p_o, t_o) + (p_L - p_o)v_L^o - (t - t_o)\eta_L^o + \frac{1}{2} \left| -(p_L - p_o)^2 v_L^o \bar{\kappa}_L^o \right. \\ \left. + 2(p_L - p_o)(t - t_o)v_L^o \alpha_L^o - (t - t_o)^2 \frac{c_{p_L}^o}{t_o} \right| \quad (6-45) \end{aligned}$$

where the subscript L refers to the liquid phase.

The chemical potentials appearing in equations (6-44) and (6-45) are regarded as defined by equations having the form of equation (6-38). For a bulk system ($c = 0$) at the bulk melting temperature, t_o , and at the pressure p_o , we have from equation (6-43):

$$\mu_C(p_o, t_o) = \mu_L(p_o, t_o) \quad (6-46)$$

We also have

$$\eta_L^o - \eta_C^o = \frac{L_o}{t_o} \quad (6-47)$$

where L_o is the latent heat of fusion per gram.

Subtracting equation (6-44) from equation (6-45) and making use of equations (6-46) and (6-47), we have to first order

$$\begin{aligned} \mu_L(p_L, t) - \mu_C(p_C, t) &= (p_L - p_o)v_L^o - (p_C - p_o)v_C^o + \frac{L_o}{t_o}(t_o - t) \\ &= p_L v_L^o - p_C v_C^o + p_o(v_C^o - v_L^o) + \frac{L_o}{t_o}(t_o - t) \quad (6-48) \end{aligned}$$

For the materials investigated, the second order terms in equation (6-48) may be shown to be small. The pressures p_L and p_C are typically much

greater than an atmosphere for the crystallite sizes investigated in these experiments, so the term in p_o is conveniently neglected. Writing

$$v_L^o = \frac{1}{\rho_L} \quad \text{and} \quad v_C^o = \frac{1}{\rho_C}$$

where ρ_L and ρ_C are the densities of the liquid and crystal (at a pressure and temperature which need not be specified to the order of accuracy employed)

we may write equation (6-48) in the form

$$\mu_L(p_L, t) - \mu_C(p_C, t) = \frac{p_L}{\rho_L} - \frac{p_C}{\rho_C} + \frac{L_o}{t_o} (t_o - t) \quad (6-49)$$

From equations (6-42) and (6-49), denoting the specific surface work by σ_{CL} , we obtain

$$- \frac{p_C}{\rho_C} + \frac{p_L}{\rho_C} + \frac{2c}{\rho_C} \sigma_{CL} = \frac{p_L}{\rho_L} - \frac{p_C}{\rho_C} + \frac{L_o}{t_o} (t_o - t)$$

so that

$$\frac{2c}{\rho_C} \sigma_{CL} = p_L \left(\frac{1}{\rho_L} - \frac{1}{\rho_C} \right) + \frac{L_o}{t_o} (t_o - t) \quad (6-50)$$

Equation (6-50) is a condition for the equilibrium of a (spherical) crystalline-liquid interface in a single-component system.

6.3 The application of thermodynamics to models resembling the melting of a metallic crystallite

6.3.1 General considerations

(i) Anisotropy of the specific surface work, σ , and the equilibrium form

The crystalline-liquid and crystalline-vapour specific surface free energies, σ_{CL} and σ_C respectively, are both functions of the orientation of the surface with respect to the underlying crystal lattice. As a consequence of this, a small crystal must assume a unique shape - the "equilibrium form" - if its surface free energy is to be a minimum for a given volume. The construction which gives this equilibrium form is due to Wulff (1901) - see also the theoretical examination of this problem by Herring (1951). A number of experimental investigations of the dependence of the crystalline-vapour specific surface free energy, σ_C , on orientation have been made - see the accounts by Shewmon and Robertson (1963); Defay, Prigogine, Bellemans and Everett (1966), pg. 306; and Dunning (1967), pgs. 285-289. Sundquist (1964a, 1964b) has attempted to prepare small crystals having the equilibrium form and examine them directly.

It is likely that small crystals of the materials investigated in the present experiments undergo appreciable changes of shape when heated to temperatures a little below their melting temperatures, as a consequence of volume-diffusion or surface-migration mechanisms of the type envisaged by Herring (1949, 1950a, 1950b, 1952). Surface energies would be the motivation for such changes, and the crystals might even attain an equilibrium form before melting. Moreover, the form of any crystalline-liquid interface existing during the actual melting of a crystallite, may be expected to reflect the anisotropy of the crystalline-liquid specific surface free energy, σ_{CL} . In the absence of detailed information on the dependence of σ_C and σ_{CL} on orientation, no account can be taken of these effects, and the anisotropy is ignored in the present considerations. Recent theoretical work, taking account of anisotropic surface energies in dealing with problems concerning the influence of surface on the physical properties of a material, may be seen in the generalisation of the Gibbs-Thomson equation by Johnson (1965)

and in the work of Lacmann (1962).

(ii) Temperature dependence of the specific surface work, σ

The crystalline-liquid, crystalline-vapour and liquid-vapour specific surface free energies, σ_{CL} , σ_C and σ_L , respectively, are temperature dependent quantities. Experimental determinations of the temperature dependence have only been made for the last of these - see, for example, the work on lead, tin and indium by Melford and Hoar (1956-57). Even these determinations are fraught with difficulties, as may be seen from the comparison by Cahill and Kirshenbaum (1964) of the data of a dozen different workers (including Melford and Hoar) on the surface tension of liquid tin. Cahill and Kirshenbaum suggest the following formula for the temperature dependence of the surface tension of liquid tin:

$$\sigma_L = 581.2 - 7.424 \times 10^{-2} T \quad \text{dyne/cm.}$$

where T is the absolute temperature.

Theoretically, the temperature dependence of σ may be approached through the Gibbs adsorption equation - see equation (6-24) - by calculating the surface entropy. An empirical relationship between the surface tension, molar volume and the temperature due to Eötvös (1886) has attracted much theoretical attention - see Defay, Prigogine, Bellemans and Everett (1966), pg. 153. Work on the disordering of crystal surfaces and the surface modification of thermal vibrations has made available theoretical estimates of the temperature dependence of the crystalline-vapour (or strictly crystalline-vacuum) specific surface free energy, σ_C - see Dunning (1967), pgs. 294-299; and see especially Karge, Heyer and Pound (1967). A discussion of the roughening of a crystalline-liquid interface has been given by Jackson (1957) - see also Jackson (1959).

The available work may be briefly summarised by saying that for a particular material the crystalline-vapour and liquid-vapour specific surface free energies show comparable temperature dependences, which for the materials investigated in the present experiments may be expected to amount to an increase of 1 - 3 % for every 100 °C decrease in

temperature.

(iii) Curvature dependence of the specific surface work, σ

The specific surface works σ_{CL} , σ_C and σ_L , as defined by equation (6-20) in terms of the superficial quantities defined in § 6.2.1, are "excess" energies introduced to permit the convenience of a hypothetical system in which the inhomogeneous capillary layer is replaced by homogeneous extensions of the bulk phases on either side of the interface. As thus defined they may be expected to be dependent on the curvature of the interface, and this curvature dependence will itself be effected by the choice of the dividing surface to which the excess energies are referred - see Buff (1951), pg. 1593.

The liquid-vapour specific surface work, σ_L , when referred to the surface of tension is called the surface tension. Extensive theoretical investigations have been made to determine the dependence of the surface tension on the curvature of the surface: see Tolman (1949); Kirkwood and Buff (1949); Koenig (1950); Buff and Kirkwood (1950); Buff (1951, 1952); McLellan (1953); Buff (1955); Turnbull (1956), pgs. 260-261; Bellemans (1963); Defay, Prigogine, Bellemans and Everett (1966), pgs. 256-258; and Flood (1967), pgs. 46-54. The order of magnitude of the dependence may be gauged from the estimated figures for water quoted in Defay, Prigogine, Bellemans and Everett (op. cit.): these show a 3 % decrease in the surface tension for a droplet of 100 Å radius, and a 24 % decrease for a droplet of 10 Å radius.

The crystalline-liquid and crystalline-vapour specific surface works, σ_{CL} and σ_C , are usually referred to the dividing surface for which the superficial density of mass of the principle constituent of the crystal is zero (the " $\Gamma = 0$ surface"). Some indication of the difficulties of evaluating the curvature dependence of these quantities may be obtained by considering the size dependence of σ_C (assumed isotropic) for a spherical crystallite of a pure metal having a very low vapour pressure (the vapour phase is ignored).

For a small metallic crystallite at 0 °K, omitting zero point energy, we may write

$$s \sigma_C(0) = \Delta\phi$$

where s is the area of the $\Gamma = 0$ surface

$\sigma_C(0)$ is the specific surface free energy at 0°K

and $\Delta\Phi$ is the difference between the binding energy of the crystallite and the binding energy associated with the same metallic mass when it is part of an extended crystal.

The binding energy is defined as the increase in potential energy when the atoms, initially at rest in their mean positions in the crystal, are dispersed to infinite separation. Clearly, if the difference between the binding energies is not proportional to the area s , then the specific surface free energy at 0°K , $\sigma_C(0)$, is size dependent. The connection between the binding energy of a crystal and its surface energy is discussed by Dunning (1967), pgs. 274-282.

In the pseudo-potential formalism as developed by Harrison (1966), the cohesive energy of a metal appears as the sum of three terms: a contribution due to a pair-central interaction between the metallic ions which is evaluated by a lattice-summation procedure, a conduction-electron contribution which is dependent on the position of the metallic ions and is related to the band structure, and a conduction-electron contribution which is independent of the location of the metallic ions being dependent only on the total volume occupied by the ions. However, theoretical estimates of the surface energy of metals - see appendix 3 for a bibliography - have mostly been made on the basis of the simpler Sommerfeld model. In this, a metal is represented as a medium with a uniform distribution of positive charge and a compensating number of electrons: this model has been referred to by Herring (1952) - see appendix 3 - as the "jellium model" of a metal. Probably the best calculations on this basis are those by Stratton (1953) - see appendix 3 - in which the surface free energy of a metal in the normal state at 0°K , $\sigma_C(0)$, is obtained as the sum of three terms:

$$\sigma_C(0) = \sigma_1 + \sigma_2 + \sigma_3$$

where σ_1 and σ_2 are the electron kinetic energy contributions for an infinite surface barrier, and the correction for a finite barrier, respectively

and σ_3 is a small potential energy contribution arising from the surface electric double layer.

In the earlier treatment by Huang and Wyllie (1949) - see appendix 3 - a further contribution to the surface energy $\sigma_C(0)$, arising from the repulsive interaction of the metal ions, is discussed. Both Stratton, and Huang and Wyllie consider that the change in σ_C due to a finite temperature will be due in the main to the thermal excitation of the lattice waves.

On the basis of the "jellium model", Sugiyama (1960), pg. 974 - see appendix 3 - has discussed the "dependence of spherical surface energy on its radius" for "a spherical metal with a given radius R_0 ". He obtained the following expression for the surface energy at 0 °K, $\sigma_C(0)$ (excluding ion-ion interaction) :

$$\sigma_C(0) = \beta \frac{k_F^4}{160\pi} = \beta \sigma_s$$

where $\sigma_s = \frac{k_F^4}{160\pi}$ is curvature independent

k_F is the Fermi momentum

and for large R_0 , $\beta \approx 1$, nearly independently of R_0 . For small radii, β may depend on R_0 : Sugiyama's estimate of the radius at which this could become significant is $24r_s$, where r_s is the Wigner-Seitz radius. A comparison of this estimate with the figures quoted above for the surface tension of water droplets suggests that the dependences of σ_C and σ_L on curvature become important at similar radii. Moreover, in order to examine the curvature dependence of σ_L for a metallic droplet, electron contributions of the type discussed above must be considered.

To compliment the work of Sugiyama, many additional factors require investigation. For instance, relaxation of the crystal surface may distort the entire lattice for a very small crystal. The "jellium model" takes no account of ion-ion interactions. Furthermore, at finite temperatures, surface roughening and modification of the thermal vibrational modes influence surface energies - see (ii) above. The results of the present work will be interpreted on the assumption that the various excess energies are independent of temperature and curvature,

though the limitations of such an approach should be kept in mind.

(iv) Equilibrium considerations

An aggregate of metallic crystallites which is melted under the conditions prevailing in the experiments described here, is never in equilibrium with respect to the transfer of material through the vapour phase. There is a continuous loss of metal through the vapour phase, both by adsorption onto the cold surfaces of the diffraction camera and by removal through the pumping system. The existence of crystallites of varying sizes in close proximity, after a melting observation, indicates that even very locally the crystallites and vapour phase cannot be regarded as constituting a system in thermodynamic equilibrium: the highering of the vapour pressure according to the Kelvin equation precludes the existence of small crystallites of differing radii in equilibrium.

As has been observed by Hanszen (1960), the equilibrium of a system consisting of an aggregate of small crystallites and their vapour requires that all the crystallites be of equal size, and even then the equilibrium is not a stable one. Melting considerations based on a model such as that employed by Hanszen, in which the melting temperature of a crystallite was identified as that temperature at which an aggregate of crystallites and droplets of identical mass can exist in metastable equilibrium with its vapour (essentially the same model as was employed by Pawlow - see § 1.1 (pg. 5)), are not applicable to the melting of an aggregate under the conditions prevailing in the present experiments.

Calculations based on the known equilibrium vapour pressures of lead, bismuth and indium, even allowing for such higherings of the vapour pressure which occur, in accordance with the Kelvin equation, as a result of the small size of the crystallites, indicate that the time taken for any appreciable change in the size of a crystallite will be large compared with the duration of a melting temperature determination: this is true even for the smallest crystallites examined in the present experiments. The time taken for the melting of an individual crystallite is clearly very small compared with the times involved in the attainment of equilibrium by the aggregate as a whole, by the transfer of material through the vapour phase. It is therefore appropriate when considering

the melting of such an aggregate, to investigate the equilibrium of the system contained within a small envelope enclosing an individual crystallite and a portion of its surrounding vapour phase. Because of the low vapour pressures of lead, bismuth and indium, and the low pressure of the residual gases, it is possible to neglect the mass and energy associated with the vapour phase. Moreover, we may regard the metallic mass of such a system as constant, and the chemical potentials of the residual gases in the vapour phase as invariant insofar as they may be adsorbed at the crystallite surface. Assuming that the free exchange of heat between such a system and its surroundings constrains a uniform temperature t throughout the system, a necessary and sufficient condition for equilibrium is

$$\delta(\epsilon_T - t\eta_T) = 0 \quad (6-51)$$

for all reversible variations of the system contained within the fixed envelope (see Gibbs (1928), pg. 90), where ϵ_T and η_T are the total energy and entropy of the system.

(v) Influence of the substrate on the melting of a small crystallite

This has been discussed qualitatively in § 5.4.1. A quantitative expression for the influence of the substrate on the melting temperature of a small crystallite could be obtained by examining the possible modes of melting of a crystallite having the form of a spherical cap (as is done in § 6.3.3 and § 6.3.4 for a spherical crystallite), but this will not be attempted here. However, such a model will later be examined - see § 6.4.2 and figure 42 - in connection with heterogeneous nucleation of a cap-shaped liquid droplet. As may be seen from table 5 (pg. 117), the factor K , by which the observed crystallite radius must be multiplied in order to get the radius of a (hypothetical) spherical crystallite having the same volume as the actual crystallite, does not differ appreciably from unity. The experimental results have been interpreted on the assumption that the crystallites are spheres having radii equal to the observed crystallite radii.

(vi) Influence of the residual gases on the melting of a small crystallite

This has been discussed qualitatively in § 5.4.3. If it is assumed that the gases are merely adsorbed at the crystallite surface, their

influence can be estimated quantitatively via the Gibbs adsorption equation - see Flbod (1967), pg. 26. Such considerations have been made by Hanszen (1960). Only single-component systems will be examined here.

6.3.2 The "two-state" model

Consider a one-component system having a fixed volume and consisting of a single spherical crystallite completely surrounded by its vapour. Suppose the system is of comparable size with the crystallite, and is completely isolated except with respect to the free exchange of heat with its surroundings, which constrains a uniform temperature t throughout. The equilibrium of the system requires - c.f. equation (6-51) - that for all possible variations

$$\delta(\epsilon_T - t\eta_T) \geq 0 \quad (6-52)$$

where ϵ_T and η_T are the total energy and entropy of the system.

If the process of melting is envisaged as the spread of a liquid-solid interface through the crystal, there will in general be an energy barrier (consequent upon the energy associated with the interface) to the melting of a crystallite when it is at the temperature, t_{TS} , at which its Helmholtz free energy is equal to that of a liquid droplet of the same mass. In the present state of knowledge of melting mechanisms, it is not possible to say whether the molten state could be attained by a process of disordering which did not involve the movement of such an interface. If it is assumed that the melting of the crystallite to a liquid droplet does not involve the surmounting of an appreciable energy barrier - that is any barrier can be overcome by statistical fluctuations - then the crystallite will melt at the temperature t_{TS} . As will be seen, for the mode of melting envisaged in § 6.3.3, such an assumption can only be justified for a very small crystallite. The "two-state" model is thus not strictly a model of melting, but rather an analysis of the consequences of an assumption which can only be justified by an appeal to statistical mechanics. The assumption is essentially that described by T.L. Hill - see Hill (1963), pg. 115 - as the "two-state" approximation, and the results of the analysis here are in agreement with those obtained by Hill.

We will now calculate the total Helmholtz free energies of our system, $(\epsilon_T - t\eta_T)_{\text{CRYSTALLINE}}$ and $(\epsilon_T - t\eta_T)_{\text{LIQUID}}$, in the two cases when the condensed metallic mass is wholly crystalline and when it is wholly molten. The dividing surface which makes the superficial density of mass vanish (the " $\Gamma = 0$ surface") will be employed for the crystal-vapour interface, and the surface of tension for the liquid-vapour interface. Referred to these dividing surfaces, we define the quantities:

$s_C, r_C, \epsilon_C^s, \eta_C^s$ and σ_C - area, radius, superficial energy, superficial entropy and specific surface work, respectively, of the crystal-vapour dividing surface (σ_C is assumed to be independent of the radius and orientation of the surface)

$\epsilon_C, \eta_C, m, v_C, p_C$ and μ_C - (internal) energy, entropy, mass, volume, pressure and chemical potential, respectively, of the homogeneous crystalline region extending up to the dividing surface

$s_L, r_L, \epsilon_L^s, \eta_L^s, m_L^s$ and σ_L - area, radius, superficial energy, superficial entropy, superficial mass and surface tension, respectively, of the liquid-vapour dividing surface

$\epsilon_L, \eta_L, m_L, v_L, p_L$ and μ_L - (internal) energy, entropy, mass, volume, pressure and chemical potential, respectively, of the homogeneous liquid phase extending up to the dividing surface.

Neglecting the energy associated with the vapour phase, we may write

$$(\epsilon_T - t\eta_T)_{\text{CRYSTALLINE}} = \epsilon_C - t\eta_C + \epsilon_C^s - t\eta_C^s$$

But for the homogeneous crystalline region - see Gibbs (1928), pg. 77 - we have

$$\epsilon_C - t\eta_C = -p_C v_C + \mu_C m$$

and from equations (6-5) and (6-20), we have for the $\Gamma = 0$ surface

$$\epsilon_C^s - t\eta_C^s = \sigma_C s_C$$

therefore

$$(\epsilon_T - t\eta_T)_{\text{CRYSTALLINE}} = -p_C v_C + \mu_C^m + \sigma_C s_C \quad (6-53)$$

Similarly

$$(\epsilon_T - t\eta_T)_{\text{LIQUID}} = -p_L v_L + \mu_L^m + \mu_L^m s + \sigma_L s_L$$

But, neglecting the mass associated with the vapour phase, we have

$$m = m_L + m_L^s \quad (6-54)$$

therefore

$$(\epsilon_T - t\eta_T)_{\text{LIQUID}} = -p_L v_L + \mu_L^m + \sigma_L s_L \quad (6-55)$$

The "two-state" melting temperature, t_{TS} , is the temperature at which

$$(\epsilon_T - t\eta_T)_{\text{CRYSTALLINE}} = (\epsilon_T - t\eta_T)_{\text{LIQUID}}$$

$$\text{i.e.} \quad (\mu_L - \mu_C)m = -p_C v_C + p_L v_L + \sigma_C s_C - \sigma_L s_L$$

But, from equation (6-49), we have to first order

$$\mu_L - \mu_C = \frac{p_L}{\rho_L} - \frac{p_C}{\rho_C} + \frac{L_o}{t_o} (t_o - t)$$

also, from equation (6-54)

$$m = \rho_C v_C = m_L \left(1 + \frac{m_L^s}{m_L} \right) = \rho_L v_L \left(1 + \frac{m_L^s}{m_L} \right) \quad (6-56)$$

therefore

$$\frac{\rho_C^L}{t_o} (t_o - t_{TS}) \rho_C^V v_C = \sigma_C^s s_C - \sigma_L^s s_L - p_L^V v_L \frac{m_L^s}{m_L}$$

But, from equation (6-33), if we neglect the pressure of the vapour, we may write

$$p_L = \frac{2\sigma_L}{r_L}$$

and

$$p_L^V v_L \frac{m_L^s}{m_L} = \frac{2\sigma_L}{r_L} v_L \frac{m_L^s}{m_L} = \frac{2}{3} \sigma_L^s s_L \frac{m_L^s}{m_L}$$

therefore

$$\frac{\rho_C^L}{t_o} (t_o - t_{TS}) v_C = \sigma_C^s s_C - \sigma_L^s \left(1 + \frac{2m_L^s}{3m_L} \right) s_L \quad (6-57)$$

In equation (6-57), the term in m_L^s/m_L is curvature dependent, and as it appears here may be envisaged as a curvature dependent correction to the surface tension. It will be neglected, which approximation may be justified in view of the lack of an adequate framework to examine the assertion that σ_C is independent of curvature for the $\Gamma = 0$ surface. This yields

$$\frac{\rho_C^L}{t_o} (t_o - t_{TS}) v_C = \sigma_C^s s_C - \sigma_L^s s_L \quad (6-58)$$

To the same degree of approximation we have from (6-56)

$$\rho_C^V v_C = \rho_L^V v_L$$

so that, from (6-58), we may deduce

$$t_o - t_{TS} = \frac{t_o}{L_o} \left(\frac{3\sigma_C}{r_C \rho_C} - \frac{3\sigma_L}{r_L \rho_L} \right) \quad (6-59)$$

Hill - see Hill (1963), pgs. 1, 41, and 129-132 - assumes a surface contribution to the total Gibbs free energy of a spherical crystallite, of the form

$$a(p,T) N^{2/3} = \gamma(p,T) A$$

where p is the pressure exerted by an inert fluid reservoir in which the crystallite is considered to be immersed

T is the absolute temperature

N is the number of molecules in the crystallite

A is the surface area of the crystallite

and a and γ are functions independent of N ; γ being a specific surface free energy.

Hill has derived the following equation for the "two-state" melting temperature, T_{TS} - see Hill (1963), pgs. 114-132; and pg. 131, equation (5-151)

$$T_{TS} = T_{\infty} + \frac{N^{-1/3} \Delta a(p_{\infty}, T_{\infty})}{\Delta s_{\infty}} \quad (6-60)$$

where p_{∞} and T_{∞} are the values of p and T at which the two macroscopic phases are in equilibrium, and may be taken to be p_0 and t_0 as defined in § 6.2.4

and $\Delta a(p_{\infty}, T_{\infty})$ and Δs_{∞} are given by the equations

$$\Delta a(p_{\infty}, T_{\infty}) = N^{-2/3} \left(\gamma_L A_L - \gamma_S A_S \right)$$

and

$$\Delta s_{\infty} = s_L - s_S$$

where the subscripts L and S denote liquid and solid

γ_L and γ_S are the specific surface free energies at p_{∞} , T_{∞}

and s_L and s_S are the entropies per molecule at p_{∞} , T_{∞} .

If we write

$$\Delta s_{\infty} = m \frac{L_{\infty}}{T_{\infty}}$$

where m is the mass of a molecule in grams

and L_∞ is the latent heat of fusion per gram

equation (6-60) can be written

$$T_\infty - T_{TS} = - \frac{T_\infty}{L_\infty} \frac{\gamma_L^A L - \gamma_S^A S}{Nm}$$

Employing r_S , r_L , ρ_S and ρ_L to denote the radii and densities of the solid crystallite and liquid droplet (both assumed spherical), we obtain

$$\begin{aligned} T_\infty - T_{TS} &= \frac{T_\infty}{L_\infty} \frac{\gamma_S \frac{3}{r_S} \frac{4}{3} \pi r_S^3 - \gamma_L \frac{3}{r_L} \frac{4}{3} \pi r_L^3}{Nm} \\ &= \frac{T_\infty}{L_\infty} \left(\frac{3\gamma_S}{r_S \rho_S} - \frac{3\gamma_L}{r_L \rho_L} \right) \end{aligned} \quad (6-61)$$

Equation (6-61) may be compared with equation (6-59).

6.3.3 The "liquid-shell" model (refer to figure 38 pg. 131)

(i) Derivation of pertinent relationships

The system considered in § 6.3.2 will now be investigated when the crystallite is partially melted: the system is regarded as consisting of a spherical crystalline core enclosed in a concentric liquid shell and completely surrounded by its vapour. The dividing surface which makes the superficial density of mass vanish will be employed for the crystal-liquid interface, and the surface of tension for the liquid-vapour interface. Referred to these dividing surfaces, we define the quantities:

s_{CL} , r_{CL} and σ_{CL} - area, radius and specific surface work, respectively, of the crystal-liquid dividing surface (σ_{CL} is assumed to be independent of the radius and orientation of the surface)

s_L' , r_L' and m_L^s - area, radius and superficial mass, respectively, of the liquid-vapour dividing surface

m_C' , v_C' , p_C' and μ_C' - mass, volume, pressure and chemical potential, respectively, of the homogeneous crystalline region extending up to the dividing surface

m_L' , v_L' , p_L' and μ_L' - mass, volume, pressure and chemical potential, respectively, of the homogeneous liquid shell extending up to the dividing surfaces.

Other quantities used below are as defined on pg. 156.

A consideration of the equilibrium of the system in accordance with equation (6-52), leads only to relationships already derived in § 6.2. Distinguishing quantities which refer to an equilibrium state of the system by a double prime, we may write equation (6-50) in particular

$$\frac{2}{r_{CL}'' \rho_C} \sigma_{CL} = p_L'' \left(\frac{1}{\rho_L} - \frac{1}{\rho_C} \right) + \frac{L_o}{t_o} (t_o - t)$$

Making use of equation (6-33), and neglecting the pressure of the vapour, we obtain

$$\frac{2\sigma_{CL}}{r_{CL}''} = \frac{2\sigma_L}{r_L''} \left(\frac{\rho_C}{\rho_L} - 1 \right) + \frac{\rho_C L_o}{t_o} (t_o - t) \quad (6-62)$$

To arrive at a better understanding of the nature of this equilibrium and its relevance to the melting of a spherical crystallite and to the solidification of a spherical droplet, it will prove convenient to write the total Helmholtz free energy of the system, not necessarily in equilibrium, $(\epsilon_T - t\eta_T)_{r_{CL}}$, in the two forms

$$(\epsilon_T - t\eta_T)_{r_{CL}} = (\epsilon_T - t\eta_T)_{\text{CRYSTALLINE}} + \Delta f_m \quad (6-63)$$

and

$$(\epsilon_T - t\eta_T)_{r_{CL}} = (\epsilon_T - t\eta_T)_{\text{LIQUID}} + \Delta f_s \quad (6-64)$$

The quantities Δf_m and Δf_s are the free energies of formation of a liquid shell on a crystallite, and of a crystalline core in a liquid droplet, respectively.

We may write, compare equation (6-53),

$$\begin{aligned}
 (\epsilon_T - t\eta_T)_{r_{CL}} &= -p_C'v_C' + \mu_C'm_C' + \sigma_{CL}s_{CL} \\
 &\quad - p_L'v_L' + \mu_L'm_L' + \mu_L'm_L^{s'} + \sigma_L s_L'
 \end{aligned}
 \tag{6-65}$$

Neglecting, as before, the mass of the vapour phase, we have

$$\begin{aligned}
 m &= m_C' + m_L' + m_L^{s'} \\
 &= m_C' + m_L' \left(1 + \frac{m_L^{s'}}{m_L'} \right)
 \end{aligned}$$

Neglecting $m_L^{s'}/m_L'$ compared with unity, we obtain

$$m = m_C' + m_L' \tag{6-66}$$

From equations (6-63), (6-65), (6-53) and (6-66), we have

$$\begin{aligned}
 \Delta f_m &= -p_C'v_C' - p_L'v_L' + p_C v_C + \sigma_{CL}s_{CL} + \sigma_L s_L' - \sigma_C s_C \\
 &\quad + (\mu_C' - \mu_C)m_C' + (\mu_L' - \mu_C) \left(\begin{matrix} m - m_C' \\ \text{or} \\ m_L' \end{matrix} \right)
 \end{aligned}
 \tag{6-67}$$

But from equation (6-44) we have, to first order,

$$\mu_C'(p_C', t) = \mu_C(p_o, t_o) + (p_C' - p_o)v_C^o - (t - t_o)\eta_C^o \tag{6-68}$$

and

$$\mu_C(p_C, t) = \mu_C(p_o, t_o) + (p_C - p_o)v_C^o - (t - t_o)\eta_C^o \tag{6-69}$$

where $v_C^o = \frac{1}{\rho_C}$

Subtracting equation (6-69) from (6-68)

$$\mu_C' - \mu_C = \frac{p_C' - p_C}{\rho_C} \quad (6-70)$$

Further, from equation (6-49), we have

$$\mu_L' - \mu_C = \frac{p_L'}{\rho_L} - \frac{p_C}{\rho_C} + \frac{L_O}{t_O} (t_O - t) \quad (6-71)$$

Moreover

$$m = \rho_C v_C \quad m_C' = \rho_C v_C' \quad m_L' = \rho_L v_L' \quad (6-72)$$

From equations (6-67), (6-70), (6-71) and (6-72), we find

$$\begin{aligned} \Delta f_m &= -p_C' v_C' - p_L' v_L' + p_C v_C + \sigma_{CL} s_{CL} + \sigma_L s_L' - \sigma_C s_C + (p_C' - p_C) v_C' \\ &\quad + \frac{p_L'}{\rho_L} \rho_L v_L' + \left(-\frac{p_C}{\rho_C} + \frac{L_O}{t_O} (t_O - t) \right) \rho_C (v_C - v_C') \\ &= \sigma_{CL} s_{CL} + \sigma_L s_L' - \sigma_C s_C + \frac{\rho_C L_O}{t_O} (t_O - t) (v_C - v_C') \end{aligned} \quad (6-73)$$

From equations (6-64), (6-65) and (6-55), we may show in a similar way

$$\Delta f_s = \sigma_{CL} s_{CL} + \sigma_L s_L' - \sigma_L s_L - \frac{\rho_C L_O}{t_O} (t_O - t) v_C' \quad (6-74)$$

The quantities Δf_m and Δf_s must, clearly, have stationary values for $r_{CL} = r_{CL}''$, where r_{CL}'' is the equilibrium radius given in equation (6-62): this may be demonstrated by differentiation. The stationary values are maxima, and will be denoted by $\Delta f_m''$ and $\Delta f_s''$.

It will prove convenient to introduce at this point the quantity δ , defined by the equation

$$\delta = \frac{\rho_C}{\rho_L} - 1 \quad (6-75)$$

This quantity is (discounting any temperature dependence of the densities) identical to the volume change on melting

$$\Delta V_m = \frac{V_{\text{liquid}} - V_{\text{solid}}}{V_{\text{solid}}}$$

tabulated in Smithells' "Metals Reference Book" (1967).

From equations (6-66) and (6-72), we deduce

$$\rho_L (r_L'^3 - r_{CL}^3) = \rho_C (r_C^3 - r_{CL}^3) \quad (6-76)$$

From equation (6-76) we may derive, to first order in δ ,

$$r_L'^2 = r_C^2 \left[1 + \frac{2}{3} \delta \left(1 - \frac{r_{CL}^3}{r_C^3} \right) \right] \quad (6-77)$$

which is a good approximation for the metals lead, bismuth and indium for which $|\delta| \sim 0.03$.

Further, defining the quantity K by the equation

$$K = \frac{\rho_C^L}{t_o} (t_o - t) \quad (6-78)$$

we may now write equations (6-73) and (6-74) in the forms

$$\Delta f_m = \sigma_{CL} s_{CL} + (\sigma_L - \sigma_C) s_C + \left(K + \frac{2\sigma_L}{r_C} \delta \right) (v_C - v_C') \quad (6-79)$$

and

$$\Delta f_s = \sigma_{CL} s_{CL} - \left(K + \frac{2\sigma_L}{r_C} \delta \right) v_C' \quad (6-80)$$

to first order in δ .

Equation (6-62) may be written, to first order in δ ,

$$\frac{2\sigma_{CL}}{r_{CL}''} = K + \frac{2\sigma_L}{r_C} \delta \quad (6-81)$$

and hence the following expressions may be obtained for $\Delta f_m''$ and $\Delta f_s''$

$$\Delta f_m'' = \frac{16}{3} \pi \sigma_{CL}^3 \frac{1}{\left(K + \frac{2\sigma_L}{r_C} \delta\right)^2} + \left(K + \frac{2\sigma_L}{r_C} \delta\right) v_C + (\sigma_L - \sigma_C) s_C \quad (6-82)$$

and

$$\Delta f_s'' = \frac{16}{3} \pi \sigma_{CL}^3 \frac{1}{\left(K + \frac{2\sigma_L}{r_C} \delta\right)^2} \quad (6-83)$$

The formulae for Δf_m and Δf_s in equations (6-73) and (6-74), or in equations (6-79) and (6-80), cannot be expected to properly represent the true free energies of formation, unless the thickness of the liquid shell is sufficiently large for its properties to approximate to those within a bulk liquid phase. Although equation (6-79) implies that the energy of formation of a very thin liquid shell is approximately $(\sigma_{CL} + \sigma_L - \sigma_C) s_C$, it is assumed here that equations (6-73) and (6-74) only become valid for $r_C - r_{CL} \geq \lambda$, where λ is some critical thickness of the order of a few tens of Ångstrom units.

The free energy of formation of a liquid shell of critical thickness (such that $r_C - r_{CL} = \lambda$) on a spherical crystallite is, from equation (6-79)

$$\begin{aligned} (\Delta f_m)_\lambda &= \sigma_{CL} 4\pi(r_C - \lambda)^2 + (\sigma_L - \sigma_C) s_C \\ &\quad + \left(K + \frac{2\sigma_L}{r_C} \delta\right) \left[\frac{4}{3} \pi r_C^3 - \frac{4}{3} \pi (r_C - \lambda)^3\right] \end{aligned}$$

which may be written

$$\begin{aligned}
 (\Delta f_m)_\lambda &= (\sigma_{CL} + \sigma_L - \sigma_C) s_C \\
 &+ \lambda s_C \left[\left(\frac{\rho_C L_O}{t_O} (t_O - t) + \frac{2\sigma_L}{r_C} \delta \right) \left(1 - \frac{\lambda}{r_C} + \frac{1}{3} \frac{\lambda^2}{r_C^2} \right) - \frac{2\sigma_{CL}}{r_C} \left(1 - \frac{\lambda}{2r_C} \right) \right]
 \end{aligned} \quad (6-84)$$

If t_λ is the temperature at which the equilibrium radius is $r_C - \lambda$, we obtain from equation (6-81)

$$\frac{\rho_C L_O}{t_O} (t_O - t_\lambda) = \frac{2\sigma_{CL}}{r_C - \lambda} - \frac{2\sigma_L}{r_C} \delta \quad (6-85)$$

which may be written

$$t_O - t_\lambda = \frac{2t_O}{\rho_C L_O} \left(\frac{\sigma_{CL}}{r_C - \lambda} - \frac{\sigma_L}{r_C} \delta \right) \quad (6-86)$$

When λ is small compared with r_C , so that terms in λ/r_C may be neglected, reference to equation (6-85) shows that the term $\lambda s_C []$ in equation (6-84) is positive or negative depending upon whether the temperature t is less than or greater than t_λ , and vanishes when $t = t_\lambda$.

The condition that $(\Delta f_m)_\lambda = 0$ may be written

$$\begin{aligned}
 t_O - t &= \frac{2t_O}{\rho_C L_O} \left[\frac{\sigma_{CL}}{r_C} \left(1 - \frac{\lambda}{2r_C} \right) \left(1 - \frac{\lambda}{r_C} + \frac{1}{3} \frac{\lambda^2}{r_C^2} \right)^{-1} - \frac{\sigma_L}{r_C} \delta \right. \\
 &\quad \left. - \frac{\sigma_{CL} + \sigma_L - \sigma_C}{2\lambda} \left(1 - \frac{\lambda}{r_C} + \frac{1}{3} \frac{\lambda^2}{r_C^2} \right)^{-1} \right]
 \end{aligned} \quad (6-87)$$

and when λ is small compared with r_C , we may write this condition approximately

$$t_O - t = \frac{2t_O}{\rho_C L_O} \left[\frac{\sigma_{CL}}{r_C - \frac{\lambda}{2}} - \frac{\sigma_L}{r_C} \delta - \frac{\sigma_{CL} + \sigma_L - \sigma_C}{2\lambda} \left(1 - \frac{\lambda}{r_C} \right)^{-1} \right] \quad (6-88)$$

(ii) The melting temperature of a small crystallite

The way in which the total Helmholtz free energy of the system varies with the radius, r_{CL} , of the crystalline core is represented schematically in figure 39 for six discrete values of the temperature: four of these temperatures - including the two designated as t_1 and t_2 - are not specifically defined. The values of $(\Delta f_m)_\lambda$ have been taken to be positive at the two temperatures t_{TS} and t_2 and the free energy has been dotted in the region $r_C - \lambda < r_{CL} < r_C$: it has been assumed that the free energy is a smooth function of r_{CL} in this region. Of the six temperatures considered, t_1 is the lowest and t_λ the highest.

It is seen from figure 39, that if the system is in the liquid state ($r_{CL} = 0$) at the relatively low temperature t_1 , then only a small free energy barrier Δf_s separates the system from the attainment of the much lower energy level represented by complete solidification. If the system is in the liquid state at the temperature t_λ , then as the temperature is lowered towards t_1 , the system moves up the line $r_{CL} = 0$ until a temperature is reached at which the energy barrier becomes small enough for there to be an appreciable probability of its being surmounted by a statistical fluctuation. Such ideas form the basis of nucleation theory, and are discussed quantitatively in § 6.4.

If the system is in the crystalline state ($r_{CL} = r_C$) at the relatively high temperature t_2 , then only a small free energy barrier Δf_m separates the system from the attainment of the much lower energy level represented by complete melting. If the system is in the crystalline state at the temperature t_1 , then as the temperature is increased towards t_λ , the system moves down the line $r_{CL} = r_C$ (provided $(\Delta f_m)_\lambda$ remains positive) until a temperature is reached at which the energy barrier becomes small enough for there to be an appreciable probability of its being surmounted by a statistical fluctuation. An estimate of the height of the barrier at which this probability may be expected to become appreciable may be made on the basis of absolute rate theory; a figure of some 35kt being appropriate to a crystallite of radius $25 \text{ \AA}$ and 40kt to a crystallite of radius $500 \text{ \AA}$, where k is Boltzmann's constant and t the absolute temperature. For the larger crystallites this energy is certainly small, so for the larger

* See Turnbull and Fisher, 1949

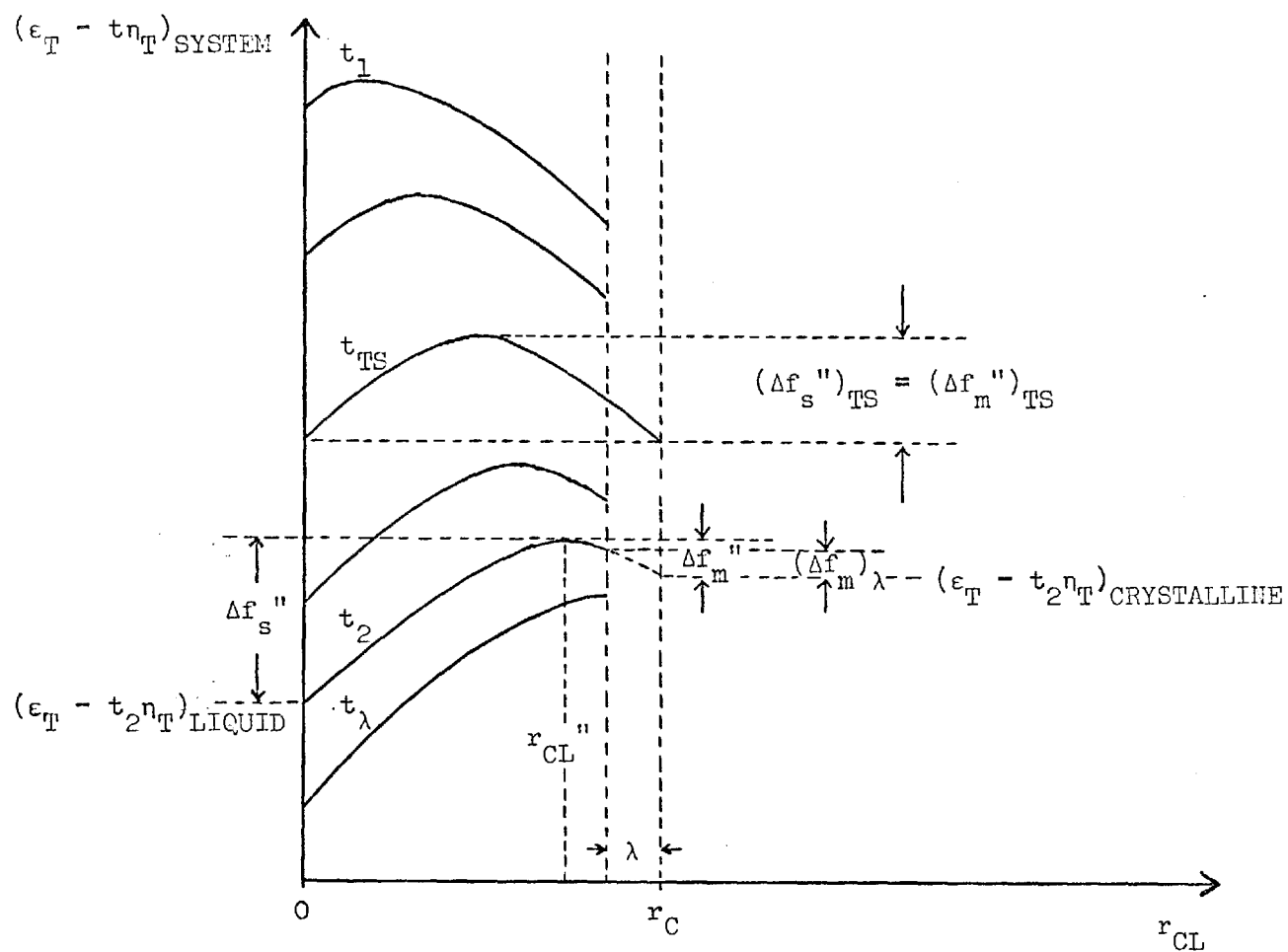


Figure 39. The "liquid-shell" model: the dependence of the total Helmholtz free energy of the system on the radius, r_{CL} , of the crystalline core

crystallites we may assume that for melting to take place the free energy barrier must vanish. In applying this criterion to obtain an expression for the melting temperature of a crystallite we may distinguish two possible cases.

(a) The free energy of formation of the liquid shell of critical thickness λ (see equation (6-84)) is zero or negative at the temperature t_λ , i.e.

$$\left[(\Delta f_m)_\lambda \right]_{t=t_\lambda} \leq 0 \quad (6-89)$$

In this case we may identify the melting temperature of the crystallite with the temperature t_λ defined by equation (6-85) or (6-86) - see also figure 39.

As indicated above, if λ is small compared with r_c , the term $\lambda s_c []$ in equation (6-84) is approximately zero when $t = t_\lambda$: therefore equation (6-89) will appertain provided

$$\sigma_c \geq \sigma_L + \sigma_{CL} \quad (6-90)$$

since this makes the term $(\sigma_{CL} + \sigma_L - \sigma_c)s_c$ in equation (6-84) zero or negative.

Equation (6-90) may be compared with the criterion for complete wetting discussed in § 1.2 - see equation (1-2). Turnbull has stated - see Turnbull (1956), pg. 292 :

"... the magnitude ... of the overheating, required for sensible nucleation of liquid droplets in perfect crystals, should be only a little less than that of the undercooling which causes sensible homogeneous nucleation of crystals. In ordinary experience, crystals do not overheat perceptibly because, as a consequence of the relation

$$\sigma_{\beta v} \geq \sigma_{\alpha v} + \sigma_{\alpha \beta} \quad (6-91)$$

(where β , v and α denote, respectively, crystal, vapour and liquid), there is no thermodynamic barrier to liquid nucleation at the external

clean surface of the crystal."

It should be noted that equation (6-91) applies to the values of the quantities $\sigma_{\beta v}$, $\sigma_{\alpha v}$ and $\sigma_{\alpha\beta}$ at the bulk melting point.

If

$$\sigma_C > \sigma_L + \sigma_{CL} \quad (6-92)$$

then $(\Delta f_m)_\lambda$ will become negative at a temperature below t_λ , so that there will be a minimum of the free energy of the system, as r_{CL} varies, in the vicinity of $r_{CL} = r_C - \lambda$. This implies that as the temperature is raised, a stable liquid layer will form on the crystallite while the bulk of the crystallite remains solid until the temperature t_λ is reached. Under these circumstances, t_λ may properly be regarded as the melting temperature of the crystallite. However, we are drawn to the conclusion (if equation (6-92) pertains) that even the bulk material should exhibit a very great "surface roughening" at temperatures a little below the melting point. It may be noted that calculations of the degree of surface roughening as a function of the temperature have been made, from a statistical mechanical viewpoint, by a number of authors - see, for example, Burton, Cabrera and Frank (1951); Mullins (1959); and Valenta and Sukiennicki (1966). The surface roughening of face-centred-cubic metals has recently been investigated by Karge, Heyer and Pound (1967). (b) There is still a free energy barrier to the formation of a liquid shell of critical thickness, on raising the temperature of the crystallite to t_λ , i.e.

$$\left[(\Delta f_m)_\lambda \right]_{t=t_\lambda} > 0 \quad (6-93)$$

Under these circumstances we may expect the criterion

$$(\Delta f_m)_\lambda = 0 \quad (6-94)$$

to yield an appropriate expression for the melting temperature. Thus for

crystallites for which r_C is large compared with λ , equation (6-88) should yield the proper melting temperature.

When terms in λ/r_C may be neglected, reference to equation (6-84) indicates that equation (6-93) requires

$$\sigma_C < \sigma_L + \sigma_{CL} \quad (6-95)$$

The condition (6-95) might come about as a result of a lowering of the values of σ_C and σ_L , due to the adsorption at the surface of a crystallite of the residual gases in the vacuum. In this connection, the interesting proposal of Holloman and Turnbull (1953) that "it should be possible to substantially superheat tiny ice crystals covered with a coherent coating of silver iodide" may be noted - c.f. Powell and Fletcher in "Discussion (1965)". In view of the rather small dependence of σ_C , σ_L and σ_{CL} on the temperature - see § 6.3.1(ii) (pg. 149) - the influence of temperature on the relative values of σ_C and $(\sigma_L + \sigma_{CL})$ is likely to be slight.

The conclusions concerning the melting temperature of a small crystallite arrived at in (a) and (b) above would have to be rejected, if it could be shown that an asymmetric mechanism of melting allowed the attainment of the molten state at a temperature lower than is predicted by equation (6-86) or (6-88). Such an asymmetric model of melting is investigated in § 6.3.4.

The dependence of the Helmholtz free energy of the system on the radius, r_{CL} , of the crystalline core at the two-state melting temperature, t_{TS} , is indicated in figure 39. For a crystallite that is small enough for there to be an appreciable probability per ^{unit time} ~~second~~ that the energy barrier $(\Delta f_m)_{TS} = (\Delta f_s)_{TS}$ will be surmounted as a result of a statistical fluctuation, its melting and solidification temperatures may both be taken to be t_{TS} . At a temperature slightly greater than t_{TS} , the crystallite will spend the majority of its time in the liquid state; and at a temperature slightly below t_{TS} , it will spend the majority of its time in the crystalline state. It thus appears that the melting and solidification temperatures of a large crystallite should differ

appreciably, but that this difference should become smaller and eventually disappear as the crystallite radius decreases.

6.3.4 The "asymmetric-melting" model

Consider the system examined in § 6.3.2 and § 6.3.3 : suppose that the crystallite is partially melted as shown in figure 40(a), with spherical interfaces separating the various regions. For the crystal-liquid and crystal-vapour interfaces, we will employ the dividing surfaces which make the superficial density of mass vanish: for the liquid-vapour interface we will employ the surface of tension. Of the quantities defined above in § 6.3.2 and § 6.3.3, the quantities s_{CL} , r_{CL} , s_L' , r_L' , m_L^s , m_C' , v_C' , p_C' , μ_C' , m_L' , v_L' , p_L' , μ_L' and Δf_m defined on pages 160 and 161, are now regarded as applying to this new partially-melted configuration: other quantities are as defined previously. We define the additional quantities:

s_C' - area of the crystal-vapour dividing surface

h_C , h_L and h_{CL} - see figure 40(a).

The total Helmholtz free energy of the system, not necessarily in equilibrium, $(\epsilon_T - t\eta_T)_{h_C, r_{CL}}$, may be written in the two forms

$$(\epsilon_T - t\eta_T)_{h_C, r_{CL}} = (\epsilon_T - t\eta_T)_{\text{CRYSTALLINE}} + \Delta f_m \quad (6-96)$$

$$= -p_C'v_C' + \mu_C'm_C' + \sigma_C s_C' + \sigma_{CL}s_{CL} \quad (6-97)$$

$$- p_L'v_L' + \mu_L'm_L' + \mu_L^s m_L^s + \sigma_L s_L'$$

where Δf_m is (now) the free energy of formation of a liquid cap on a spherical crystallite.

With the same approximations as were made in § 6.3.3(i), we may obtain

$$m = m_C' + m_L' \quad (6-98)$$

$$m = \rho_C v_C \quad m_C' = \rho_C v_C' \quad m_L' = \rho_L v_L' \quad (6-99)$$

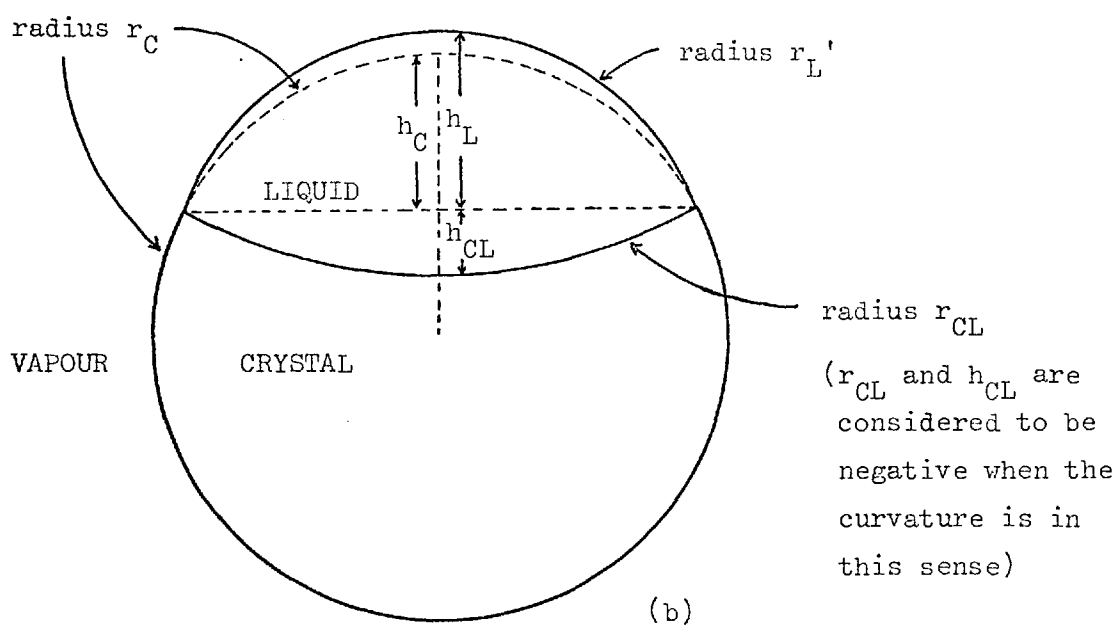
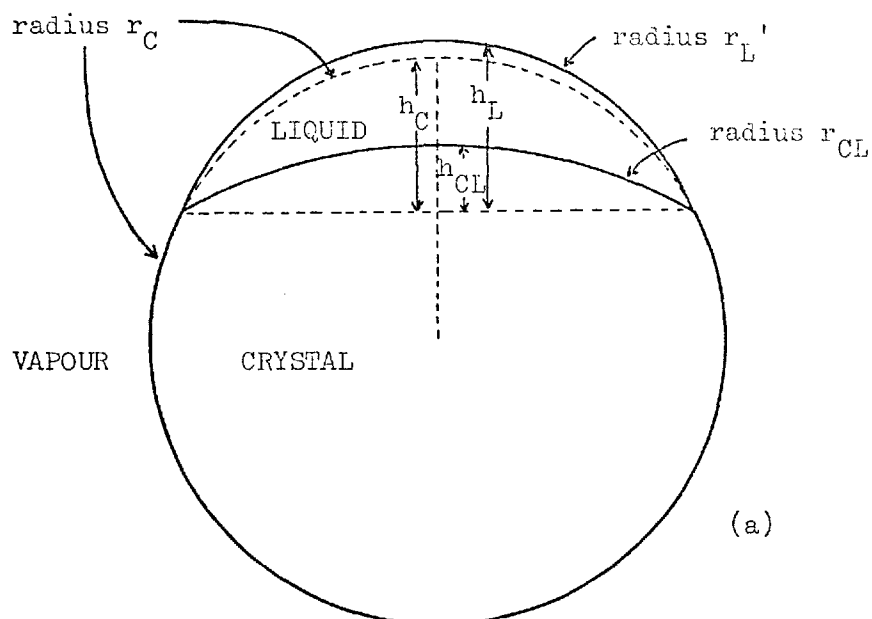


Figure 40 (a) and (b). The "asymmetric-melting" model

and

$$\Delta f_m = \sigma_{CL} s_{CL} + \sigma_L s_L' - \sigma_C (s_C - s_C') + \frac{\rho_{CL}^L}{t_o} (t_o - t)(v_C - v_C') \quad (6-100)$$

compare equations (6-66), (6-72) and (6-73).

We also have

$$s_{CL} = 2\pi r_{CL} h_{CL} \quad (6-101)$$

$$s_L' = 2\pi r_L' h_L' \quad (6-102)$$

$$s_C - s_C' = 2\pi r_C h_C \quad (6-103)$$

$$v_C - v_C' = \pi h_C^2 (r_C - \frac{1}{3} h_C) - \pi h_{CL}^2 (r_{CL} - \frac{1}{3} h_{CL}) \quad (6-104)$$

$$X_1 \equiv h_C (2r_C - h_C) - h_{CL} (2r_{CL} - h_{CL}) = 0 \quad (6-105)$$

$$X_2 \equiv h_L (2r_L' - h_L) - h_{CL} (2r_{CL} - h_{CL}) = 0 \quad (6-106)$$

$$\begin{aligned} X_3 \equiv & \rho_L \pi h_L^2 (r_L' - \frac{1}{3} h_L) - \rho_C \pi h_C^2 (r_C - \frac{1}{3} h_C) \\ & + (\rho_C - \rho_L) \pi h_{CL}^2 (r_{CL} - \frac{1}{3} h_{CL}) = 0 \end{aligned} \quad (6-107)$$

where the functions X_1 , X_2 and X_3 are defined by the identities in equations (6-105), (6-106) and (6-107).

The functions X_1 and X_2 are zero by geometrical necessity; and the function X_3 is also zero, as may be demonstrated from equations (6-98) and (6-99).

With reference to equations (6-101) to (6-104) and equation (6-78), we may write equation (6-100) in the form

$$\Delta f_m = \sigma_{CL} 2\pi r_{CL} h_{CL} + \sigma_L 2\pi r_L' h_L - \sigma_C 2\pi r_C h_C + K \left[\pi h_C^2 \left(r_C - \frac{1}{3} h_C \right) - \pi h_{CL}^2 \left(r_{CL} - \frac{1}{3} h_{CL} \right) \right] \quad (6-108)$$

In order to identify the melting temperature which may properly be ascribed to the asymmetric-melting model, we now turn our attention to a consideration of the equilibrium of the system. Whereas the conditions for thermodynamic equilibrium of the liquid-shell model comprised only relationships previously derived in § 6.2, we shall see that one relationship in addition to those of § 6.2 must be satisfied, to secure the equilibrium of the asymmetric-melting configuration. This relationship - equation (6-115) below - may be regarded as defining the value of h_C at equilibrium.

The equilibrium of the system requires that the total Helmholtz free energy of the system have a stationary value with respect to all infinitesimal reversible variations of the system contained within the fixed envelope - see page 154. When the temperature of the system is regarded as fixed, reference to equation (6-96) shows that the total Helmholtz free energy of the system will be stationary with respect to infinitesimal variations of the crystal-liquid interface, when Δf_m is stationary with respect to such variations. An investigation of the equilibrium of the system with respect to variations of the crystal-liquid interface may therefore take the form of an examination of the stationarity of Δf_m with respect to such variations. It will be instructive to consider first the stationarity of Δf_m with respect to variations in the crystal-liquid interface for which r_{CL} varies while h_C is regarded as fixed: this leads once again to the equation which defines the value of r_{CL} at equilibrium. We will afterwards examine the stationarity of Δf_m with respect to the variation of h_C .

Employing Lagrange's method of multipliers, and considering the stationarity of the quantity

$$U = \Delta f_m + \lambda_1 X_1 + \lambda_2 X_2 + \lambda_3 X_3$$

we obtain as the condition for the stationarity of Δf_m on varying r_{CL} , r_L' , h_{CL} and h_L (one independent), the four equations

$$\frac{\partial \Delta f_m}{\partial \mu} + \lambda_1 \frac{\partial X_1}{\partial \mu} + \lambda_2 \frac{\partial X_2}{\partial \mu} + \lambda_3 \frac{\partial X_3}{\partial \mu} = 0 \quad (6-109)$$

for $\mu = r_{CL}, r_L', h_{CL}, h_L$ in turn

Here r_C , σ_{CL} , σ_L , σ_C , K and h_C are regarded as constant. On eliminating λ_1 , λ_2 and λ_3 , we obtain

$$\frac{2\sigma_{CL}}{r_{CL}''} = \frac{2\sigma_L}{r_L''} \left(\frac{\rho_C}{\rho_L} - 1 \right) + K \quad (6-110)$$

where the values of r_{CL} and r_L' for which Δf_m is stationary are distinguished by a double prime. Equation (6-110) is a condition for thermodynamic equilibrium which we have already encountered - compare equations (6-50) and (6-62). Let t_{rC} denote the temperature at which the radius r_{CL}'' is equal to the crystallite radius, r_C .

Suppose $h_C < r_C$. Then it follows as a geometrical necessity that $r_{CL} > r_C$ (or $-r_C < r_{CL} < 0$, see below). If the temperature, t , is less than t_{rC} , there is no stationary value of Δf_m as r_{CL} varies: Δf_m decreases monotonically as r_{CL} decreases towards r_C . If $t > t_{rC}$, it may be demonstrated (most simply by neglecting terms of the order of the density difference between the solid and the liquid) that the stationary value of Δf_m for $r_{CL} = r_{CL}''$ is, in fact, a minimum for both positive (i.e. $t < t_0$) and negative (i.e. $t > t_0$) values of K , provided that negative values of r_{CL} are interpreted as indicating that the curvature of the crystal-liquid interface is in the opposite sense - see figure 40(b).

We may conclude that, at any particular temperature, the asymmetric-melting mechanism which represents the lowest free energy path between the wholly-crystalline and wholly-liquid states of the system, is that involving the passage through the crystallite of a crystal-liquid

interface of (fixed) radius r_{CL}'' . In order to investigate the nature of any free energy barrier to the melting of the crystallite in this manner, we now examine how Δf_m varies with h_C at constant temperature, when $r_{CL} = r_{CL}''$. For simplicity, the double prime which has been used to distinguish equilibrium values is now dropped.

The condition for the stationarity of Δf_m on varying h_C , r_L' , h_{CL} and h_L (one independent) is obtained by putting $\mu = h_C$, r_L' , h_{CL} and h_L , in turn, in equation (6-109): hence, on eliminating λ_1 , λ_2 and λ_3 , we obtain

$$\begin{aligned} & \left(2\sigma_{CL}r_{CL} - Kh_{CL}r_{CL} - \frac{2\sigma_L}{\rho_L r_L'} (\rho_C - \rho_L)h_{CL}r_{CL} \right) (r_C - h_C) \\ & + 2\sigma_L(r_{CL} - h_{CL})(r_C - h_C) - 2\sigma_C r_C (r_{CL} - h_{CL}) \\ & + K \left(h_C(2r_C - h_C) - h_{CL}(r_C - h_C) \right) (r_{CL} - h_{CL}) - \\ & \frac{2\sigma_L}{\rho_L r_L'} \left(\rho_L h_L (r_C - h_C) + (\rho_C - \rho_L)h_{CL}(r_C - h_C) - \rho_C h_C(2r_C - h_C) \right) (r_{CL} - h_{CL}) = 0 \end{aligned} \quad (6-111)$$

The application of equation (6-110) enables us to divide equation (6-111) through immediately by a factor $(r_{CL} - h_{CL})$. On rearranging, the equation may be written

$$\begin{aligned} & 2(\sigma_{CL} + \sigma_L - \sigma_C)r_C - 2\sigma_{CL}h_C + K \left(h_C r_C + (h_C - h_{CL})(r_C - h_C) \right) \\ & - 2\sigma_L h_C \left(1 - \frac{\rho_C r_C}{\rho_L r_L'} \right) - \frac{2\sigma_L}{\rho_L r_L'} \left(\rho_L h_L + (\rho_C - \rho_L)h_{CL} - \rho_C h_C \right) (r_C - h_C) = 0 \end{aligned} \quad (6-112)$$

Substituting for $2\sigma_{CL}$ from equation (6-110) in the second term of equation (6-112), and rearranging, we obtain

$$\begin{aligned}
& 2(\sigma_{CL} + \sigma_L - \sigma_C)r_C + K \left[(h_C - h_{CL})r_C - h_C(r_{CL} - r_C + h_C - h_{CL}) \right] \quad (6-113) \\
& - \frac{2\sigma_L}{\rho_L r_L'} \left[h_C(\rho_L r_L' - \rho_C r_C) + (\rho_L h_L - \rho_C h_C)(r_C - h_C) \right. \\
& \quad \left. + (\rho_C - \rho_L) \left[h_{CL}(r_C - h_C) + h_C r_{CL} \right] \right] = 0
\end{aligned}$$

Employing equation (6-115), we may write equation (6-113) in the form

$$\begin{aligned}
& 2(\sigma_{CL} + \sigma_L + \sigma_C)r_C + \left[K + \frac{2\sigma_L}{r_L'} \delta \right] \left[(h_C - h_{CL})r_C - h_C(r_{CL} - r_C + h_C - h_{CL}) \right] \\
& - \frac{2\sigma_L}{r_L'} \left[h_C(r_L' - r_C) + (h_L - h_C)(r_C - h_C) \right] = 0 \quad (6-114)
\end{aligned}$$

Making use of the equation

$$h_C(2r_C - h_C) = h_L(2r_L' - h_L)$$

- compare equations (6-105) and (6-106) - we may write the last term in equation (6-114) in the form

$$- \frac{2\sigma_L}{r_L'} \left[\frac{1}{2}(h_L - h_C)^2 - (h_L - h_C)(r_L' - r_C) \right]$$

which term is of second order in δ . To first order in δ , equation (6-114) may be written

$$2(\sigma_{CL} + \sigma_L - \sigma_C)r_C \quad (6-115)$$

$$+ \left[K + \frac{2\sigma_L}{r_L'} \delta \right] \left[(h_C - h_{CL})r_C - h_C(r_{CL} - r_C + h_C - h_{CL}) \right] = 0$$

This is a necessary condition for the equilibrium of the asymmetric-melting configuration: it may be regarded as defining the value of h_C for which Δf_m is a maximum. We may write equation (6-115) in a more illuminating form if we introduce the thickness of the liquid cap, λ' , defined by the equation

$$\lambda' = h_C - h_{CL} \quad (6-116)$$

We deduce, from equation (6-105), the relationships

$$h_C = \frac{\lambda'(2r_{CL} + \lambda')}{2(r_{CL} - r_C + \lambda')} \quad \text{and} \quad h_{CL} = \frac{\lambda'(2r_C - \lambda')}{2(r_{CL} - r_C + \lambda')} \quad (6-117)$$

Employing equations (6-116) and (6-117), equation (6-115) may be written

$$2(\sigma_{CL} + \sigma_L - \sigma_C)r_C + \lambda' \left[K + \frac{2\sigma_L}{r_L'} \delta \right] \left(r_C - r_{CL} - \frac{\lambda'}{2} \right) = 0$$

and making use of equation (6-110), we obtain

$$\sigma_{CL} + \sigma_L - \sigma_C + \frac{\lambda'}{2} \left[\left(K + \frac{2\sigma_L}{r_L'} \delta \right) \left(1 - \frac{\lambda'}{2r_C} \right) - \frac{2\sigma_{CL}}{r_C} \right] = 0 \quad (6-118)$$

Rearranging equation (6-118), and making use of the definition of K in equation (6-78), we obtain

$$t_o - t = \frac{2\tau_o}{\rho_{CL}^L} \left[\frac{\sigma_{CL}}{r_C - \frac{\lambda'}{2}} - \frac{\sigma_L}{r_L'} \delta - \frac{\sigma_{CL} + \sigma_L - \sigma_C}{\lambda'} \left(1 - \frac{\lambda'}{2r_C} \right)^{-1} \right] \quad (6-119)$$

We may expect that equation (6-108) will not properly represent the free energy of formation of the liquid cap, unless the thickness of the liquid cap is sufficient for its properties to approximate to those within a bulk liquid phase. It is assumed here that equation (6-108) is only valid for $\lambda' \geq \lambda$, where λ is the critical thickness of the order of a few tens of Angstrom units referred to in § 6.3.3.

If T_λ is the temperature at which $\lambda' = \lambda$, then from equation (6-119) we obtain, to first order in δ ,

$$t_o - T_\lambda = \frac{2t_o}{\rho_{CL}^L} \left[\frac{\sigma_{CL}}{r_C - \frac{\lambda}{2}} - \frac{\sigma_L}{r_C} \delta - \frac{\sigma_{CL} + \sigma_L - \sigma_C}{\lambda} \left(1 - \frac{\lambda}{2r_C} \right)^{-1} \right] \quad (6-120)$$

We may introduce the thickness of the crystalline material, x , defined by the equation

$$x = 2r_C - \lambda' \quad (6-121)$$

The way in which the total Helmholtz free energy of the system varies with the thickness of the crystalline material, x , is represented schematically in figure 41 for three discrete values of the temperature.

We see that if the free energy of formation of the liquid cap of critical thickness λ is zero or negative at the temperature T_λ , i.e.

$$\left[(\Delta f_m)_\lambda \right]_{t=T_\lambda} \leq 0 \quad (6-122)$$

then we may identify the melting temperature of the crystallite with the temperature T_λ defined by equation (6-120).

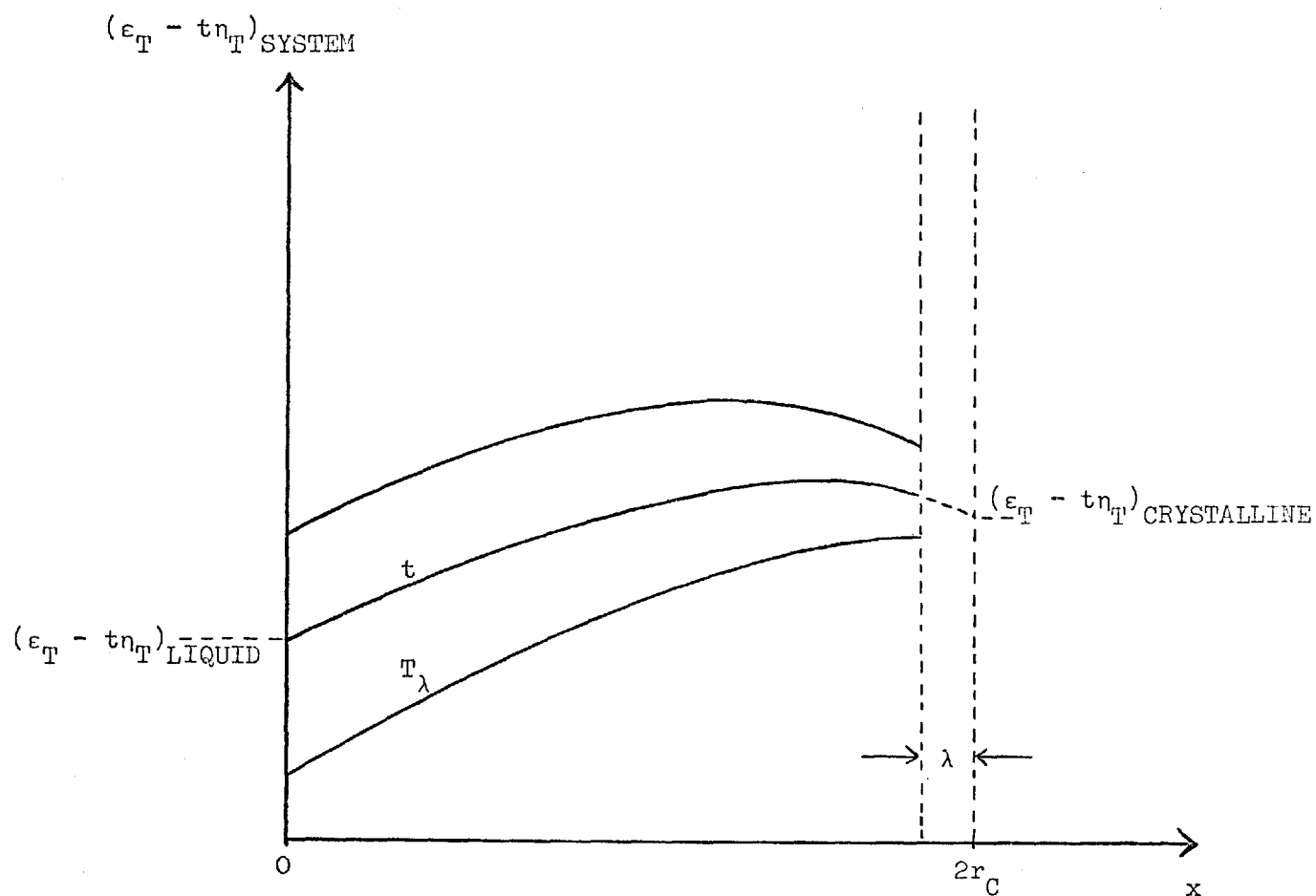


Figure 41. The "asymmetric-melting" model: the dependence of the total Helmholtz free energy of the system on the thickness, x , of the crystalline material

For a particular crystallite radius r_C , the temperature t_{rC} defined on page 176 is somewhat greater than the temperature t_λ defined on page 166. When t_λ may be identified as the melting temperature of the liquid-shell model (i.e. when case (a) on page 169 pertains), it follows from the observations on page 176 that the asymmetric-melting model cannot be regarded as a competitive mechanism of melting. Furthermore, on comparing equations (6-120) and (6-88), we see that when $\sigma_C < \sigma_L + \sigma_{CL}$, the temperature T_λ is greater than the temperature t defined by equation (6-88). We may therefore conclude that the asymmetric-melting mechanism is not competitive with the liquid-shell model even when case (b) on page 170 pertains.

6.4 Nucleation theory and solidification

6.4.1 Homogeneous nucleation theory

In the theory of homogeneous nucleation in condensed systems as developed by Turnbull and Fisher (1949), the local free energy change, ΔF_i , associated with the formation of a region of i atoms of a new phase β in a parent phase α , is taken to have the form

$$\frac{\Delta F_i}{kt} = Ai^{2/3} - Bi \quad (6-123)$$

where k is Boltzmann's constant

t is the absolute temperature

A is proportional to the interfacial free energy per unit area of α - β interface

and B is proportional to the bulk free energy difference between β and α in the absence of surfaces.

The theory of Turnbull and Fisher leads to the following expression for the frequency of formation, I , of stable crystal nuclei per volume of supercooled liquid

$$I = n^* \left(\frac{A}{9\pi} \right)^{1/2} \frac{nkt}{h} \exp \left(- \frac{\Delta F_A + \Delta F^*}{kt} \right) \quad (6-124)$$

where n^* is the number of atoms in the surface of a nucleus of critical size

n is the number of atoms per volume of liquid

k is Boltzmann's constant

h is Planck's constant

ΔF_A is the free energy of activation per atom for transport across the liquid-crystal interface

and ΔF^* is the free energy for formation of a critical nucleus, and is given by

$$\Delta F^* = kt \frac{4A^3}{27B^2} \quad (6-125)$$

Turnbull and Fisher's expression for the local free energy change, ΔF_i , associated with the formation of a spherical crystalline nucleus, may be written

$$\Delta F_i = 4\pi r_{CL}^2 \sigma_{CL} + \frac{4}{3} \pi r_{CL}^3 \Delta F_v \quad (6-126)$$

where r_{CL} is the radius of the nucleus

σ_{CL} is the interfacial free energy per unit area of crystal-liquid interface

and ΔF_v is the free energy change per volume for the transition liquid $\rightarrow$ crystal.

By writing equation (6-126) in the form of equation (6-123), we may infer

$$A = \frac{\sigma_{CL}}{kt} (36\pi\Omega^2)^{1/3} \quad (6-127)$$

and

$$B = - \frac{\Delta F_v}{kt} \Omega \quad (6-128)$$

where Ω is the volume per atom in the crystal.

With reference to equation (6-125), the free energy of formation of a critical nucleus, ΔF^* , may now be written

$$\Delta F^* = \frac{16\pi}{3} \frac{\sigma_{CL}^3}{(\Delta F_v)^2} \quad (6-129)$$

Turnbull - see Turnbull (1950) - takes the following (approximate) expression for ΔF_v

$$\Delta F_v = \frac{\lambda \Delta t}{t_o} \quad (6-130)$$

where λ is the heat of fusion per unit volume of the solid

$\Delta t = t - t_o$

t is the absolute temperature

and t_0 is the bulk melting temperature.

Turnbull's expression for ΔF_v in equation (6-130) is identical, apart from a difference in sign, with the definition of K in equation (6-78). Comparison of equations (6-126) and (6-80) shows that there is an additional term in equation (6-80) of the order of the density difference between the solid and the liquid: this term may be regarded as arising from the change in the liquid-vapour surface area consequent upon the formation of the crystalline nucleus. When equation (6-80) is written in the form of equation (6-123), we obtain

$$A = \frac{\sigma_{CL}}{kt} (36\pi\Omega^2)^{1/3} \quad (6-131)$$

and

$$B = \frac{\Omega}{kt} \left(K + \frac{2\sigma_L}{r_C} \delta \right) \quad (6-132)$$

Because the free energy of formation of a crystalline core, Δf_s , given by equation (6-80) can be written in the form of equation (6-123) (i.e. as the sum of two parts, one of which is proportional to $i^{2/3}$ and the other to i), it follows that the arguments developed by Turnbull and Fisher (1949) remain valid for a system in which the term in δ in equation (6-80) is not negligible. In particular, the nucleation frequency, I , will still be given by equation (6-124), where ΔF^* is, from equations (6-125), (6-131) and (6-132), given by

$$\Delta F^* = \frac{16\pi}{3} \frac{\sigma_{CL}^3}{\left(K + \frac{2\sigma_L}{r_C} \delta \right)^2} \quad (6-133)$$

The expression for ΔF^* in equation (6-133) is, of course, identical with the expression for Δf_s in equation (6-83).

An equation which is formally equivalent to equation (6-133) has been obtained by Laumann - see Laumann (1962), pg. 811 equation (16) - as the free energy of formation of a critical nucleus appropriate to the

theory of Turnbull and Fisher. In view of the wide use which has been made of equation (6-129), we may at once point out that for a supercooled liquid droplet of some 25 microns radius (typical of the droplet sizes investigated by Turnbull et al.), the term involving δ in equation (6-133) is extremely small, compared with the value of K at the temperature at which homogeneous nucleation occurs. The term involving δ does, however, become important for the very much smaller droplet radii investigated in the present experiments.

From equations (6-124) and (6-133), we obtain

$$I = n^* \left(\frac{A}{9\pi} \right)^{\frac{1}{2}} \frac{nkt}{h} \exp \left(- \frac{\Delta F_A}{kt} \right) \exp \left[- \frac{16\pi\sigma_{CL}^3}{3kt \left(K + \frac{2\sigma_L}{r_C} \delta \right)^2} \right] \quad (6-134)$$

Following Turnbull and Fisher - see Turnbull and Fisher (1949), pg. 73 - we take

$$n^* \left(\frac{A}{9\pi} \right)^{\frac{1}{2}} \sim 1 \quad (6-135)$$

Following Turnbull - see Turnbull (1950), pgs. 1022 and 1026 - we take

$$\exp \left(- \frac{\Delta F_A}{kt} \right) \sim 10^{-2} \quad (6-136)$$

Equation (6-134) may therefore be written, approximately

$$I = \frac{nkt}{h} 10^{-2} \exp \left[- \frac{16\pi\sigma_{CL}^3}{3kt \left(K + \frac{2\sigma_L}{r_C} \delta \right)^2} \right] \quad (6-137)$$

Here we may recall that I is the frequency of formation of critical nuclei per volume of supercooled liquid.

The frequency of nucleation, I^* , in our liquid droplet of radius r_L is

$$I^* = \frac{4}{3} \pi r_L^3 I \quad (6-138)$$

From equations (6-137) and (6-138), we may write, since $r_L \approx r_C$,

$$I^* = \frac{4\pi}{3} n \frac{k}{h} 10^{-2} r_C^3 t \exp \left[- \frac{16\pi\sigma_{CL}^3}{3kt \left(K + \frac{2\sigma_L}{r_C} \delta \right)^2} \right] \quad (6-139)$$

6.4.2 Heterogeneous nucleation

Figure 42 shows a liquid droplet, having a contact angle θ_2 with the (plane) surface of the substrate on which the droplet rests, and containing a crystalline core (a nucleus) which has a contact angle θ_1 with the substrate: both the droplet and its crystalline core are supposed to have the form of a segment of a sphere. Our considerations here pertain to the system contained within a fixed envelope encompassing the droplet, a portion of its surrounding vapour phase, and part of the substrate on which the droplet rests. The system may be regarded as completely isolated, except with respect to the free exchange of heat with its surroundings, which constrains a uniform temperature t throughout.

For the crystal-substrate, crystal-liquid, substrate-liquid and substrate-vapour interfaces, we choose the dividing surfaces which make the superficial density of mass of the component of the droplet vanish. For the liquid-vapour interface, we choose the surface of tension. Referred to these dividing surfaces, we define the quantities:

s_L , r_L and σ_L - area, radius and surface tension, respectively, of the liquid-vapour dividing surface

s_L^0 and r_L^0 - area and radius, respectively, of the liquid-vapour dividing surface when the crystalline core is completely melted

m_L , v_L and ρ_L - mass, volume and density, respectively, of the homogeneous liquid phase extending up to the dividing surfaces

m_L^0 and v_L^0 - mass and volume, respectively, of the homogeneous liquid phase when the crystalline core is completely melted

s_{CL} , r_{CL} and σ_{CL} - area, radius and specific surface work, respectively, of the crystal-liquid dividing surface

m_C , v_C and ρ_C - mass, volume and density, respectively, of the homogeneous crystalline region extending up to the dividing surfaces

s_{CS} and σ_{CS} - area and specific surface work, respectively, of the crystal-substrate dividing surface

s_{SL} and σ_{SL} - area and specific surface work, respectively, of the substrate-liquid dividing surface

s_{SL}^0 - area of the substrate-liquid dividing surface when the crystalline

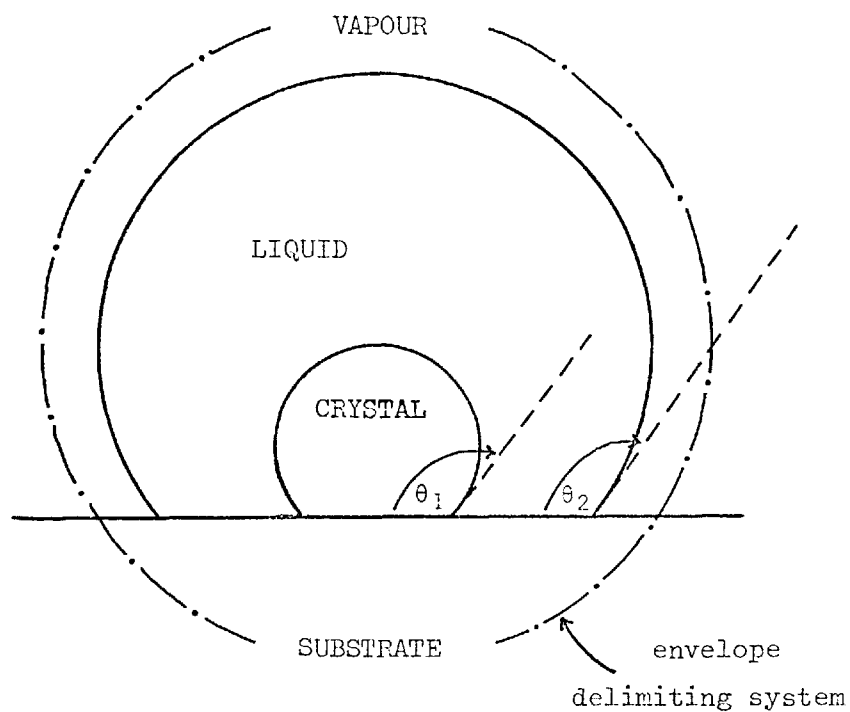


Figure 42. Model considered in connection with heterogeneous nucleation of a liquid droplet

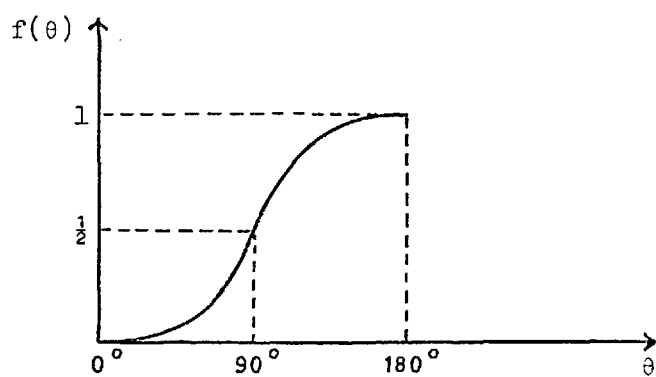


Figure 43. The function $f(\theta)$, defined by equation (6-140), for values of θ between 0° and 180°

core is completely melted

σ_S - specific surface work of the substrate-vapour dividing surface.

Other thermodynamic quantities appearing below are as previously defined.

It is convenient to define the functions $f(\theta)$, $g(\theta)$ and $h(\theta)$ by the equations

$$f(\theta) \equiv \frac{1}{4}(1 - \cos \theta)^2(2 + \cos \theta) \quad (6-140)$$

$$g(\theta) \equiv \frac{1}{2}(1 - \cos \theta) \quad (6-141)$$

$$h(\theta) \equiv \sin^2 \theta \quad (6-142)$$

The functions $f(\theta)$, $g(\theta)$ and $h(\theta)$ are related by the identity

$$4g(\theta) - \cos \theta h(\theta) \equiv 4f(\theta) \quad (6-143)$$

The relationships obtained immediately below, as far as equation (6-159), are merely preliminaries to deriving the free energy expressions which follow equation (6-159).

We may write

$$v_L^o = \frac{4}{3} \pi r_L^3 f(\theta_2) \quad (6-144)$$

$$v_L + v_C = \frac{4}{3} \pi r_L^3 f(\theta_2) \quad (6-145)$$

$$v_C = \frac{4}{3} \pi r_{CL}^3 f(\theta_1) \quad (6-146)$$

$$s_L^o = 4\pi r_L^2 g(\theta_2) \quad (6-147)$$

$$s_L = 4\pi r_L^2 g(\theta_2) \quad (6-148)$$

$$s_{CL} = 4\pi r_{CL}^2 g(\theta_1) \quad (6-149)$$

$$s_{SL}^0 = \pi r_L^2 h(\theta_2) \quad (6-150)$$

$$s_{SL} + s_{CS} = \pi r_L^2 h(\theta_2) \quad (6-151)$$

$$s_{CS} = \pi r_{CL}^2 h(\theta_1) \quad (6-152)$$

From equations (6-149), (6-152) and (6-143), we deduce

$$s_{CL} - \cos \theta_1 s_{CS} = 4\pi r_{CL}^2 f(\theta_1) \quad (6-153)$$

From equations (6-147), (6-148), (6-150), (6-151) and (6-143), we deduce

$$(s_L - s_L^0) - \cos \theta_2 (s_{SL} + s_{CS} - s_{SL}^0) = 4\pi(r_L^2 - r_L^2 \cos^2 \theta_2) f(\theta_2) \quad (6-154)$$

Neglecting the superficial mass associated with the liquid-vapour interface, and any change in the mass of the vapour phase, we may write

$$m_L^0 = m_L + m_C$$

from which we deduce

$$\rho_L v_L^0 = \rho_L v_L + \rho_C v_C \quad (6-155)$$

With reference to equation (6-75), equation (6-155) may be written

$$v_L^0 = v_L + v_C + \delta v_C \quad (6-156)$$

From equations (6-156), (6-144), (6-145) and (6-146), we obtain

$$r_L^3 f(\theta_2) = r_L^3 f(\theta_2) + \delta r_{CL}^3 f(\theta_1)$$

$$\text{i.e.} \quad r_L^3 = r_L^3 \left(1 - \delta \frac{r_{CL}^3 f(\theta_1)}{r_L^3 f(\theta_2)} \right) \quad (6-157)$$

From equation (6-157) we obtain, to first order in δ ,

$$r_L^2 = r_{L^0}^2 \left(1 - \frac{2}{3} \delta \frac{r_{CL}^3}{r_{L^0}^3} \frac{f(\theta_1)}{f(\theta_2)} \right)$$

$$\text{i.e. } r_L^2 - r_{L^0}^2 = - \frac{2}{3} \delta \frac{r_{CL}^3}{r_{L^0}^3} \frac{f(\theta_1)}{f(\theta_2)} \quad (6-158)$$

From equations (6-154), (6-158) and (6-146), we obtain

$$(s_L - s_{L^0}) - \cos \theta_2 (s_{SL} + s_{CS} - s_{SL}^0) = - \frac{2}{r_{L^0}} \delta v_C \quad (6-159)$$

The increase, Δf_s , in the total Helmholtz free energy of the system, when the crystalline core is formed inside the liquid droplet, is

$$\Delta f_s = \sigma_{CL} s_{CL} + (\sigma_{CS} - \sigma_{SL}) s_{CS} + \sigma_L (s_L - s_{L^0})$$

$$+ (\sigma_{SL} - \sigma_S) (s_{SL} + s_{CS} - s_{SL}^0) - \frac{\rho_{CL}^L}{t_C} (t_o - t) v_C \quad (6-160)$$

We may assume that the conditions for equilibrium at the two three-phase boundaries are satisfied, i.e.

$$\sigma_{CS} - \sigma_{SL} = - \sigma_{CL} \cos \theta_1 \quad (6-161)$$

and

$$\sigma_{SL} - \sigma_S = - \sigma_L \cos \theta_2 \quad (6-162)$$

The equations (6-161) and (6-162), which may be derived as conditions for the equilibrium of the system, play a role comparable with that of equation (6-110) in § 6.3.4. They may be regarded as ensuring that the energy of formation of a critical nucleus (derived below) is, indeed, the

minimum free energy of formation.

From equations (6-160), (6-161), (6-162), (6-153) and (6-159), we obtain

$$\Delta f_s = \sigma_{CL} 4\pi r_{CL}^2 f(\theta_1) - \sigma_L \frac{2}{r_L^0} \delta v_C - \frac{\rho_{CL}^L}{t_0} (t_0 - t) v_C \quad (6-163)$$

Suppose r_C is the radius of the crystallite into which the liquid droplet will solidify: then, to a good approximation, we may substitute r_C for r_L^0 in equation (6-163). Introducing the quantity K defined by equation (6-78), and employing equation (6-146), we may write equation (6-163) in the form

$$\Delta f_s = \sigma_{CL} f(\theta_1) 4\pi r_{CL}^2 - \left[K + \frac{2\sigma_L}{r_C} \delta \right] f(\theta_1) \frac{4}{3} \pi r_{CL}^3 \quad (6-164)$$

By differentiating equation (6-164) w.r.t. r_{CL} , we find that the maximum value, ΔF^* , of Δf_s , as r_{CL} varies, is

$$\Delta F^* = \frac{16\pi}{3} \frac{\sigma_{CL}^3 f(\theta_1)}{\left[K + \frac{2\sigma_L}{r_C} \delta \right]^2} \quad (6-165)$$

However, it is more important to observe that equation (6-164) may be written in the form of equation (6-123). To do this, we note that

$$\frac{4}{3} \pi r_{CL}^3 f(\theta_1) = i\Omega \quad (6-166)$$

where i is the number of atoms in the crystalline phase

and Ω is the volume per atom in the crystal.

From equation (6-166), we have

$$r_{CL}^2 = \left(\frac{3}{4\pi} \frac{\Omega}{f(\theta_1)} \right)^{2/3} i^{2/3} \quad (6-167)$$

We obtain

$$A = \frac{\sigma_{CL} [f(\theta_1)]^{1/3}}{kt} (36\pi\Omega^2)^{1/3} \quad (6-168)$$

and

$$B = \frac{\Omega}{kt} \left(K + \frac{2\sigma_L}{r_C} \delta \right) \quad (6-169)$$

which may be compared with equations (6-131) and (6-132). From equations (6-125), (6-168) and (6-169) we may now derive equation (6-165).

Parallel to equation (6-134), we may write for the frequency, I_S , of formation of stable crystal nuclei per area of substrate-liquid interface

$$I_S = n^* \left(\frac{A}{9\pi} \right)^{1/2} \frac{n_S kt}{h} \exp \left(- \frac{\Delta F_A}{kt} \right) \exp \left[- \frac{16\pi\sigma_{CL}^3 f(\theta_1)}{3kt \left(K + \frac{2\sigma_L}{r_C} \delta \right)^2} \right] \quad (6-170)$$

where n^* is the number of atoms in the crystal-liquid interface of a nucleus of critical size

n_S is the number of atoms in the substrate-liquid interface per unit area

A is given by equation (6-168)

and other quantities are as previously defined.

Equation (6-170) is identical, apart from the term in δ , with the expressions for the frequency of heterogeneous nucleation derived by Turnbull - see Turnbull (1952), pg. 411; and Turnbull (1956), pg. 277. This was not, necessarily, to be expected, as the geometrical configuration of the model considered here differs from that employed by Turnbull: nothing corresponding to the contact angle between the liquid droplet and the substrate appears in Turnbull's work, as he assumes that nucleation occurs on inclusions (impurities) contained within the droplet surface.

With approximations similar to those leading to equation (6-137), we obtain - c.f. Turnbull (1950), pg. 1023

$$I_S = \frac{n_S k t}{h} 10^{-2} \exp \left[- \frac{16 \pi \sigma_{CL}^3 f(\theta_1)}{3 k t \left(K + \frac{2 \sigma_L}{r_C} \delta \right)^2} \right] \quad (6-171)$$

The nucleation frequency, I_S^* , in our liquid droplet of radius r_L^o is

$$I_S^* = \pi r_L^{o2} h(\theta_2) I_S \quad (6-172)$$

From equations (6-171) and (6-172), we may write, since $r_L^o \approx r_C$,

$$I_S^* = \pi n_S \frac{k}{h} 10^{-2} r_C^2 h(\theta_2) t \exp \left[- \frac{16 \pi \sigma_{CL}^3 f(\theta_1)}{3 k t \left(K + \frac{2 \sigma_L}{r_C} \delta \right)^2} \right] \quad (6-173)$$

CHAPTER 7

EXAMINATION OF THE EXPERIMENTAL RESULTS IN THE LIGHT OF THEORY, AND CONCLUSIONS

In applying the macroscopic concepts of thermodynamics to systems representing very small crystals, it may be observed that the larger the system, the more likely it is that theoretical predictions will be valid. It follows that, in choosing the values of parameters to accord the predictions of theory with the experimental results, those fits are to be preferred which agree ^{with} the experimental results for large crystallite sizes.

7.1 Melting

It was concluded in § 6.3.4 (see pg. 182) that the asymmetric-melting model is not competitive with the liquid-shell model as a mechanism of melting. Without a full analysis of the modes of melting of a model of the kind examined in § 6.4.2, it is deemed most expedient to interpret the experimental results on the melting of small metallic crystals in terms of the liquid-shell model - see § 6.3.3. With regard to this model, it will be noted that two cases are distinguished - (a) and (b) of § 6.3.3(ii) - depending upon the relative magnitudes of the quantities σ_C and $\sigma_L + \sigma_{CL}$. The melting temperature, t_λ , which pertains to case (a) is given by equation (6-86); and the melting temperature, t , which pertains to case (b) is given by equation (6-87). Without reference to the experimental results, there is no criterion for deciding whether case (a) or case (b) may be expected to apply. The choice between the melting point formulae (6-86) and (6-87) has therefore been made, according to which gives the more satisfactory fit to the experimental results.

(i) Lead

In comparing the predictions of the liquid-shell model with the experimental results for the melting temperature of small lead crystals, it was found that the more satisfactory fit is obtained from equation (6-86). Making use of the data given in table 6, equation (6-86) becomes

Mechanical equivalent of heat, $J = 4.1855 \text{ erg/cal.}_{15}$

	Lead	Bismuth	Indium
Melting point ($^{\circ}\text{C}$)	327.4	271.3	156.4
Melting point, t_o ($^{\circ}\text{K}$)	600.6	544.5	429.6
* Density of solid at melting point, ρ_c (gm./cc.)	10.97	9.72	7.17
* Latent heat (k cal./gm. atom)	1.19	2.60	0.78
* Latent heat, L_o (erg/gm.)	24.04×10^7	52.07×10^7	28.43×10^7
* $\frac{2t_o}{\rho_c L_o}$ ($^{\circ}\text{K cm.}^3 \text{ erg}^{-1}$)	4.555×10^{-7}	2.152×10^{-7}	4.215×10^{-7}
* Fractional increase in volume on melting, δ	0.035	- 0.0335	0.020
* Surface tension of liquid metal at melting point, σ_L (erg cm. $^{-2}$)	480	390	559
* $\sigma_L \delta$ (erg cm. $^{-2}$)	16.8	- 13.065	11.18

* Taken or derived from Smithells' "Metals Reference Book" (1967)

Table 6. Data used in interpreting the experimental results on the melting of small metallic crystals.

for lead

$$t_o - t_\lambda = 45.55 \left[\frac{\sigma_{CL}}{r_C - \lambda} - \frac{16.8}{r_C} \right] \quad (7-1)$$

where t_o °K is the melting temperature of bulk lead

λ is a critical liquid-shell thickness, of the order of a few tens of Angstrom units

t_λ °K is the melting temperature of a crystallite of radius r_C
 σ_{CL} erg cm.⁻² is the crystal-liquid specific interfacial free energy

and r_C and λ are measured in Å.

A fit to the experimental results on the basis of equation (7-1) is shown in figure 32. The values $\lambda = 30$ Å and $\sigma_{CL} = 40$ erg cm.⁻² have been chosen. As may be seen, the equation represents the experimental results well over a wide range of crystallite radii. Somewhat less satisfactory fits may be obtained with values of λ of 25 Å or 35 Å and corresponding values of σ_{CL} of 47 and 36 erg cm.⁻², respectively. It is concluded that, for all but the smallest lead crystals examined, the experimental results for the melting temperature of small lead crystals may be understood by the application of thermodynamics to a model representing the melting of a small crystal. The following value is inferred for the crystal-liquid interfacial free energy, σ_{CL}

$$\sigma_{CL} = 40 \pm 7 \text{ erg cm.}^{-2} \quad (7-2)$$

(ii) Bismuth

The experimental results for the melting temperatures of small bismuth crystals may be better represented on the basis of the liquid-shell model, if it is assumed that case (b) pertains. From the data of table 6, equation (6-87) may be written for bismuth

$$t_o - t = 21.52 \left[\frac{\sigma_{CL}}{r_C} \left(1 - \frac{\lambda}{2r_C} \right) - \frac{\Delta\sigma}{2\lambda} \right] \left[1 - \frac{\lambda}{r_C} + \frac{1}{3} \frac{\lambda}{r_C^2} \right]^{-1} + \frac{13.07}{r_C} \quad (7-3)$$

where $t_o^{\circ}\text{K}$ is the melting temperature of bulk bismuth
 $t^{\circ}\text{K}$ is the melting temperature of a crystallite of radius r_C
 λ is a critical liquid-shell thickness, of the order of a few tens
of Angstrom units
 r_C and λ are measured in $\text{\AA}$
 $\Delta\sigma = \sigma_{CL} + \sigma_L - \sigma_C$
 $\sigma_{CL} \text{ erg cm.}^{-2}$ is the crystal-liquid specific interfacial free
energy
 $\sigma_L \text{ erg cm.}^{-2}$ is the liquid-vapour specific interfacial free energy
and $\sigma_C \text{ erg cm.}^{-2}$ is the crystal-vapour specific interfacial free
energy.

A fit to the experimental results on the basis of equation (7-3) is shown in figure 33. The values $\lambda = 30 \text{ \AA}$, $\sigma_{CL} = 55 \text{ erg cm.}^{-2}$ and $\Delta\sigma = 39 \text{ erg cm.}^{-2}$ have been chosen. It will be seen that the theoretical curve represents the experimental plots of the first-melting temperature adequately down to crystallite radii of some $60 \text{ \AA}$. It is to be expected that the critical thickness, λ , will be sensibly the same for the three metals investigated; the value of λ quoted ($30 \text{ \AA}$) was chosen to be consistent with that inferred from the lead results, though somewhat closer fits may be obtained with a slightly larger value of λ . For the value of λ chosen, plausible fits to the experimental results may also be obtained with rather larger values of σ_{CL} (and correspondingly larger values of $\Delta\sigma$), up to a value of σ_{CL} of some 80 erg cm.^{-2} .

It is concluded that the experimental results for the melting temperature of small bismuth crystals may be interpreted in terms of the liquid-shell model, if it is assumed that $\sigma_C < \sigma_L + \sigma_{CL}$. On this basis the following values are inferred for the crystal-liquid interfacial free energy, σ_{CL} , and for what may be termed "the change in superficial free energy associated with surface melting", $\Delta\sigma$,

$$\sigma_{CL} = 55 \text{ erg cm.}^{-2} \quad (7-4)$$

and

$$\Delta\sigma = \sigma_{CL} + \sigma_L - \sigma_C = 39 \text{ erg cm.}^{-2} \quad (7-5)$$

Taking the value of σ_L to be 390 erg cm.^{-2} , as quoted in table 6, we may also infer

$$\sigma_C = 1106 \text{ erg cm.}^{-2} \quad (7-6)$$

(iii) Indium

An investigation of the melting of thin condensed films of indium has recently been made by Boiko, Pugachev and Bratsykhin (1969). They found that the melting temperature of an aggregate of indium crystallites having a "most probable" diameter, L , of $400 \text{ \AA}$ is some 140°C , and that the melting temperature of an aggregate decreases with L to a value of some 64°C when $L = 100 \text{ \AA}$. These results do not accord very well with the present findings, though they do suggest that in interpreting the experimental results on the melting of small crystals of indium in terms of the liquid-shell model, case (a) may be assumed to pertain. From the data of table 6, we may write equation (6-36) for indium

$$t_o - t_\lambda = 42.15 \left[\frac{\sigma_{CL}}{r_C - \lambda} - \frac{11.18}{r_C} \right] \quad (7-7)$$

where t_o $^\circ \text{K}$ is the melting temperature of bulk indium

λ is a critical liquid-shell thickness, of the order of a few tens of Angstrom units

t_λ $^\circ \text{K}$ is the melting temperature of a crystallite of radius r_C

$\sigma_{CL} \text{ erg cm.}^{-2}$ is the crystal-liquid specific interfacial free energy

and r_C and λ are measured in $\text{\AA}$.

It is felt that a fit to the experimental results for the melting temperature of small crystals of indium on the basis of equation (7-7) would not be pertinent, however, as equation (7-7) cannot be expected to properly represent the melting temperature of the very small crystals for which melting temperatures were obtained experimentally. If a value $\lambda = 30 \text{ \AA}$ is assumed for indium (in line with the value used to interpret the results for lead), then this critical thickness is only a little less

than the greatest crystallite radius ($38 \text{ \AA}$) for which a melting temperature has been determined.

It will be observed that the experimental results for the melting temperatures of small crystals of lead and bismuth are not adequately described theoretically for the smallest crystallites investigated. It is therefore worthwhile to re-examine certain limitations in our theoretical approach, already alluded to in the text. The introduction of a critical thickness for the liquid shell may be seen as the recognition of a limitation in applying the macroscopic concepts of thermodynamics to a small system. By this device, the possibility of evaluating the free energy of the system, when the thickness of the liquid shell is insufficient for its properties at any point to approximate to those of a bulk phase, is precluded. Moreover, it would clearly be unphysical to assume that the generation of a liquid shell no matter how thin, is associated with a discrete free energy change of $\sigma_{CL} + \sigma_L - \sigma_C$ per unit area. In considering the initial generation or final disappearance of the crystalline core, this latter difficulty of a sudden discrete change in the free energy of the system does not arise. It has therefore been felt that, in line with current treatments of nucleation problems, it is unnecessary to place a specific restriction on the size of the crystalline phase; though results inferred when the crystalline core is very small should be approached with caution.

In this context we may note, that if we assume that the macroscopic concepts of thermodynamics may properly be applied within the framework constructed, then there is the possibility of refining our theoretical approach by taking account of the kinetic effects discussed in § 6.3.3(ii) (pg. 167). Instead of assuming that the Helmholtz free energy barrier to melting must vanish at the melting temperature, we may assume that it is only necessary that the barrier be reduced to a value at which there is an appreciable probability of its being surmounted as a result of a statistical fluctuation. The consequences of such an assumption are to lower the predicted melting temperature by an amount which increases rapidly with decreasing crystallite size, so that the melting temperature falls more sharply for crystallite radii less than some $60 \text{ \AA}$.

7.2 Solidification

Two mechanisms for the solidification of a small liquid droplet were considered theoretically in § 6.4. The frequency, I^* , of homogeneous nucleation of a liquid droplet is given by equation (6-139) of § 6.4.1. The frequency, I_S^* , of droplet nucleation by the heterogeneous mechanism examined in § 6.4.2, is given by equation (6-173). In order to associate a solidification temperature with a liquid droplet on the basis of nucleation theory, it is necessary to make some assumption concerning the value of the nucleation frequency I^* (or I_S^*) at which the probability of nucleation may be regarded as "appreciable". In interpreting the results of the present experiments on the solidification of small metallic droplets, it has been (somewhat arbitrarily) assumed that the solidification temperature of a liquid droplet may be identified with that temperature for which the nucleation frequency is 10^{-1} per sec. The appropriate choice clearly depends on the time scale of the experiment: if a liquid droplet is cooled sufficiently slowly, there may be an appreciable probability of nucleation occurring even at temperatures for which the nucleation frequency is relatively small. The rate of cooling in the present experiments was some 0.1°K per second.

It is, perhaps, worthwhile to indicate briefly how a precise criterion for choosing I^* may be arrived at. For a particular liquid droplet and a given rate of cooling, it is possible to derive an expression for the temperature ($t_{0.8}$, say) at which the probability that the droplet will have solidified attains a value of 0.8 (say). Suppose that the droplet is cooled from the bulk melting temperature, t_0 , at a constant rate of $k^\circ\text{K}$ per second. Then after a time τ sec., the temperature, t , is given by

$$t = t_0 - k\tau \quad (7-8)$$

We may now write for the nucleation frequency, I^*

$$I^* = I^*(\tau) \quad (7-9)$$

Suppose $P(\tau)$ is the probability that the droplet has not solidified after a time τ sec.; then considering a small interval of time $\delta\tau$, we may write

$$\frac{P(\tau) - P(\tau + \delta\tau)}{P(\tau)} = I^*(\tau) \delta\tau \quad (7-10)$$

From equation (7-10), on proceeding to the limit $\delta\tau \rightarrow 0$ and integrating, we obtain

$$\log_e P(\tau) = - \int_0^\tau I^*(\tau) d\tau \quad (7-11)$$

When $P(\tau) = 0.2$, we obtain from equation (7-11)

$$\int_0^\tau I^*(\tau) d\tau = 1.6 \quad (7-12)$$

Equation (7-12) may be used to determine the temperature $t_{0.8}$ and the corresponding frequency.

(i) Lead

Employing the data in tables 6 and 7, equation (6-139) may be written for lead

$$I^* = 2.689 \times 10^7 r_c^3 t \exp \left[- \frac{1213.7 \sigma_{CL}^3}{t(0.4390\{t_0 - t\} + 336/r_c)^2} \right] \quad (7-13)$$

where I^* per sec. is the frequency of homogeneous nucleation of a liquid droplet

r_c Å is the radius of the crystallite into which the droplet solidifies

t °K is the temperature of the liquid droplet

t_0 °K is the melting temperature of bulk lead

Boltzmann's constant, $k = 1.3805 \times 10^{-16}$ erg/ $^{\circ}$ K

Planck's constant, $h = 6.6254 \times 10^{-27}$ erg sec.

Avogadro's number, $N_o = 6.0228 \times 10^{23}$ per mole

$\frac{16\pi}{3k} = 1.2137 \times 10^{17}$ erg $^{-1}$ $^{\circ}$ K

	Lead	Bismuth
* $\frac{\rho_{CL_o}}{t_o}$ ($^{\circ}$ K $^{-1}$ cm. $^{-3}$ erg)	4.390×10^6	9.295×10^6
* Density of liquid at melting point, ρ_L (gm./cc.)	10.60	10.06
Atomic weight, W	207.21	209.00
Number of atoms per volume of liquid, $n = \frac{\rho_L N_o}{W}$	3.081×10^{22}	2.899×10^{22}
$\frac{4\pi}{3} n \frac{k}{h} 10^{-2}$	2.689×10^{31}	2.530×10^{31}
Number of atoms in substrate-liquid interface per sq. cm., $n_s = n^{2/3}$	9.828×10^{14}	9.437×10^{14}
$\pi n_s \frac{k}{h} 10^{-2}$	6.433×10^{23}	6.178×10^{23}

* Taken or derived from Smithells' "Metals Reference Book" (1967)

Table 7. Data used in interpreting the experimental results on the solidification of small metallic droplets.

and σ_{CL} erg cm.⁻² is the crystal-liquid specific interfacial free energy.

A fit to the experimental results on the basis of equation (7-13) is shown in figure 32. The values $I^* = 10^{-1}$ per sec. and $\sigma_{CL} = 31.45$ erg cm.⁻² have been chosen. As will be seen, the expression (7-13) for the frequency of homogeneous nucleation, predicts a gradual increase in the solidification temperature as droplet radius decreases, in contrast to the trend of the experimental results. However, insofar as equation (7-13) predicts that the solidification temperature is sensibly independent of droplet radius over a wide range of droplet radii, the agreement between theory and experiment may be regarded as satisfactory.

To obtain an impression of the error which should be associated with the value of σ_{CL} inferred, we suppose firstly that the value assumed for I^* may be in error by as much as a factor of 10. With the values $I^* = 10^{-(1 \pm 1)}$ per sec., it is found that the values of σ_{CL} which must be chosen, in order that the solidification temperature predicted for (say) a droplet of radius $300 \text{ \AA}$ shall remain unchanged (at 235°C), are 31.45 ± 0.56 erg cm.⁻². We suppose secondly that, whereas the value of σ_{CL} chosen predicts a solidification temperature of 235°C for a droplet of radius $300 \text{ \AA}$, the actual solidification temperature of such a droplet may differ from this by as much as 3°C . It is found that the values of σ_{CL} which must be chosen, in order that the solidification temperatures predicted for a droplet of radius $300 \text{ \AA}$ shall be $235 \pm 3^\circ\text{C}$, are 31.45 ± 0.60 erg cm.⁻² (with $I^* = 10^{-1}$ per sec.). We may combine these two possible sources of error, to obtain an error in σ_{CL} of some 0.8 erg cm.⁻².

If the term $336/r_C$ in equation (7-13), which arises from the change in the surface area of the droplet consequent upon the formation of a critical nucleus, is discarded; then equation (7-13) predicts a gradual decrease in the solidification temperature as droplet radius decreases (from 235°C when $r_C = 300 \text{ \AA}$, to 227°C when $r_C = 40 \text{ \AA}$; with $I^* = 10^{-1}$ per sec. and $\sigma_{CL} = 30.88$ erg cm.⁻²). There is little comfort in this from a theoretical viewpoint, however, partly because it is quite arbitrary, and partly because the agreement between theory and experiment is only marginally improved. Although precise determinations were not

made, it was observed that the solidification temperatures of even the thinnest films investigated were several degrees below their melting temperatures: thus a very sharp decrease in the solidification temperature occurs on approaching very small droplet radii.

It is concluded that homogeneous nucleation theory provides a satisfactory interpretation of the experimental results on the solidification of small lead droplets, for all but the smallest droplets examined. The following value is inferred for the crystal-liquid interfacial free energy, σ_{CL}

$$\sigma_{CL} = 31.5 \pm 0.8 \text{ erg cm.}^{-2} \quad (7-14)$$

From the data in tables 6 and 7, the expression (6-173) for the frequency, I_S^* , of droplet nucleation by the heterogeneous mechanism examined in § 6.4.2, may be written for lead

$$I_S^* = 6.433 \times 10^7 r_C^2 \sin^2 \theta_2 t \exp \left[\frac{-1213.7 \sigma_{CL}^3 f(\theta_1)}{t(0.4390\{t_o - t\} + 336/r_C)^2} \right] \quad (7-15)$$

where I_S^* per sec. is the frequency of heterogeneous nucleation of a liquid droplet

r_C Å is the radius of the crystallite into which the droplet solidifies

θ_2 is the contact angle between the lead droplet and the substrate on which it rests

t °K is the temperature of the droplet

t_o °K is the melting temperature of bulk lead

σ_{CL} erg cm.⁻² is the crystal-liquid specific interfacial free energy

θ_1 is the contact angle of a crystalline nucleus with the substrate

and f is a function defined by equation (6-140).

A fit to the experimental results on the basis of equation (7-15) is shown in figure 32. The values $I_S^* = 10^{-1}$ per sec., $\sin^2 \theta_2 = 1$ and $\sigma_{CL}^3 f(\theta_1) = 27590 \text{ erg}^3 \text{ cm.}^{-6}$ have been chosen. As may be seen, for a suitable choice of parameters, the expression (7-15) for the frequency of heterogeneous nucleation, predicts a dependence of the solidification temperature on droplet radius which is very similar to that obtained from homogeneous nucleation theory. Insofar as equation (7-15) predicts that the solidification temperature is sensibly independent of droplet radius over a wide range of droplet radii, the agreement between theory and experiment may be regarded as satisfactory.

The value of $\sin^2 \theta_2$ chosen, assumes that the contact angle, θ_2 , between a lead droplet and the substrate on which it rests is 90° . Some idea of the contact angle to be expected between a lead droplet and the substrate, may be obtained from the measurements of the contact angles between resolidified lead crystallites and their substrates described in § 5.3 - see table 5 (pg. 117). The contact angle between liquid lead and graphite at 800°C , calculated from data quoted by Munson (1967), is 139° : with this value for θ_2 , we would have $\sin^2 \theta_2 = 0.44$. To obtain an impression of the error which may be associated with the value of $\sigma_{CL}^3 f(\theta_1)$ inferred, as a consequence of the uncertainty as to the precise value of the contact angle θ_2 , we suppose that the value $\sin^2 \theta_2 = 1$ assumed is in error, and that a value $\sin^2 \theta_2 = 0.1$ is appropriate. The value $\sin^2 \theta_2 = 0.1$ corresponds to a contact angle, θ_2 , of 162° , and it is considered most unlikely that the actual value of θ_2 is larger than this. It is found that the value of $\sigma_{CL}^3 f(\theta_1)$ which must be chosen, in order that the solidification temperature predicted for (say) a droplet of radius $300 \text{ \AA}$ shall remain unchanged (at 235°C), is $25920 \text{ erg}^3 \text{ cm.}^{-6}$. It is also found that with this value of $\sigma_{CL}^3 f(\theta_1)$, and the value $\sin^2 \theta_2 = 0.1$, the solidification temperature predicted for a droplet of radius $60 \text{ \AA}$ is changed (lowered) by only 0.3°C . Thus the uncertainty as to the precise value of the contact angle θ_2 makes very little difference to the quality of the theoretical fit to the experimental results. A change in the value of $\sin^2 \theta_2$ from 1 to 0.1 is equivalent to a change in the value of I_S^* from 10^{-1} to 1, so far as the solidification temperatures inferred from equation (7-15) are concerned.

Thus we may conclude, that the uncertainty as to the precise value of I_S^* which is appropriate, makes very little difference to the quality of the theoretical fit to the experimental results.

To obtain an impression of the error which should be associated with the value $\sigma_{CL}^3 f(\theta_1) = 27590 \text{ erg}^3 \text{ cm.}^{-6}$ inferred, we suppose firstly that the value assumed for I_S^* may be in error by as much as a factor of 10. With the values $I_S^* = 10^{-(1 \pm 1)}$ per sec., it is found that the values of $\sigma_{CL}^3 f(\theta_1)$ which must be chosen, in order that the solidification temperature predicted for (say) a droplet of radius $300 \text{ \AA}$ shall remain unchanged (at 235°C), are $27590 \pm 1670 \text{ erg}^3 \text{ cm.}^{-6}$. We suppose secondly that, whereas the value of $\sigma_{CL}^3 f(\theta_1)$ chosen predicts a solidification temperature of 235°C for a droplet of radius $300 \text{ \AA}$, the actual solidification temperature of such a droplet may differ from this by as much as 3°C . It is found that the values of $\sigma_{CL}^3 f(\theta_1)$ which must be chosen, in order that the solidification temperatures predicted for a droplet of radius $300 \text{ \AA}$ shall be $235 \pm 3^\circ \text{C}$, are $27590 \pm 1560 \text{ erg}^3 \text{ cm.}^{-6}$. If we combine the error arising from the uncertainty in the value of the contact angle θ_2 , with the errors arising from the uncertainty in I_S^* and the uncertainty in the actual solidification temperature of (say) a droplet of radius $300 \text{ \AA}$, we may obtain a value of some $2800 \text{ erg}^3 \text{ cm.}^{-6}$ for the overall error in $\sigma_{CL}^3 f(\theta_1)$.

It is concluded that heterogeneous nucleation theory provides a satisfactory interpretation of the experimental results on the solidification of small lead droplets, for all but the smallest droplets examined. The following value is inferred for the quantity $\sigma_{CL}^3 f(\theta_1)$

$$\sigma_{CL}^3 f(\theta_1) = 27600 \pm 2800 \text{ erg}^3 \text{ cm.}^{-6} \quad (7-16)$$

The function $f(\theta_1)$ has a maximum value of unity - see figure 43 - when the contact angle, θ_1 , of a crystalline nucleus with the substrate is 180° . When $\theta_1 = 180^\circ$, we obtain from equation (7-16)

$$\sigma_{CL} = 30.2 \pm 1.0 \text{ erg cm.}^{-2} \quad (7-17)$$

For a contact angle θ_1 of 180° , the free energy of formation of a critical nucleus in the heterogeneous model of nucleation examined in § 6.4.2, becomes identical to the free energy of formation of a critical nucleus in the homogeneous model of nucleation considered in § 6.4.1. Nevertheless, the two models remain distinct, as a consequence of the differing underlying assumptions concerning possible sites for nucleation: in the heterogeneous model, nucleation is supposed to occur only at the substrate-liquid interface, whereas in the homogeneous model it may occur anywhere within the droplet. It is for this reason that the value of σ_{CL} in equation (7-17) is lower than that in equation (7-14).

There is a value of the contact angle θ_1 , for which the values of σ_{CL} inferred from homogeneous and heterogeneous nucleation theory are identical. If we denote this angle by ψ , then from equations (7-16) and (7-14) we obtain

$$\frac{27600}{f(\psi)} = 31.5^3$$

so that, with reference to equation (6-140), we obtain

$$\psi = 125^\circ$$

If the contact angle, θ_1 , between a crystalline nucleus and the substrate is greater than ψ , then the interpretation of the experimental results on the basis of heterogeneous nucleation theory is unacceptable: it requires a value of σ_{CL} less than that given by equation (7-14), which implies that the frequency, I^* , of homogeneous nucleation exceeds the frequency, $I_S^* = 10^{-1}$, of heterogeneous nucleation. We may conclude that if $\theta_1 > \psi$, then the experimental results should be interpreted on the basis of homogeneous nucleation theory; whereas if $\theta_1 < \psi$, then they should be interpreted on the basis of heterogeneous nucleation theory. It follows that the value $\sigma_{CL} = 31.5 \text{ erg cm.}^{-2}$, inferred from homogeneous nucleation theory, represents the smallest value of σ_{CL} compatible with both homogeneous and heterogeneous nucleation theory.

(ii) Bismuth

Employing the data in tables 6 and 7, the expression (6-139) for the frequency, I^* , of homogeneous nucleation may be written for bismuth

$$I^* = 2.530 \times 10^7 r_c^3 t \exp \left[- \frac{1213.7 \sigma_{CL}^3}{t(0.9295\{t_o - t\} - 261.3/r_c)^2} \right] \quad (7-18)$$

where I^* per sec. is the frequency of homogeneous nucleation of a liquid droplet

r_c Å is the radius of the crystallite into which the droplet solidifies

t °K is the temperature of the droplet

t_o °K is the melting temperature of bulk bismuth

and σ_{CL} erg cm.⁻² is the crystal-liquid specific interfacial free energy.

A fit to the experimental results on the basis of equation (7-18) is shown in figure 33. The values $I^* = 10^{-1}$ per sec. and $\sigma_{CL} = 46.00$ erg cm.⁻² have been chosen. As will be seen, the expression (7-18) for the frequency of homogeneous nucleation predicts that the solidification temperature is sensibly independent of droplet radius over a wide range of droplet radii: this finding is not unsatisfactory in the light of the single experimental result obtained for a droplet radius of some 720 Å. However, the gradual decrease in the solidification temperature predicted, as droplet radius decreases, is not sufficient to accomodate the much steeper trend of the experimental results. This is despite the term $261.3/r_c$ in equation (7-18), which arises from the change in the surface area of the droplet consequent upon the formation of a critical nucleus: this term tends to progressively lower the predicted solidification temperature, as droplet radius decreases.

To obtain an impression of the error which may be associated with the value of σ_{CL} inferred, we suppose firstly that the value assumed for I^* may be in error by as much as a factor of 10, and secondly that the actual solidification temperature of (say) a droplet of radius 470 Å may differ from that predicted (183.6 °C) by as much as 6 °C. We may combine

the error ($\sim 0.8 \text{ erg cm.}^{-2}$) arising from the uncertainty in I^* , with the error ($\sim 2.0 \text{ erg cm.}^{-2}$) arising from the uncertainty in the actual solidification temperature, to obtain a value of some 2.2 erg cm.^{-2} for the overall error in σ_{CL} .

When the experimental results for the solidification temperatures of small droplets of bismuth are interpreted on the basis of homogeneous nucleation theory, the following value is inferred for the crystal-liquid interfacial free energy, σ_{CL}

$$\sigma_{CL} = 46.0 \pm 2.2 \text{ erg cm.}^{-2} \quad (7-19)$$

From the data in tables 6 and 7, the expression (6-173) for the frequency, I_S^* , of droplet nucleation by the heterogeneous mechanism examined in § 6.4.2, may be written for bismuth

$$I_S^* = 6.178 \times 10^7 r_C^2 \sin^2 \theta_2 t \exp \left[\frac{-1213.7 \sigma_{CL}^3 f(\theta_1)}{t(0.9295\{t_o - t\} - 261.3/r_C)^2} \right] \quad (7-20)$$

where I_S^* per sec. is the frequency of heterogeneous nucleation of a liquid droplet

r_C Å is the radius of the crystallite into which the droplet solidifies

θ_2 is the contact angle between the bismuth droplet and the substrate on which it rests

t °K is the temperature of the droplet

t_o °K is the melting temperature of bulk bismuth

$\sigma_{CL} \text{ erg cm.}^{-2}$ is the crystal-liquid specific interfacial free energy

θ_1 is the contact angle of a crystalline nucleus with the substrate

and f is a function defined by equation (6-140).

A fit to the experimental results on the basis of equation (7-20) is shown in figure 33. The values $I_S^* = 10^{-1}$ per sec., $\sin^2 \theta_2 = 1$ and

$\sigma_{CL}^3 f(\theta_1) = 85710 \text{ erg}^3 \text{ cm.}^{-6}$ have been chosen. As may be seen, for a suitable choice of parameters, the expression (7-20) for the frequency of heterogeneous nucleation predicts a dependence of the solidification temperature on droplet radius which is very similar to that obtained from homogeneous nucleation theory.

The value of $\sin^2 \theta_2$ chosen assumes that the contact angle, θ_2 , between a bismuth droplet and the substrate on which it rests is 90° . Some idea of the contact angle to be expected between a bismuth droplet and the substrate, may be obtained from the measurements of the contact angles between resolidified bismuth crystallites and their substrates described in § 5.3 - see table 5 (pg. 117). To obtain an impression of the error which may be associated with the value of $\sigma_{CL}^3 f(\theta_1)$ inferred, as a consequence of the uncertainty as to the precise value of the contact angle θ_2 , we suppose that the value $\sin^2 \theta_2 = 1$ assumed is in error, and that a value of 0.1 is appropriate. The value $\sin^2 \theta_2 = 0.1$ corresponds to a contact angle, θ_2 , of 162° , and it is considered most unlikely that the actual value of θ_2 is larger than this. It is found that the value of $\sigma_{CL}^3 f(\theta_1)$ which must be chosen, in order that the solidification temperature predicted for (say) a droplet of radius $470 \text{ \AA}$ shall remain unchanged (at 188.6°C), is $80600 \text{ erg}^3 \text{ cm.}^{-6}$. It is also found that with this value of $\sigma_{CL}^3 f(\theta_1)$ and the value $\sin^2 \theta_2 = 0.1$, the solidification temperature predicted for (say) a droplet of radius $30 \text{ \AA}$ is changed (lowered) by only 0.5°C . Thus the uncertainty as to the precise value of the contact angle θ_2 makes very little difference to the quality of the theoretical fit to the experimental results. A change in the value of $\sin^2 \theta_2$ from 1 to 0.1 is equivalent to a change in the value of I_S^* from 10^{-1} to 1, so far as the solidification temperatures inferred from equation (7-20) are concerned. Thus we may conclude, that the uncertainty as to the precise value of I_S^* which is appropriate, makes very little difference to the quality of the theoretical fit to the experimental results.

To obtain an impression of the error which should be associated with the value $\sigma_{CL}^3 f(\theta_1) = 85710 \text{ erg}^3 \text{ cm.}^{-6}$ inferred, we suppose firstly that the value assumed for I_S^* may be in error by as much as a factor of 10. With the values $I_S^* = 10^{-(1 \pm 1)}$ per sec., it is found that the

values of $\sigma_{CL}^3 f(\theta_1)$ which must be chosen, in order that the solidification temperature predicted for (say) a droplet of radius $470 \text{ \AA}$ shall remain unchanged (at 188.6°C), are $85710 \pm 5110 \text{ erg}^3 \text{ cm.}^{-6}$. We suppose secondly that, whereas the value of $\sigma_{CL}^3 f(\theta_1)$ chosen predicts a solidification temperature of 188.6°C for a droplet of radius $470 \text{ \AA}$, the actual solidification temperature of such a droplet may differ from this by as much as 6°C . It is found that the values of $\sigma_{CL}^3 f(\theta_1)$ which must be chosen, in order that the solidification temperatures predicted for a droplet of radius $470 \text{ \AA}$ shall be $188.6 \pm 6^\circ \text{C}$, are $85710 \pm 11100 \text{ erg}^3 \text{ cm.}^{-6}$. We may combine the error ($5110 \text{ erg}^3 \text{ cm.}^{-6}$) arising from the uncertainty in the value of the contact angle θ_2 , with the error ($5110 \text{ erg}^3 \text{ cm.}^{-6}$) arising from the uncertainty in I_S^* and the error ($11100 \text{ erg}^3 \text{ cm.}^{-6}$) arising from the uncertainty in the actual solidification temperature, to obtain a value of some $13000 \text{ erg}^3 \text{ cm.}^{-6}$ for the overall error in $\sigma_{CL}^3 f(\theta_1)$.

When the experimental results for the solidification temperatures of small droplets of bismuth are interpreted on the basis of heterogeneous nucleation theory, the following value is inferred for the quantity $\sigma_{CL}^3 f(\theta_1)$

$$\sigma_{CL}^3 f(\theta_1) = 86000 \pm 13000 \text{ erg}^3 \text{ cm.}^{-6} \quad (7-21)$$

The function $f(\theta_1)$ has a maximum value of unity - see figure 43 - when the contact angle, θ_1 , of the crystalline nucleus with the substrate is 180° . When $\theta_1 = 180^\circ$, we obtain from equation (7-21)

$$\sigma_{CL} = 44.1 \pm 2.3 \text{ erg cm.}^{-2} \quad (7-22)$$

For a contact angle θ_1 of 180° , the free energy of formation of a critical nucleus in the heterogeneous model of nucleation examined in § 6.4.2, becomes identical to the free energy of formation of a critical nucleus in the homogeneous model of nucleation considered in § 6.4.1. Nevertheless, the two models remain distinct, as a consequence of the

differing underlying assumptions concerning possible sites for nucleation: in the heterogeneous model, nucleation is supposed to occur only at the substrate-liquid interface, whereas in the homogeneous model it may occur anywhere within the droplet. It is for this reason that the value of σ_{CL} in equation (7-22) is lower than that in equation (7-19).

There is a value of the contact angle θ_1 , for which the values of σ_{CL} inferred from homogeneous and heterogeneous nucleation theory are identical. If we denote this angle by ϕ , then from equations (7-21) and (7-19) we obtain

$$\frac{86000}{f(\phi)} = 46.0^3$$

so that, with reference to equation (6-140), we obtain

$$\phi = 125^\circ$$

If the contact angle, θ_1 , between a crystalline nucleus and the substrate is greater than ϕ , then the interpretation of the experimental results on the basis of heterogeneous nucleation theory is unacceptable: it requires a value of σ_{CL} less than that given by equation (7-19), which implies that the frequency, I^* , of homogeneous nucleation exceeds the frequency, $I_S^* = 10^{-1}$, of heterogeneous nucleation. We may conclude that if $\theta_1 > \phi$, then the experimental results should be interpreted on the basis of homogeneous nucleation theory; whereas if $\theta_1 < \phi$, then they should be interpreted on the basis of heterogeneous nucleation theory. It follows that the value $\sigma_{CL} = 46.0 \text{ erg cm.}^{-2}$, inferred from homogeneous nucleation theory, represents the smallest value of σ_{CL} compatible with both homogeneous and heterogeneous nucleation theory.

Our comparison of the experimental results on the solidification of small metallic droplets with predictions based on nucleation theory shows, that whilst the trend of the experimental results for the melting temperatures of the larger droplets may be accorded with current ideas in

nucleation theory, the agreement between theory and experiment is most unsatisfactory for the smaller droplets investigated. In applying homogeneous nucleation theory to a small liquid droplet, it has here been implicitly assumed that any position (any atom) in the droplet is as suitable as any other, as a site for the formation of a critical nucleus: however, the position of an atom with respect to the droplet surface may well influence its suitability as a nucleation centre, and this consideration becomes important as soon as the size of the critical nucleus is comparable with the size of the droplet. (Quite equivalent remarks may be made concerning heterogeneous nucleation, in that the location of a nucleation site on the substrate-liquid interface with respect to the liquid-vapour interface, may well effect its suitability as a nucleation centre.) It is therefore pertinent to calculate the size of a critical nucleus. From equations (6-81) and (6-78), we may derive the following equation for the radius, r_{CL}^* , of a critical nucleus

$$r_{CL}^* = \frac{2\sigma_{CL}}{\frac{\rho_{CL}^L}{t_0} (t_0 - t) + \frac{2\sigma_L}{r_C} \delta} \quad (7-23)$$

From equation (7-23) and the data in tables 6 and 7, we obtain for a lead droplet of radius 200 Å at 235 °C:

$$\begin{aligned} r_{CL}^* &= 0.4744 \sigma_{CL} \text{ Å} \\ &= 14.91 \text{ Å} \quad \text{with } \sigma_{CL} = 31.5 \text{ erg cm.}^{-2} \end{aligned}$$

and for a bismuth droplet of radius 200 Å at 188.6 °C:

$$\begin{aligned} r_{CL}^* &= 0.2652 \sigma_{CL} \text{ Å} \\ &= 12.18 \text{ Å} \quad \text{with } \sigma_{CL} = 46.0 \text{ erg cm.}^{-2} \end{aligned}$$

* For definition see page 183

It should be borne in mind that the question of the "suitability" of a site as a nucleation centre does not necessarily involve only a consideration of the free energy of formation of a critical nucleus at that site, but may also involve a consideration of the rates of all the reversible reactions (involving the gain and loss of atoms by nuclei smaller than the critical nucleus) as a consequence of which a critical nucleus is supposed to be formed - see Turnbull and Fisher (1949). It is clear that a careful examination of the statistical assumptions underlying equations (6-134) and (6-170) of § 6.4 must be undertaken, before a successful interpretation of the size dependence of the solidification temperature of very small droplets can be expected.

7.3 Discussion

The important parameter which may be estimated from the present experimental data on the size dependence of the melting and solidification temperatures of small metallic particles, is the crystal-liquid interfacial free energy, σ_{CL} .

(i) Lead

In the course of the theoretical examination of the experimental results in § 7.1 and § 7.2, the following imputations were made: From the results on the melting of small lead crystals:

$$\sigma_{CL} = 40 \pm 7 \text{ erg cm.}^{-2} \quad (7-2)$$

From the results on the solidification of small lead droplets:

$$\text{homogeneous nucleation} \quad \sigma_{CL} = 31.5 \pm 0.8 \text{ erg cm.}^{-2} \quad (7-14)$$

$$\text{heterogeneous nucleation} \quad \sigma_{CL}^3 f(\theta_1) = 27600 \pm 2800 \text{ erg}^3 \text{ cm.}^{-6} \quad (7-16)$$

where θ_1 is the contact angle between a crystalline nucleus and the substrate.

If it is assumed that the solidification results are properly interpreted in terms of heterogeneous nucleation theory, and that the

contact angle, θ_1 , between a crystalline nucleus and the substrate is some 85° , then from equation (7-16) we find $\sigma_{CL} \approx 40 \text{ erg cm.}^{-2}$, in close agreement with the value inferred from the melting temperature results.

The above values of the crystal-liquid interfacial free energy, σ_{CL} , for lead, may be compared with the value $33.3 \text{ erg cm.}^{-2}$ estimated by Turnbull (1950d). Turnbull's estimate was obtained, on the basis of homogeneous nucleation theory, from data on the maximum supercooling of pure-lead droplets some 25 microns in radius.

(ii) Bismuth

In interpreting the experimental results on the melting and solidification of small particles of bismuth in § 7.1 and § 7.2, the following imputations were made:

From the results on the melting of small bismuth crystals:

$$\sigma_{CL} = 55 \text{ erg cm.}^{-2} \quad (7-4)$$

$$\sigma_{CL} + \sigma_L - \sigma_C = 39 \text{ erg cm.}^{-2} \quad (7-5)$$

$$\text{and (with } \sigma_L = 390 \text{ erg cm.}^{-2}) \quad \sigma_C = 406 \text{ erg cm.}^{-2} \quad (7-6)$$

where σ_C and σ_L are, respectively, the crystal-vapour and liquid-vapour interfacial free energies

and an impression of the uncertainty in the value of σ_{CL} is given in § 7.1(ii).

From the results on the solidification of small bismuth droplets:

$$\text{homogeneous nucleation} \quad \sigma_{CL} = 46.0 \pm 2.2 \text{ erg cm.}^{-2} \quad (7-19)$$

$$\text{heterogeneous nucleation} \quad \sigma_{CL}^3 f(\theta_1) = 86000 \pm 13000 \text{ erg}^3 \text{ cm.}^{-6} \quad (7-21)$$

where θ_1 is the contact angle between a crystalline nucleus and the substrate.

If it is assumed that the solidification results are properly interpreted in terms of heterogeneous nucleation theory, and that the contact angle, θ_1 , between a crystalline nucleus and the substrate is some 91° , then from equation (7-21) we find $\sigma_{CL} = 55 \text{ erg cm.}^{-2}$, in close agreement with the value inferred from the melting temperature results.

The above values of the crystal-liquid interfacial free energy, σ_{CL} , for bismuth, may be compared with the value $54.4 \text{ erg cm.}^{-2}$ estimated by Turnbull (1950d). Turnbull's estimate was obtained, on the basis of homogeneous nucleation theory, from data on the maximum supercooling of pure-bismuth droplets some 25 microns in radius.

The materials selected for investigation in the present experiments - lead, bismuth and indium - were chosen because of their comparatively low melting points, and low vapour pressures in the crystalline state:

	Melting point ($^\circ\text{C}$)	Vapour pressure * (torr)
Lead	327.4	4.2×10^{-9} at 327.4°C
Bismuth	271.3	2.1×10^{-10} at 271.3°C
Indium	156.4	1.0×10^{-11} at 640°C

* The data is taken from "Vapour Pressure curves of the Elements", prepared by R.E. Honig (R.C.A. Laboratories: Princeton, N.J.).

The selection of materials having comparatively low melting temperatures, minimised the risks of contamination by volatile impurities contained in the furnace or of contamination by the material of the furnace itself - c.f. § 5.4.3 (pg. 123). Low temperatures are also easier to attain and measure accurately. It would be interesting to conduct a similar investigation to that reported here, on the same materials, under conditions of ultra-high vacuum. The effect of introducing a controlled partial pressure of (say) argon or oxygen could then be studied.

The present investigations on the size dependence of the melting

and solidification temperatures of small particles were restricted to materials having very low vapour pressures in the crystalline state, in order to avoid excessive evaporation of the deposits. However, a great range of materials, both elements and compounds, having somewhat higher vapour pressures could be studied, if their evaporation from thin deposits could be prevented. A technique which might achieve this, would be to condense a thin deposit of the material to be investigated on to (say) a carbon substrate under vacuum, and then to condense a thin film of carbon on top of the deposit, so as to sandwich the deposit between two layers of carbon. The technique might be tried, firstly, with the materials investigated here; and the results could be compared with those presented here, in order to ascertain whether imbedding the particles in carbon had any influence on the melting and solidification phenomena.

7.4 Conclusions

Observations of the melting and solidification of aggregates of metallic particles were made, under vacuum, using electron diffraction techniques. The residual gas pressures prevailing during the experiments were in the range 5×10^{-6} to 10^{-6} torr (except in those instances where hydrogen was admitted). No systematic attempt was made to investigate the influence of the residual gases on the melting and solidification temperatures determined, and it should not be assumed that similar results would necessarily be obtained under higher vacuum conditions.

An experimental relationship between the melting temperature of a small crystal and its size is inferred for each of the metals lead, bismuth and indium. The findings are compared with theoretical predictions based on a thermodynamic model - the "liquid-shell" model. The model incorporates a critical liquid-shell thickness, λ , to which a value of $30 \text{ \AA}$ has been assigned in interpreting the experimental results. The model is so conceived as to render it inapplicable to a crystallite whose radius is less than λ , indeed it may be regarded as unsuitable for estimating the melting temperature of a crystallite whose radius is less than some $50 \text{ \AA}$. For larger crystallite radii, however, the model is capable of providing a satisfactory interpretation of the experimental results. It is to be expected that in the near future it will be possible

to approach the melting of a small metallic crystal from a statistical viewpoint, along the lines indicated in § 6.1. A better understanding of the melting of a very small crystal should then be attainable, perhaps using a model based on the work of Lennard-Jones and Devonshire.

An experimental relationship between the solidification temperature of a small droplet and its radius is inferred for the metals lead and bismuth. The findings are compared with predictions based on nucleation theory. Whilst the trend of the experimental results for the larger droplet radii may be accorded with current ideas in nucleation theory, the agreement between theory and experiment is most unsatisfactory for the smaller droplet radii investigated. It is clear that a more careful examination of the underlying statistical assumptions than that made here will be required, before nucleation theory can be successfully applied to predicting the solidification temperature of a very small droplet.

Values of the crystal-liquid specific interfacial free energies have been imputed to lead and bismuth. For each metal, the agreement between the separate values inferred, respectively, from the melting temperature results and from the solidification temperature results, is fair. The values also compare quite well with those derived by Turnbull, from observations on the maximum supercooling of much larger droplets.

ACKNOWLEDGEMENTS

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C.J. Coombes

Derby, 1969.

APPENDIX 1

THE CRYSTAL STRUCTURES OF LEAD, BISMUTH, INDIUM AND INDIUM SESQUIOXIDE, OF THE COMMON OXIDES OF LEAD, AND OF COPPER (see § 4.2, § 5.4.2 and § 5.4.3)

The reciprocals of the plane spacings of lead, bismuth, indium and indium sesquioxide, are calculated from published data on their crystalline structures. Comparisons are made with values inferred from measurements of the sharp-ring, electron-diffraction patterns obtained from the polycrystalline aggregates investigated in the present experiments.

The reciprocals of the crystal plane spacings of the common oxides of lead, and of metallic copper, calculated from published data, are also presented (see § 5.4.2 and § 5.4.3).

The diameter, D , of a ring in the electron-diffraction pattern from a polycrystalline deposit, and the plane spacing, d , of the crystal planes from which the ring arises, are related by the equation

$$D d = 2 \lambda L \quad (\text{A1-1})$$

where λ is the wavelength associated with the monochromatic electron beam

and L is the distance of the photographic emulsion from the specimen.

(1) Lead

Crystalline lead has a face-centred-cubic structure, with four atoms per cell, and cell side

$$a (= b = c) = 4.9505 \text{ \AA}$$

The data is taken from Wyckoff (1963), Volume I, pg. 10.

For a cubic system, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given by

$$\frac{1}{d_{hkl}} = \frac{1}{a} (h^2 + k^2 + l^2)^{\frac{1}{2}} \quad (\text{A1-2})$$

From data of Wyckoff		Present experiments	
Miller indices	1/d	Ring diameters	1/d [†]
(hkl)	(Å ⁻¹)	D (cm.)	(Å ⁻¹)
111	0.3499	1.60	0.352
200	0.4040	1.84	0.404
220	0.5713	2.60	0.572
311	0.6700	3.05	0.670
222	0.6997	3.17	0.697
400	0.8080		
331	0.8805	4.01	0.881
420	0.9034	4.13	0.908
422	0.9896	4.50	0.989

[†] With $2\lambda L = 4.55 \times 10^{-8} \text{ cm.}^2$

Table A1.1. The reciprocals of the plane spacings of lead.

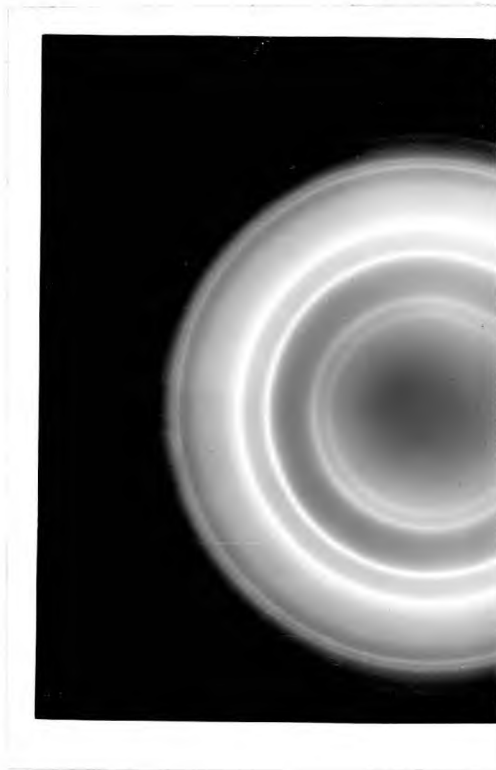


Figure A1.1. Transmission electron diffraction pattern produced by a polycrystalline lead deposit.

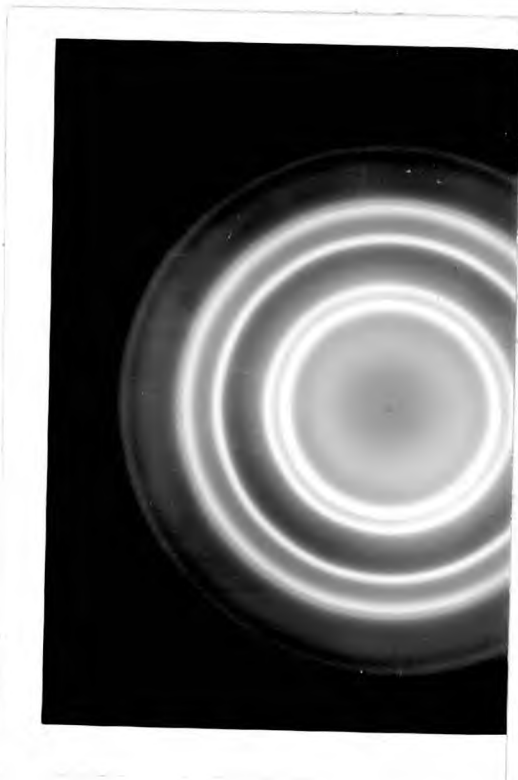


Figure A1.2. Transmission electron diffraction pattern produced by a polycrystalline indium deposit

Structure factor considerations limit possible diffractions to those for which h , k and l are either all odd integers or all even integers.

The reciprocals of the plane spacings of lead, calculated from the data of Wyckoff, are shown in table A1.1 for those planes giving rise to the first 9 diffraction rings of polycrystalline lead: alongside are shown the values calculated using equation (A1-1) from ring diameters measured in the present experiments. The electron-diffraction pattern arising from polycrystalline lead is shown (enlarged) in figure A1.1.

(2) Bismuth

There is evidence for the existence of eight solid phases of bismuth - see Strong (1960), pgs. 69 and 74 - but the only one stable in bulk form at pressures below some 18,500 atmospheres has a rhombohedral structure, with two atoms per cell, and cell parameters (at 25 °C)

$$\text{cell side} \quad a (= b = c) = 4.7459 \text{ \AA}$$

$$\text{interaxial angle} \quad \alpha (= \beta = \gamma) = 57^\circ 14.2'$$

The structure may equally well be represented as hexagonal, with six atoms per cell, and cell sides (at 25 °C)

$$a' (= b') = 4.54590 \text{ \AA}$$

$$c' = 11.86225 \text{ \AA}$$

The data is taken from Wyckoff (1963), Volume I, pg. 32.

For a rhombohedral structure, the plane spacing in real space, d_{hkl} , of the planes having the Miller indices (hkl) is - see Vainshtein (1964), Appendix 1, pg. 393 - given by

$$\frac{1}{d_{hkl}} = \frac{1}{a} \left[\frac{1 + \cos \alpha}{(1 - \cos \alpha)(1 + 2\cos \alpha)} \right]^{\frac{1}{2}} \\ \times \left[h^2 + k^2 + l^2 + 2(hk + kl + lh) \frac{\cos^2 \alpha - \cos \alpha}{\sin^2 \alpha} \right]^{\frac{1}{2}}$$

For the equivalent hexagonal structure, the plane spacing in real space, $d_{h'k'l'}$, of planes having the Miller indices $(h'k'l')$ is

$$\frac{1}{d_{h'k'l'}} = \frac{2}{\sqrt{3}} \frac{1}{a} \left(h'^2 + k'^2 + h'k' + l'^2 \frac{3a^2}{4c^2} \right)^{\frac{1}{2}}$$

The Miller indices of corresponding planes in the two systems are related by the equations

$$h' = 1 - k$$

$$k' = h - 1$$

$$l' = h + k + 1$$

The bismuth structure is developed from the D_{3d}^5 space group - see "International Tables for X-ray Crystallography" (1952), pgs. 272-3.

Structure factor considerations in the rhombohedral system of bismuth do not give rise to any forbidden diffractions: however, the structure is close to body-centred, so the polycrystalline diffraction rings arising from planes whose Miller indices (hkl) satisfy the equation

$$h + k + l = 2n + 1 \quad n \text{ an integer}$$

may be expected to be weak. In the equivalent hexagonal system, structure factor considerations limit possible diffractions to those for which

$$-h' + k' + l' = 3n \quad n \text{ an integer}$$

The reciprocals of the plane spacings of crystalline bismuth, calculated from the data of Wyckoff given above, are shown in table A1.2 for those planes giving rise to the first 42 diffraction rings of polycrystalline bismuth; they are indexed in both the rhombohedral and hexagonal systems. Alongside are shown the $1/d$ values calculated from the ring pattern of one of the bismuth deposits examined in the present experiments, as it appeared after condensation of the deposit, and after one melting and resolidification. The letters beside the ring diameters give an indication of the relative intensities of the rings:

From data of Wyckoff			Present experiments			
Rhombohedral	Hexagonal		Initial pattern		After melting once	
indices	indices	1/d	Ring diameters	1/d [†]	Ring diameters	1/d ^{††}
(hkl)	(h'k'l')	($\text{\AA}^{-1}$)	D (cm.)	($\text{\AA}^{-1}$)	D (cm.)	($\text{\AA}^{-1}$)
111*	003	0.2529			1.168 M	0.2567
100*	101	0.2676	1.211 M	0.2667		
110	102	0.3049	1.389 VS	0.3059	1.391 S	0.3057
211	104	0.4222	1.886 M	0.4154	1.919 S	0.4218
110	110	0.4399	2.005 VS	0.4416	2.010 S	0.4418
221*	105	0.4921	2.231 VW	0.4914	2.240 M	0.4923
222	006	0.5058	2.298 W	0.5062	2.314 S	0.5086
210*	113	0.5074				
111*	201	0.5149				
200	202	0.5352	2.431 VS	0.5355	2.440 S	0.5363
220	204	0.6097	2.759 S	0.6077	2.772 M	0.6092
322*	107	0.6424			2.928 MW	0.6435
311*	205	0.6601				
321	116	0.6704	3.017 W	0.6645	3.054 S	0.6712
210*	211	0.6773				
211	212	0.6928	3.147 VS	0.6932	3.155 S	0.6934
332	108	0.7207			3.284 MW	0.7218
310	214	0.7519	3.403 S	0.7496	3.421 S	0.7519
333*	009	0.7587				
211	300	0.7620	3.469 S	0.7641	3.473 S	0.7633
331*	207	0.7786			3.544 W	0.7789
320*	215	0.7933	3.609 W	0.7949	3.618 W	0.7952
221 and 300*	303	0.8029				
422	208	0.8443				
432*	119	0.8770				

Table A1.2 - continued overpage

continued from previous page

220	220	0.8799 }	4.001	M	0.8813	3.999	M	0.8789
433	1 0 10	0.8804 }						
421*	217	0.8943				4.071	W	0.8947
330 and 411*	306	0.9146 }	4.147	W	0.9134	4.165	W	0.9154
311*	223	0.9155 }						
221*	311	0.9197						
310	312	0.9312	4.237	S	0.9333	4.246	M	0.9332
431	218	0.9521				4.336	W	0.9530
443*	1 0 11	0.9615						
321	314	0.9759	4.434	S	0.9767	4.444	M	0.9767
442	2 0 10	0.9842						
410*	315	1.0081						
444	0 0 12	1.0116						
420	226	1.0149	4.602	M	1.0137	4.622	M	1.0158
311*	401	1.0195						
222	402	1.0299	4.683	M	1.0315	4.692	W	1.0312
533	2 0 11	1.0573						

† With $2\lambda L = 4.54 \times 10^{-8} \text{ cm.}^2$

†† With $2\lambda L = 4.55 \times 10^{-8} \text{ cm.}^2$

* The diffraction rings which are expected to be weak are marked with an asterisk

Table A1.2. The reciprocals of the plane spacings of bismuth

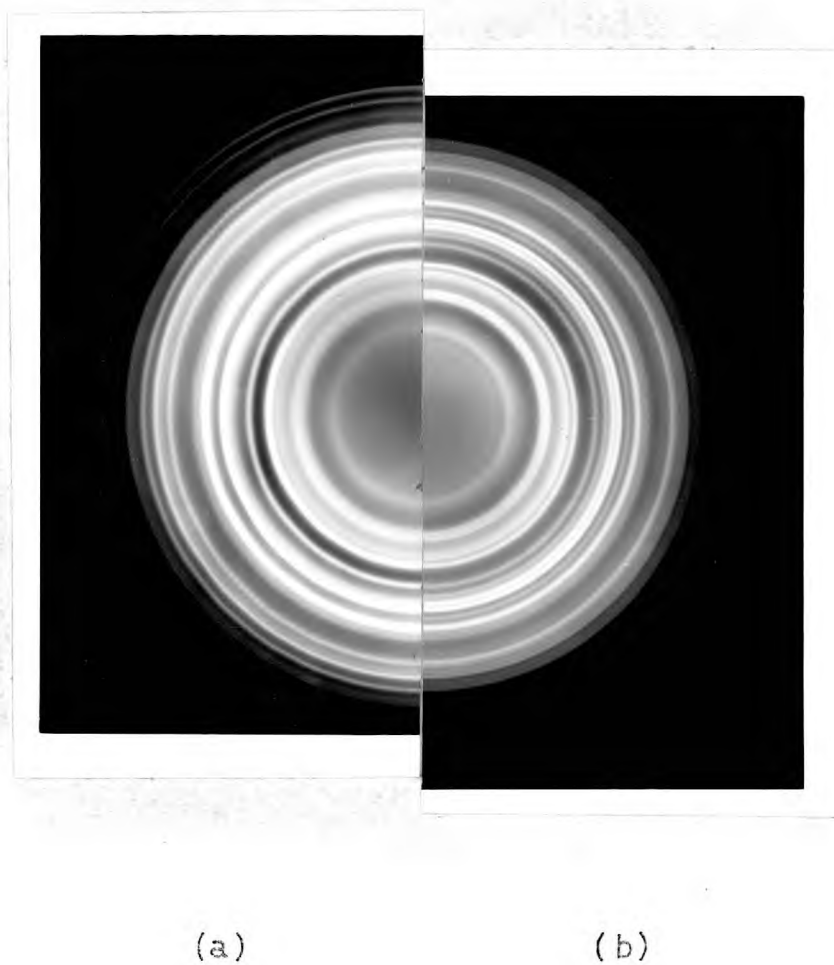


Figure A1.3. Transmission electron diffraction pattern produced by a polycrystalline bismuth deposit (on carbon)

(a) as it appeared after condensation

(b) as it appeared after one melting and resolidification.

VS - very strong; S - strong; M - medium; W - weak; VW - very weak. The electron-diffraction patterns are shown (with identical enlargements) in figure A1.3.

In the present experiments, none of the photographic records obtained of the diffraction of bismuth deposits showed evidence of the presence of any solid phase of bismuth other than the phase stable, in bulk, at ordinary pressures.

(3) Indium

The structure of crystalline indium is tetragonal, with two atoms per cell in the body-centred positions, and cell parameters

$$a (= b) = 3.244 \text{ \AA}$$

$$c = 4.938 \text{ \AA}$$

The data is taken from Wyckoff (1963), Volume I, pg. 18.

For a tetragonal system, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given - see Vainshtein (1964), Appendix 1, pg. 393 - by

$$\frac{1}{d_{hkl}} = \frac{1}{a} \left[h^2 + k^2 + l^2 \frac{a^2}{c^2} \right]^{\frac{1}{2}} \quad (\text{A1-3})$$

Structure factor considerations limit possible diffractions to those for which

$$h + k + l = 2n \quad n \text{ an integer}$$

The reciprocals of the plane spacings of crystalline indium, calculated from the data of Wyckoff, are shown in table A1.3 for those planes giving rise to the first 17 diffraction rings of polycrystalline indium: alongside are shown the values calculated using equation (A1-1) from ring diameters measured in the present experiments. The electron-diffraction pattern arising from polycrystalline indium is shown (enlarged) in figure A1.2.

From data of Wyckoff		Present experiments	
Miller indices	1/d	Ring diameters	1/d [†]
(hkl)	($\text{\AA}^{-1}$)	D (cm.)	($\text{\AA}^{-1}$)
101	0.3688	1.68	0.369
002	0.4050		
110	0.4359	1.98	0.435
112	0.5951	2.71	0.596
200	0.6165	2.81	0.618
103	0.6813	3.11	0.684
211	0.7184	3.27	0.719
202	0.7377	3.35	0.736
004	0.8160		
220	0.8719		
213	0.9188	4.19	0.921
114	0.9199		
301	0.9467	4.32	0.950
222	0.9614	4.38	0.962
310	0.9748	4.44	0.976
204	1.0180	4.65	1.022
312	1.0556	4.80	1.055

[†] With $2\lambda L = 4.55 \times 10^{-8} \text{ cm.}^2$

Table A1.3. The reciprocals of the plane spacings of indium.

(4) Indium sesquioxide, In_2O_3

Indium sesquioxide has a cubic structure of the bixbyite type, with 16 molecules per cell, and cell dimensions

$$a (= b = c) = 10.118 \text{ \AA}$$

The data is taken from Wyckoff (1963), Volume II, pg. 5.

For a cubic system, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given by equation (A1-2).

The structure of indium sesquioxide is developed from the space group T_h^7 . Structure factor considerations limit possible diffractions - see "International Tables for X-ray Crystallography" (1952), pg. 315 - to those satisfying the conditions

$$\begin{array}{ll} hkl : & h + k + l = 2n \\ & n \text{ an integer} \\ Okl : & k = 2n \quad (\text{and also } l = 2n) \\ hOl : & h = 2n \quad (\text{and also } l = 2n) \\ hkO : & h = 2n \quad (\text{and also } k = 2n) \end{array}$$

The reciprocals of the plane spacings of indium sesquioxide, calculated from the data of Wyckoff, are shown in table A1.8 for those planes giving rise to the first 20 diffraction rings of polycrystalline indium sesquioxide: alongside are shown the values calculated using equation (A1-1) from ring diameters measured in the present experiments. The letters beside the ring diameters give an indication of the relative intensities of the rings: VS - very strong; S - strong; M - medium; W - weak; VW - very weak.

(5) Lead oxide, Pb_2O_3

Lead oxide, Pb_2O_3 , has a cubic structure of the cuprite type, with two molecules per cell, and cell side

$$a (= b = c) = 5.38 \text{ \AA}$$

From data of Wyckoff		Present experiments		
Miller indices (hkl)	1/d ($\text{\AA}^{-1}$)	Ring diameters D (cm.)		1/d [†] ($\text{\AA}^{-1}$)
200	0.1977			
211	0.2421	1.10	M	0.242
220	0.2795			
222	0.3424	1.56	VS	0.344
321	0.3698	1.68	VW	0.370
400	0.3953	1.80	M	0.396
411	0.4193	1.895	W	0.417
420	0.4420			
332	0.4636	2.10	M	0.463
422	0.4842			
431	0.5040	2.28	M	0.502
521	0.5413	2.47	VW	0.544
440	0.5591	2.535	VS	0.558
433	0.5763	2.59	VW	0.570
442 and 600	0.5930			
532 and 611	0.6093	2.77	W	0.610
620	0.6251			
541	0.6405	2.90	W	0.639
622	0.6556	2.97	S	0.654
631	0.6703	3.03	W	0.667

[†] With $2\lambda L = 4.54 \times 10^{-8}$ cm.²

Table A1.4. The reciprocals of the plane spacings of indium sesquioxide.

Miller indices (hkl)	1/d ($\text{\AA}^{-1}$)	Miller indices (hkl)	1/d ($\text{\AA}^{-1}$)
110*	0.2629	331	0.8102
111	0.3220	420	0.8312
200	0.3717	332*	0.8718
211*	0.4553	422	0.9106
220	0.5257	431* and 510*	0.9478
310*	0.5878	333 and 511	0.9658
311	0.6165	521*	1.0181
222	0.6439	440	1.0515
321*	0.6955	433* and 530*	1.0838
400	0.7435	531	1.0996
330* and 411*	0.7886	442 and 600	1.1152

* The rings due exclusively to the oxygen atoms, which are expected to be very weak, are marked with an asterisk.

Table A1.5. The reciprocals of the plane spacings of Pb_2O , calculated from the data of Wyckoff.

With origin at 23, at $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ from centre (3), the lead atoms are located in the positions

$$\frac{1}{4} \frac{1}{4} \frac{1}{4} ; \frac{3}{4} \frac{3}{4} \frac{1}{4} ; \frac{3}{4} \frac{1}{4} \frac{3}{4} ; \frac{1}{4} \frac{3}{4} \frac{3}{4}$$

and the oxygen atoms in the positions

$$0 \ 0 \ 0 ; \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}$$

The data is taken from Wyckoff (1963), Volume I, no. 331.

For a cubic system, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given by equation (A1-2).

The structure of Pb_2O is developed from the space group T_h^2 . Electron scattering is predominantly from the lead atoms, and for this, structure factor considerations limit possible diffractions - see "International Tables for X-ray Crystallography" (1952), pp. 309 - to those satisfying the conditions

$$h + k = 2n \quad \text{and} \quad k + l = 2m \quad n \text{ and } m \text{ integers}$$

This yields the usual face-centred, polycrystalline ring sequence. Structure factor considerations limit diffractions from the oxygen atoms to those for which

$$h + k + l = 2n \quad n \text{ an integer}$$

and the oxygen atoms should yield a relatively-weak, body-centred, polycrystalline ring sequence.

The reciprocals of the plane spacings of Pb_2O , calculated from the data of Wyckoff, are shown in table A1.4 for those planes giving rise to the first 22 diffraction rings of polycrystalline Pb_2O . The rings due exclusively to the oxygen atoms, which are expected to be very weak, are marked with an asterisk.

(6) Red lead oxide, PbO

PbO (red) has a bimolecular tetragonal structure, with cell sides

Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)	Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)
001	0.1991	203	0.7809
101	0.3208	310	0.7955
110	0.3558	004	0.7963
002	0.3982	222	0.8154
111	0.4077	311	0.8201
102	0.4710	213	0.8205
200	0.5031	104	0.8351
112	0.5340	302	0.8533
201	0.5411	114	0.8722
211	0.5967	312	0.8896
003	0.5973	321	0.9286
202	0.6416	223	0.9290
103	0.6481	204	0.9420
212	0.6392	303	0.9625
113	0.6952	214	0.9750
220	0.7116	322	0.9906
221	0.7389	313	0.9948
301	0.7805	400	1.0063

Table A1.6. The reciprocals of the plane spacings of PbO (red), calculated from the data of Wyckoff.

$$a (= b) = 3.975 \text{ \AA}$$

$$c = 5.023 \text{ \AA}$$

With origin at $\bar{4}m2$, at $\frac{1}{4} \frac{1}{4} 0$ from centre (2/m), the lead atoms occupy the positions

$$0 \frac{1}{2} u ; \frac{1}{2} 0 \bar{u} \quad \text{with } u = 0.2385$$

and the best available evidence indicates that the oxygen atoms probably occupy the positions

$$0 0 0 ; \frac{1}{2} \frac{1}{2} 0$$

The data is taken from Wyckoff (1963), Volume I, pg. 134.

For a tetragonal system, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given by equation (A1-3).

The structure of red lead oxide is developed from the space group D_{4h}^7 . Electron scattering is predominantly from the lead atoms, and structure factor considerations limit such diffractions - see "International Tables for X-ray Crystallography" (1952). pg. 223 - to those satisfying the conditions

hkl : no conditions

hk0 : $h + k = 2n$ n an integer

Ok1 : no conditions

hhl : no conditions

The reciprocals of the plane spacings of red lead oxide, calculated from the data of Wyckoff, are shown in table A1.5 for those planes giving rise to the first 30 diffraction rings of polycrystalline red lead oxide.

(7) Yellow lead oxide, PbO

PbO (yellow) has an orthorhombic structure, with four molecules per

Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)	Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)
100	0.1698	212	0.5403
001	0.1822	301	0.5409
010	0.2094	003	0.5465
101	0.2490	310	0.5506
110	0.2696	022	0.5552
011	0.2776	221	0.5691
111	0.3254	103	0.5723
200	0.3395	311	0.5800
002	0.3644	122	0.5805
201	0.3853	013	0.5853
210	0.3989	113	0.6094
102	0.4020	302	0.6262
020	0.4188	030	0.6283
012	0.4203	203	0.6434
211	0.4385	222	0.6507
120	0.4519	130	0.6508
112	0.4533	031	0.6542
021	0.4568	320	0.6594
121	0.4873	312	0.6603
202	0.4980	131	0.6758
300	0.5093	213	0.6766
220	0.5392	400	0.6790

Table A1.7. The reciprocals of the plane spacings of PbO (yellow), calculated from the data of Wyckoff.

cell, and cell dimensions (at 27 °C)

$$\begin{aligned} a &= 5.891 \text{ \AA} \\ b &= 4.775 \text{ \AA} \\ c &= 5.489 \text{ \AA} \end{aligned}$$

The data is taken from Wyckoff (1963), Volume I, no. 137.

For an orthorhombic structure, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given by

$$\frac{1}{d_{hkl}} = \frac{1}{a} \left[h^2 + k^2 \frac{a^2}{b^2} + l^2 \frac{a^2}{c^2} \right]^{\frac{1}{2}}$$

The reciprocals of the plane spacings of yellow plumbous oxide, calculated from the data of Wyckoff, are shown in table A1.6 for those planes giving rise to the first 44 diffraction rings of polycrystalline yellow lead oxide.

(8) Lead dioxide, PbO_2

The common form of lead dioxide has a tetragonal structure, though $\alpha - \text{PbO}_2$, which can be produced by electrolysis, has a tetramolecular orthorhombic structure. The tetragonal form has two molecules per cell, and cell dimensions

$$\begin{aligned} a (= b) &= 4.946 \text{ \AA} \\ c &= 3.379 \text{ \AA} \end{aligned}$$

With origin at centre (mmm), the lead atoms are in the positions

$$0 \ 0 \ 0 ; \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}$$

and the oxygen atoms in the positions

$$u \ u \ 0 ; \bar{u} \ \bar{u} \ 0 ; \frac{1}{2} + u \ \frac{1}{2} - u \ \frac{1}{2} ; \frac{1}{2} - u \ \frac{1}{2} + u \ \frac{1}{2}$$

The data is taken from Wyckoff (1963), Volume I, no. 251.

Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)	Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)
110	0.2859	221*	0.6439
101	0.3584	112	0.6573
200	0.4044	301	0.6749
111*	0.4115	311*	0.7045
210*	0.4521	202	0.7168
211	0.5403	320*	0.7290
220	0.5719	212*	0.7448
002	0.5919	321	0.7868
310	0.6394	400	0.8087

* The rings due exclusively to the oxygen atoms, which are expected to be very weak, are marked with an asterisk.

Table A1.8. The reciprocals of the plane spacings of PbO_2 , calculated from the data of Wyckoff.

Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)	Miller indices (hkl)	$1/d$ ($\text{\AA}^{-1}$)
111	0.4801	400	1.1086
200	0.5544	331	1.2082
220	0.7840	420	1.2396
311	0.9193	422	1.3579
222	0.9602		

Table A1.9. The reciprocals of the plane spacings of copper.

For a tetragonal system, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given by equation (A1-3).

The structure of tetragonal lead dioxide is developed from the space group D_{4h}^{14} . Electron scattering is predominantly from the lead atoms, and structure factor considerations limit diffractions - see "International Tables for X-ray Crystallography" (1952), pg. 236 - to those for which

$$h + k + l = 2n \quad n \text{ an integer}$$

Diffractions arising from the relatively weak scattering of the oxygen atoms are limited by the conditions

hkl : no conditions

hk0 : no conditions

Ok1 : $k + l = 2n$ n an integer

hhl : no conditions

The reciprocals of the plane spacings of tetragonal lead dioxide, calculated from the data of Wyckoff, are shown in table A1.7 for those planes giving rise to the first 18 diffraction rings of polycrystalline lead dioxide. The rings due exclusively to the oxygen atoms, which are expected to be very weak, are marked with an asterisk.

(9) Copper

Crystalline copper has a face-centred-cubic structure, with cell side

$$a (= b = c) = 3.608 \text{ \AA}$$

For a cubic system, the plane spacing, d_{hkl} , of planes having the Miller indices (hkl) is given by equation (A1-2).

Structure factor considerations limit possible diffractions to those for which h, k and l are either all odd integers or all even integers.

The reciprocals of the plane spacings of copper are shown in table A1.9 for those planes giving rise to the first 9 diffraction rings of polycrystalline copper.

APPENDIX 2

THE OXIDATION OF LEAD, BISMUTH AND INDIUM AND THE REDUCTION OF THEIR OXIDES BY HYDROGEN (see § 5.4.2)

The Law of Mass Action is applied to the oxidation of deposits of lead, bismuth and indium at low partial pressures of oxygen, and to the reduction of certain of their oxides by gaseous hydrogen. In the case of oxidation, the partial pressure of oxygen, which will be in equilibrium with a mixture of the metal and one of its oxides at some specified temperature, is calculated for each of the three metals. In the case of reduction by hydrogen, the ratio of the partial pressure of hydrogen to that of water vapour, which will exist in equilibrium with a mixture of the metal and its oxide at some specified temperature, is calculated.

It may be noted that the Law of Mass Action only furnishes information on the equilibrium state of a reaction, and not on the speed with which that equilibrium is attained.

The mass action constant, K_p , is related to the standard free energy of a reaction, ΔG_T^O , at temperature T °K, by

$$\begin{aligned}\Delta G_T^O &= -RT \log_e K_p \\ &= -4.574 T \log_{10} K_p\end{aligned}\tag{A2-1}$$

where R is the gas constant per mole.

The thermodynamic data required for the calculations is taken from Kubaschewski, Evans and Alcock (1967), and is summarised in tables A2.1 and A2.2. The calculations are summarised in table A2.3.

	Heat of formation, ΔH_{298}° (cal. / mole)	Standard entropy, S_{298}° 243 (cal. / $^{\circ}\text{K}$ / mole)
$\langle \text{Bi}_2\text{O}_3 \rangle$	-137,200	36.2
$2\langle \text{Bi} \rangle$		27.1
$1\frac{1}{2}(\text{O}_2)$		73.5

Table A2.1. The heats of formation and standard entropies of solid bismuth sesquioxide, solid bismuth and gaseous oxygen, at 298 $^{\circ}\text{K}$

Reaction	Symbol	Standard free energy of reaction at T $^{\circ}\text{K}$, ΔG_T° (cal. / mole)	Range of validity ($^{\circ}\text{K}$)
$\langle \text{PbO} \rangle = \langle \text{Pb} \rangle + \frac{1}{2}(\text{O}_2)$	α	$52,850 + 3.45T \log_{10} T - 34.43T$	298-600
$(\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O})$	β	$-57,250 + 4.48T \log_{10} T - 2.21T$	298-2500
$\langle \text{PbO} \rangle + (\text{H}_2) = \langle \text{Pb} \rangle + (\text{H}_2\text{O})$	γ	$-4,400 + 7.93T \log_{10} T - 36.64T^{\text{a})}$	298-600
$2\langle \text{Bi} \rangle + 1\frac{1}{2}(\text{O}_2) = \langle \text{Bi}_2\text{O}_3 \rangle$	δ	$\Delta G_{298}^{\circ}(\delta) = -118,000^{\text{b})}$	(298)
$3(\text{H}_2) + 1\frac{1}{2}(\text{O}_2) = 3(\text{H}_2\text{O})$	ϵ	$-171,750 + 13.44T \log_{10} T - 6.63T$	298-2500
$\langle \text{Bi}_2\text{O}_3 \rangle + 3(\text{H}_2) = 2\langle \text{Bi} \rangle + 3(\text{H}_2\text{O})$	η	$\Delta G_{298}^{\circ}(\eta) = -45,800^{\text{c})}$	(298)
$\langle \text{In}_2\text{O}_3 \rangle + 3(\text{H}_2) = 2\{\text{In}\} + 3(\text{H}_2\text{O})$	θ	$44,960 + 3.35T \log_{10} T - 49.63T$	430-1123
$2\{\text{In}\} + 1\frac{1}{2}(\text{O}_2) = \langle \text{In}_2\text{O}_3 \rangle$	κ	$-216,710 + 10.09T \log_{10} T + 43.00T^{\text{d})}$	430-1123

Table A2.2. Standard free energies of reaction

Notes to tables A2.1 and A2.2:

Except where indicated - see a), b), c) and d) below - all data is taken directly from Kubaschewski, Evans and Alcock (1967)

The brackets around symbols denoting molar quantities have the following significance: () gaseous { } liquid < > solid

(a) Calculated from $\Delta G_T^{\circ}(\gamma) = \Delta G_T^{\circ}(\alpha) + \Delta G_T^{\circ}(\beta)$

(b) Calculated from $\Delta G_{298}^{\circ} = \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ}$ and the data of table A2.1

(c) Calculated from $\Delta G_{298}^{\circ}(\eta) = -\Delta G_{298}^{\circ}(\delta) + \Delta G_{298}^{\circ}(\epsilon)$

(d) Calculated from $\Delta G_T^{\circ}(\kappa) = -\Delta G_T^{\circ}(\theta) + \Delta G_T^{\circ}(\epsilon)$

Reaction	Temperature (°K)	Mass action constant*, K_p		
Oxidation:			p_{O_2}	(atmospheres) **
α (lead)	298	7.6×10^{-34}	$= K_p^2$	$= 5.8 \times 10^{-67}$
	600	1.5×10^{-14}		$= 2.2 \times 10^{-28}$
δ (bismuth)	298	3.8×10^{86}	$= K_p^{-2/3}$	$= 1.9 \times 10^{-58}$
κ (indium)	430	9.3×10^{94}	$= K_p^{-2/3}$	$= 4.9 \times 10^{-64}$
Reduction:			p_{H_2}/p_{H_2O}	***
γ (lead)	298	8.9×10^6	$= K_p^{-1}$	$= 1.1 \times 10^{-7}$
	600	6.2×10^4		$= 1.6 \times 10^{-5}$
η (bismuth)	298	4.0×10^{33}	$= K_p^{-1/3}$	$= 6.3 \times 10^{-12}$
θ (indium)	430	1.1×10^{-14}	$= K_p^{-1/3}$	$= 4.5 \times 10^4$

* Calculated from equation (A2-1) and the data of table A2.2

** p_{O_2} is the partial pressure of oxygen in equilibrium

*** p_{H_2}/p_{H_2O} is the ratio of the partial pressure of hydrogen, p_{H_2} , to that of water vapour, p_{H_2O} , in equilibrium

Table A2.3. Equilibrium gas pressures

APPENDIX 3

SPECIAL BIBLIOGRAPHY TO WORK ON THE SURFACE ENERGY OF METALS

(see § 1.3 and § 6.3.1(iii))

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