

SUPERCONDUCTIVITY AND STRUCTURE

IN

BETA - TUNGSTEN COMPOUNDS

A Thesis
submitted for the degree of
Doctor of Philosophy

by

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"For the present, then, we must consider three things: first that which is produced, - the second, that in which it is produced, - and third, that of which the thing produced is the natural resemblance".

- Plato (The Timaeus)

Abstract

A review of the literature reveals that the superconducting and structural properties of a β -W compound are dependent on its composition. The variations of these properties as functions of composition, however, if these have been measured, are not completely understood. The properties of the β -W phases of the four systems, Nb-Sn, V-Si, V-Ga and Nb-Al, were therefore investigated as functions of composition.

Apparatus is described which was used to measure the structural properties, lattice parameter and ordering, as functions of temperature and to investigate a structural instability at low temperatures, all by X-ray powder methods. The measurement of superconducting critical temperatures is also described. A model is developed to interpret X-ray intensity data in terms of the atomic disorder in a non-stoichiometric alloy. This model is general for any binary alloy with two types of atom site.

The results obtained are:- (1) That a first order structural transformation, to a martensitic phase, occurs in Nb-Sn and V-Ga but not in V-Si and Nb-Al. The transformation temperature is a function of lattice parameter, a sensitive indicator of composition. (2) The axial ratio of the martensite is a function of lattice parameter, and is of opposite sign on opposite sides of stoichiometry. (3) Superconducting critical temperatures are functions of lattice parameter. (4) The disorder in non-stoichiometric alloys is predominantly by substitution and not by the creation of vacancies. (5) No classical order-disorder transformation takes place, all changes in order being attributable to changes of composition during heat treatment.

The relationships between the structural and superconducting properties and the composition are explained on the basis of the hydrostatic strain in the lattice arising from the effects of atomic size in the non-stoichiometric alloys.

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Introduction

The Beta-tungsten structure alloys have been shown to have the highest known superconducting critical temperatures, fields and currents, and the alloy with the highest values of all three parameters is a ternary alloy $\text{Nb}_3(\text{Ge}, \text{Al})$. To obtain these high values it was necessary to obtain an alloy of exactly the correct composition. Studies of the effects of composition changes in ternary alloys have thus been undertaken by many laboratories. It is clear, however, from a survey of the literature that the compositional variations in the properties of binary alloys of the Beta-tungsten structure are not well understood.

In this thesis, therefore, are considered the effects of composition on the structural and superconducting properties of the four binary alloys with the highest superconducting critical temperatures, Nb-Al, V-Ga, V-Si and Nb-Al and from the results obtained the importance of the different effects involved is evaluated.

Chapter I gives a brief synopsis of the phenomenon of superconductivity together with a description of both the phenomenological and microscopic theories and in Chapter 2 the previous work on materials of the β -W structure has been reviewed. Chapter 3 describes the experimental techniques and in Chapter 4 the experimental results are detailed. Chapter 5 describes a model, general for all binary systems with two types of lattice site, which was developed to determine the type of order in non-stoichiometric alloys from X-ray intensity data. The discussion of the results, the conclusions and the suggestions for future work are given in Chapter 6.

Chapter One

Superconductivity

"The best way to become
acquainted with a subject is to
write a book about it".

- Benjamin Disraeli

1.1 The Phenomenon as observed

In 1911 at Leiden, Kammerlingh Onnes found that the electrical resistivity of mercury dropped sharply to zero at about 4°K. This phenomenon he called superconductivity (Onnes 1911, 1913). Since that date it has been shown that many metallic elements and a large number of alloys become superconductors when cooled below a critical temperature (Roberts 1961, 1966; Lynton 1962, page 5).

1.1a Critical Field and Critical Current

Silsbee (1916) showed that superconductivity is not the same as perfect conductivity. If a superconductor is subjected to a sufficiently large magnetic field H_c or a current J_c large enough to produce this field is passed through it, then the superconductivity is quenched and the normal resistance returns. The critical temperature T_c and the critical field H_c are approximately related by the expression:

$$H_c \approx H_0 \{1 - (T/T_c)^2\} \quad (1.1)$$

where H_0 is the critical field at 0°K and T is the absolute temperature (Onnes 1914; Tuyn and Onnes 1926). This relationship is illustrated in figure 1.1a.

1.1b The Meissner Effect

Below its critical temperature a superconductor behaves as a perfect diamagnet, expelling all magnetic flux. This so-called Meissner effect is reversible (Meissner and Ochsenfeld 1933) and demonstrates a further difference between a perfect conductor and a superconductor. When a perfectly conducting sphere (or cross-section of a cylinder) is passed from temperature T_1 ($T_1 > T_c$) to temperature T_2 ($T_2 < T_c$) by two different paths, the magnetic field situation at T_2 is also different. If the sphere is

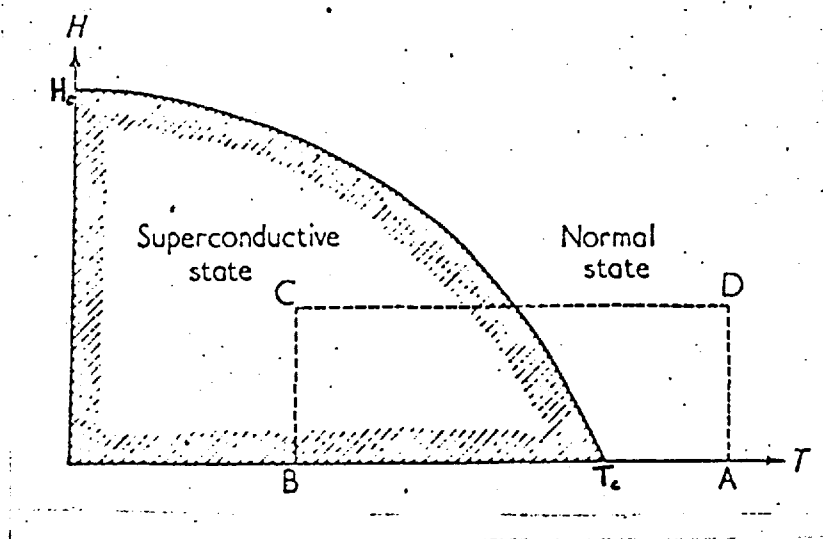


Figure 1.1a. The parabolic relation between the critical field and the critical temperature in a superconductor.

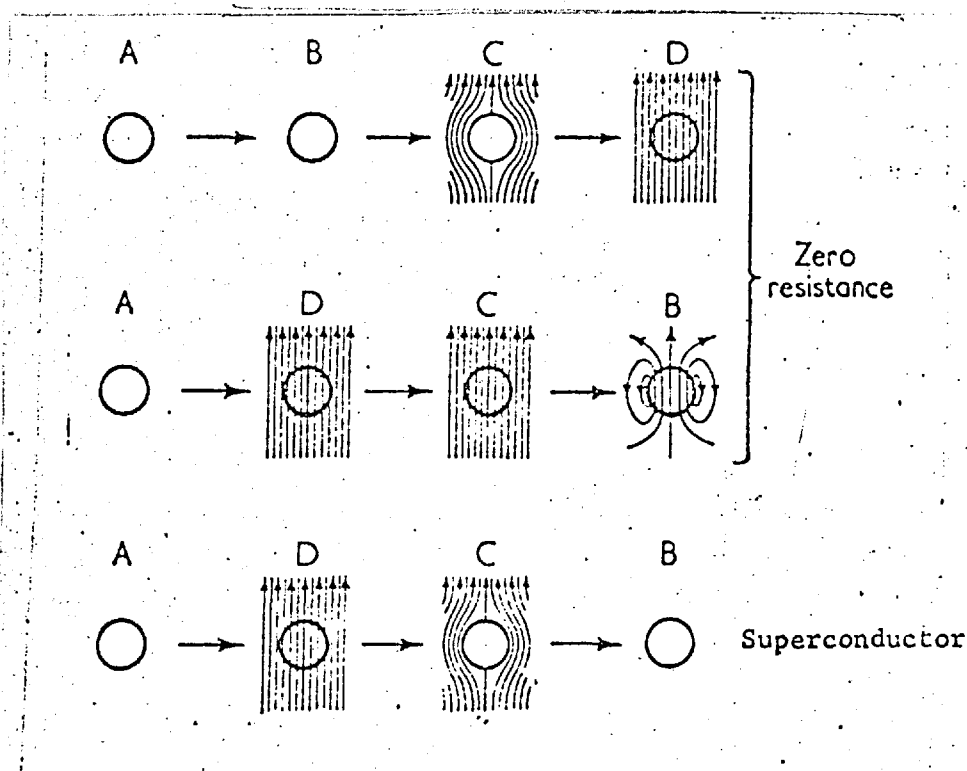


Figure 1.1b. The magnetic behaviour of a sample with zero resistance (a perfect conductor) and a superconductor when H and T are varied along the paths shown in figure 1.1a.

cooled to T_2 and then a magnetic field $H(<H_c)$ applied and removed, the sphere is left with zero magnetisation. If, however, the field is applied at T_1 and removed after cooling to T_2 the sphere has a remanent field. These are the paths $A \rightarrow B \rightarrow C \rightarrow B$ and $A \rightarrow D \rightarrow C \rightarrow B$ in figure 1.1a and the field situations at each point are shown in figures 1.1b and 1.1c respectively. If, however, the sphere is superconducting, the field situations for the path $A \rightarrow D \rightarrow C \rightarrow B$ are shown in figure 1.1d and that at T_2 is the same as for the path $A \rightarrow B \rightarrow C \rightarrow B$, because the superconductor is a perfect diamagnet. The magnetic flux B is thus zero for a superconductor below its critical temperature and hence, as can be seen from figure 1.2, it is more meaningful to plot M , the magnetisation of the sample, against H , the applied field, where $M = B - H$.

1.2 Phenomenological Theories

1.2a Thermodynamic Treatment of the Phase Transformation

The thermodynamics of the superconducting transition was examined by Gorter (1933) who predicted that the change should be reversible. A year later Gorter and Casimir (1934a) produced a full thermodynamic treatment of the transition.

When the normal and superconducting phases are in equilibrium with one another, their Gibbs free energies G must be equal. The free energy in the superconducting state is given by:

$$G_s(H_e) = G_s(0) - \int_0^V dV \int_0^{H_e} M(H_e) dH_e \quad (1.2)$$

where the subscripts s and n refer to the superconducting and normal states, H_e is the external magnetic field and the second term on the right hand side of the equation arises from consideration of the superconductor

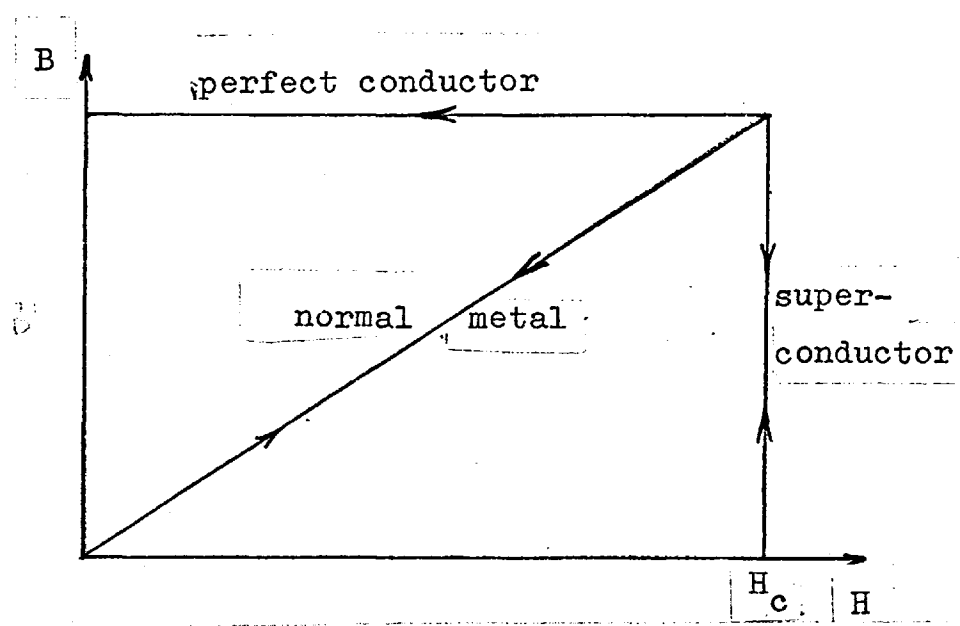


Figure 1.2a. The B - H curves for a normal metal, a perfect conductor and a superconductor.

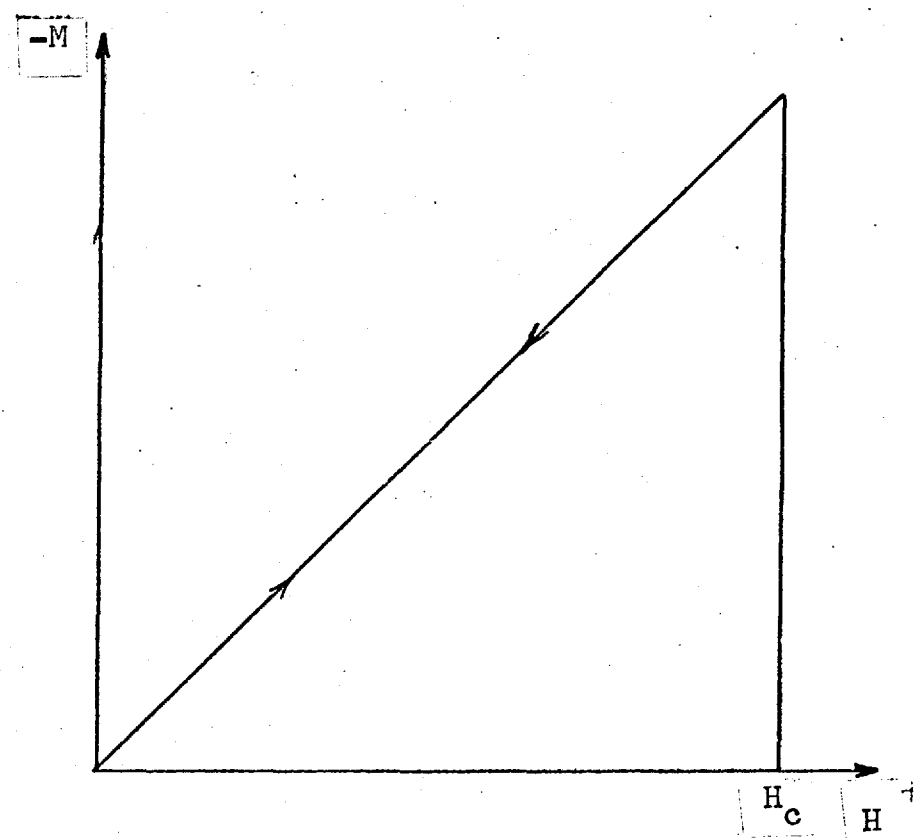


Figure 1.2b. The M - H (magnetisation) curve for a superconductor.

as a perfect diamagnet. If an ellipsoidal specimen is considered, then $M(H_e)$ is uniform and the magnetic work done per unit volume, which is the same regardless of shape, is:

$$\int_0^{H_e} M(H_e) dH_e = - \frac{H_c^2}{8\pi} \quad (1.3)$$

For particular shapes this expression can be shown to hold by using the London equations (see next section).

Therefore, for any specimen:

$$G_s(H_c) = G_s(0) + V \cdot H_c^2 / 8\pi \quad (1.4)$$

For most superconductors the normal state susceptibility is negligible and thus:

$$G_n(H_c) = G_n(0) \quad (1.5)$$

and with the equilibrium condition this gives:

$$G_n(0) - G_s(0) = V H_c^2 / 8\pi \quad (1.6)$$

Using $S = -(\partial G / \partial T)_{H,p}$ the entropy change is then given by:

$$S_n(0) - S_s(0) = - (V H_c / 4\pi) \cdot (dH_c / dT) \quad (1.7)$$

Gorter and Casimir further developed a "two-fluid" model of superconductivity, which treats the phenomenon as an ordering problem. An order parameter W is defined as the fraction of the conduction electrons in the ordered, i.e. superconducting state. The remaining $(1-W)$ electrons remain in the normal state. While this is not the physical situation, it is a fiction convenient for several arguments. The model further assumes that the entire entropy of the system arises from the normal electrons in the non-condensed state.

The free energy per unit volume of the normal electrons is that of the electrons in a normal metal:

$$g_n(T) = - \frac{1}{2} \gamma T^2 \quad (1.8)$$

where γ is the Sommerfeld constant, and the free energy of the superconducting electrons is the condensation energy relative to the normal state:

$$g_s(T) = -H_0^2/8\pi \quad (1.9)$$

The total Gibbs energy per unit volume is thus:

$$G_s(W,T) = a(1-W) g_n(T) = b(W) g_s(T) \quad (1.10)$$

In order that for any value of W the two phases can be in equilibrium at different temperatures, Gorter and Casimir (1934b) chose:

$$a(1-W) = (1-W)\alpha \text{ and } b(W) = W \quad (1.11)$$

so that:

$$G_s(W,T) = -\frac{1}{2}(1-W)\alpha \gamma T^2 - WH_0^2/8\pi \quad (1.12)$$

At $T = T_c$, $W = 0$ and hence:

$$\gamma = (1/4\pi\alpha) \cdot (H_0^2/T_c^2) \quad (1.13)$$

Substituting 1.13 into 1.12, one obtains:

$$(1-W)^{(\alpha-1)} = (T_c/T)^2 = t^{-2} \quad (1.14)$$

where $t = T/T_c$ and is the reduced temperature. Substituting back into 1.12 and differentiating with respect to temperature gives the entropy of the metal in the superconducting state:

$$S_s(W,T) = \gamma T (1-W)^\alpha = T_c t^{(1+\alpha)/(1-\alpha)} \quad (1.15)$$

From a study of the experimental data α was chosen to be equal to one half which gives:

$$S_s(T) = \gamma T_c t^3 \quad (1.16)$$

$$W(T) = 1-t^4 \quad (1.17)$$

$$\text{and } \gamma(T) = (1/2\pi) \cdot (H_0^2/T_c^2) \quad (1.18)$$

1.2b The London and Pippard Equations

F. and H. London considered that as superconductivity is an electromagnetic phenomenon it should be possible to treat it using Maxwell's equations or a modification of them.

If one considers the electromagnetic behaviour of a conductor with zero resistivity, from the equation of motion of the electrons $m \dot{\underline{v}} = e \underline{E}$ and the definition of electric current $\underline{J} = n e \underline{v}$ one obtains the relation,

$$\underline{E} = 4\pi \lambda_{LP}^2 \dot{\underline{J}}/c^2 \quad (1.19)$$

$$\text{where } \lambda_{LP}^2 = mc^2 / 4\pi ne^2 \quad (1.20)$$

Taking the curl of both sides of 1.19 and using the Maxwell equations $\nabla \times \underline{H} = 4\pi \underline{J}/c$ and $\nabla \times \underline{E} = -\dot{\underline{H}}/c$ one finds:

$$(4\pi \lambda_{LP}^2 /c) \nabla \times \dot{\underline{J}} = -\dot{\underline{H}} \quad (1.21)$$

$$\text{and } \lambda_{LP}^2 \nabla \times \nabla \times \dot{\underline{H}} = \lambda_{LP}^2 \nabla (\nabla \cdot \dot{\underline{H}}) - \lambda_{LP}^2 \nabla^2 \dot{\underline{H}} = -\dot{\underline{H}} \quad (1.22)$$

Using $\nabla \cdot \underline{H} = 0$ one further obtains:

$$\lambda_{LP}^2 \nabla^2 \dot{\underline{H}} = \dot{\underline{H}} \quad (1.23)$$

F. and H. London (1935a, 1935b, 1950) substituted n_s the number of superconducting electrons, for n and instead of 1.21 wrote:

$$(4\pi \lambda_{LP}^2 /c) \nabla \times \underline{J} = -\underline{H} \quad (1.24)$$

$$\text{whence } \lambda_{LP}^2 \nabla^2 \underline{H} = \underline{H} \quad (1.25a)$$

$$\lambda_{LP}^2 \nabla^2 \underline{J} = \underline{J} \quad (1.25b)$$

$$\lambda_{LP}^2 \nabla^2 \underline{A} = \underline{A} \quad \text{where } \underline{H} = \nabla \times \underline{A} \quad (1.25c)$$

These equations give a reasonable approximation to the magnetic behaviour of some superconductors and λ_{LP} is known as the London penetration depth, as it represents the depth through which the magnetic field falls to $1/e$ of its value at the surface of the superconductor.

If one considers, after Druyvestyn (1966), a long wire of radius r_0 in a longitudinal magnetic field, then 1.25a written in cylindrical co-ordinates becomes:

$$H(r) = H_e J_0(ir/\lambda_L)/J_0(ir_0/\lambda_L) \quad (1.26)$$

where J_0 is the Bessel function of the first kind and zero order with imaginary argument. For $r_0 \gg \lambda_L$,

$$-4\pi M = H_e \quad (1.27)$$

and it can be seen that this gives the result of equation 1.3. For $r_0 \ll \lambda_L$,

$$-4\pi M = (r_0/\lambda_L)^2 \cdot H_e/8 \quad (1.28)$$

and this gives:

$$H_c' = 2^{3/2} (\lambda_L/r_0) \cdot H_c \quad (1.29)$$

where H_c and H_c' are the critical fields for the bulk and small samples respectively. From 1.29 it can be seen that the magnetic energy per unit volume of a small specimen is lower than that of a bulk specimen. Using this as a basis, it was inferred by H. London (1935) that it should be more favourable energetically for a superconductor to divide into narrow superconducting domains separated by infinitesimally thin normal domains. However, as the Meissner state is the state found experimentally, H. London (1935) postulated the existence of a positive surface energy α_s^1 which will make the filamentary structure thermodynamically unfavourable. This can be written as $\alpha_s^1 = (1/8\pi) \cdot \xi H_c^2$ where ξ , which will be later identified as the Pippard coherence length must be greater than λ_L for a Meissner effect to be observed. Superconductors for which this condition holds are known as "Type I" superconductors. There also exist superconductors for which it does not hold and ξ is less than λ_L ; these are known as "Type II" superconductors. A more rigorous definition of Type I and Type II superconductivity is given by the Ginzburg-Landau formulation (see next section).

If one considers equation 1.20 with the "two-fluid" assumption,

$$n_s(t) = W(t) n_s(0) \quad (1.30)$$

then one obtains:

$$\lambda(t) = \lambda(0)/(1-t^4)^{\frac{1}{2}} \quad (1.31)$$

$$\text{where } \lambda(0) = (mc^2/4\pi n_s(0) e^2)^{\frac{1}{2}} \quad (1.32)$$

The values of $\lambda(0)$ predicted by equation 1.31 are five times smaller than those found by Schawlow (1958) unless unrealistic estimates of the parameters are taken. This failure of the London equations and the existence of the coherence length ξ are explained by the Pippard theory.

Pippard (1950) measured the change of penetration of a small R.F. field as a function of a D.C. magnetic field H_e at a fixed temperature. His results are shown in figure 1.3. The rise near 0°K has been explained by Bardeen (1952, 1954) as arising from a non-linear extension of the London equations. The rise near T_c however involves a change in λ with H_e at the same point as there is a noticeable change with T . Using equation 1.31 Pippard calculated the field dependence of the superconducting entropy for a superconductor of surface A as:

$$S(H_e) - S(0) = \frac{\lambda(0) \cdot A \cdot H_e^2}{4\pi T_c} \{t^3/(1-t^4)\} \quad (1.33)$$

Near the critical temperature this is an extremely large change and, as it must take place in the surface layer, it appears to result in an unreasonably high entropy density in that layer.

This high entropy density, the existence of the positive surface energy, and other experimental results led Pippard to modify the London equation 1.21. In measurements of the penetration depth in indium-tin alloys he found that λ_p was a function of concentration and that the field dependence of λ_p was more noticeable at higher indium contents.

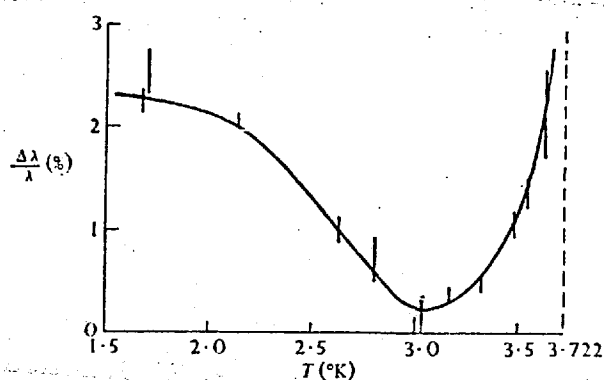


Figure 1.3. The relative shift in the penetration depth in tin between zero field and the critical field, at temperatures between 1.5°K and the critical temperature $T_c = 3.722^{\circ}\text{K}$. (Pippard 1950)

To explain these results, Pippard (1953) introduced a range of coherence ξ , dependent on the mean free path of the electron. Equation 1.21 can thus be written as:

$$\underline{J}(\underline{r}) = -(ne^2/m) \cdot \underline{A}(\underline{r}) \quad (1.34)$$

and to introduce the range of coherence Pippard wrote

$$\underline{J}(\underline{r}) = -(ne^2/m) \frac{\xi(1)}{\xi_0} \cdot \underline{A}(\underline{r}) \quad (1.35)$$

where ξ_0 is the range of coherence of the pure superconductor and l the mean free path. The exponential penetration still exists but with:

$$\lambda = \lambda_L \sqrt{\xi_0 / \xi(1)} \quad (1.36)$$

The dependence on mean free path is given by:

$$\frac{1}{\xi(1)} = \frac{1}{\xi_0} + \frac{1}{\alpha l} \quad (1.37)$$

where α is a constant approximately equal to one. A further modification was needed, however, as equation 1.35 implies that the momenta of the electrons interact over an infinite distance whereas Pippard found the range of momentum coherence to be of the order of 10^4 cm. Therefore by an analogy with the anomalous skin effect (Reuter and Sondheimer 1948) he proposed the equation:

$$\underline{J}(\underline{r}) = -(3ne / 4\pi \xi_0 m) \int \frac{\underline{R} \cdot (\underline{R} \cdot \underline{A}) e^{-R/\xi(1)}}{R^4} d\mathbf{r}' \quad (1.38)$$

where $\underline{R} = \underline{r} - \underline{r}'$.

Equation 1.38 can be evaluated in two distinct cases:-

$$\lambda = \sqrt{\xi_0 / \xi(1)} \cdot \lambda_L \quad \text{for } \xi \ll \lambda \quad (1.39a)$$

$$\lambda = \{ (\sqrt{3}/2\pi) \xi_0 \lambda_L^2 \}^{1/3} \quad \text{for } \xi \gg \lambda \quad (1.39b)$$

In the second of these, there is an infinite free path and 1.39b gives the correct magnitude of the penetration depth for pure superconductors, much larger than that predicted by the London equations.

Consider now the surface energy between the normal and superconducting phases. Assume that W increases gradually from the surface, reaching unity at a depth approximately equal to ξ . If $\xi > \lambda$, then the field penetration is significantly non-exponential. It is convenient to define the boundary where the free energy changes suddenly as the point where $W = \frac{1}{2}$. The boundary for the magnetic field, however, will not necessarily coincide with this, but will be a distance λ from the surface where the penetration is defined generally by:

$$\lambda = H_e^{-1} \int_0^\infty H(x) dx$$

The two curves are shown in figure 1.4. If $GB < GA$ then the surface energy will be positive, as there will be no field in the area BA which is normal in terms of the Gibbs free energy. However, if $GB > GA$ then the surface energy is negative (the London case is where $GA = 0$). In general GA will be approximately equal to ξ and the surface energy per unit area will be

$$\alpha_{ns} \approx H_c^2 (BA)/8\pi = (\xi - \lambda)/8\pi \quad (1.40)$$

1.2c The Ginzburg-Landau Equations

Ginzburg and Landau (1950) developed the idea of superconductivity as an ordering problem, first suggested by Gorter and Casimir (1934b), and defined their order parameter ψ where $|\psi|^2 = n_s$, the density of the superconducting electrons. ψ can also be treated as the wave function of the superconducting electrons. By using the Landau-Lifshitz theory of phase transitions (1958), Ginzburg and Landau expanded the free energy near the transition as a power series in $|\psi|^2$. In the absence of an external magnetic field the free energy density becomes:

$$g_s(0) = g_n(0) + \alpha |\psi|^2 + (\beta/2) |\psi|^4 \quad (1.41)$$

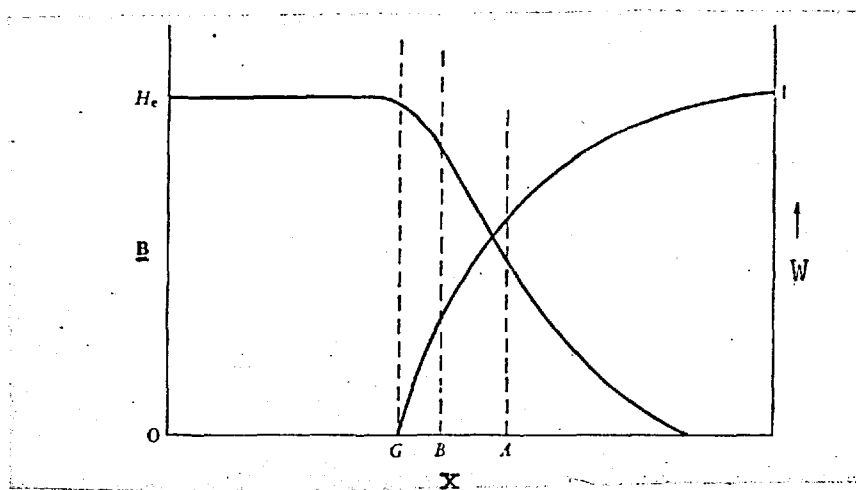


Figure 1.4. The variation of the order parameter W and the magnetic field B in the neighbourhood of the surface of a superconductor. G is the geometrical surface. The order parameter W rises from zero at G to unity for large positive x . A represents the plane at which $W=1/2$, i.e. the effective thermodynamic n-s boundary. B is the electromagnetic effective boundary. (Pippard 1951)

where α and β are functions of temperature. In equilibrium $g_s(0)$ must be a minimum and this condition gives:

$$|\psi_0|^2 = -\alpha/\beta \quad (1.42)$$

and as from equation 1.6 $g_n(0) - g_s(0) = H_c^2/8\pi$

$$H_c^2 = 4\pi\alpha^2/\beta \quad (1.43)$$

In the presence of a magnetic field H_e there is the energy term $H_e^2/8\pi$ and a further term arising from gradients in ψ which, so as to give gauge invariance, is taken to be:

$$E = \frac{1}{2m} \{-i\hbar \nabla \psi - \frac{e^*}{c} \underline{A} \psi\}^2 \quad (1.44)$$

where e^* is a charge, which is assumed to be the electronic charge. Then the free energy becomes:

$$g_s(H_e) = g_s(0) + H_e^2/8\pi + \frac{1}{2m} \{-i\hbar \nabla \psi - \frac{e^*}{c} \underline{A} \psi\}^2 \quad (1.45)$$

Ginzburg and Landau then introduced the following reduced quantities:

$$\begin{aligned} x' &= x/\lambda; & y' &= y/\lambda; & t' &= t/\lambda; \\ |\psi'|^2 &= |\psi|^2 \cdot \beta/\alpha; \\ \underline{A}' &= (e^{*2}/2mc^2 |\alpha|)^{1/2} \cdot \underline{A}; & H' &= 2^{-1/2} H/H_c \end{aligned} \quad (1.46)$$

and the parameters

$$\begin{aligned} \lambda^2 &= mc^2 \beta/4\pi e^{*2} |\alpha| \\ \kappa^2 &= (\beta/2\pi) \cdot (mc/e^*\hbar)^2 = (2e^{*2}/\hbar^2 c^2) H_c^2 \lambda^4 \end{aligned} \quad (1.47)$$

and from 1.43, $H_c^2 = 4\pi\alpha^2/\beta$. By minimising with respect to ψ and $\underline{A}$, to give the equilibrium conditions, one obtains the two Ginzburg-Landau equations;

$$\{(i/\kappa) \nabla' + \underline{A}'\}^2 \psi' = \psi' - \psi' |\psi'|^2 \quad (1.48)$$

$$\text{and: } -\nabla' \times \nabla' \times \underline{A}' = |\psi'|^2 \underline{A}' + (i/2\kappa) (\psi' * \nabla' \psi' - \psi' \nabla' \psi'^*) \quad (1.49)$$

Considering equation 1.48, for $H_e \approx 0$, $\nabla' \psi' \approx 0$ and $|\psi'|^2 \approx 1$, yields $-\nabla' \times \nabla' \times \underline{A}' = \underline{A}'$ which is the London equation (1.25c) with the penetration depth in reduced units. From 1.46 and 1.47 it can be shown that $\lambda^2 = mc^2 / 4\pi e^{*2} |\psi_0^*|^2$ and if $|\psi_0|^2 = n_s$ and $e^* = e$, λ is the London penetration depth.

To show the significance of the constant κ , one can solve 1.48 and 1.49 in the one dimensional use of a surface perpendicular to z , with H_e in the z direction, $\underline{A}$ in the y direction and ψ as a function of x only. For this effectively one dimensional geometry ψ can be chosen as real and so 1.48 and 1.49 become:

$$-\frac{1}{\kappa^2} \frac{d^2 \psi^2}{dx'^2} + \underline{A}' \psi' = \psi' - \psi' |\psi'|^2 \quad (1.50)$$

$$d^2 \underline{A}' / dx'^2 = \underline{A}' |\psi'|^2 \quad (1.51)$$

To obtain a quantitative result a solution of these equations near the normal to superconducting boundary can be considered. By obtaining an expression for the surface energy and applying the boundary conditions an expression is obtained which is soluble analytically only for κ large or small. If $\kappa \ll 1$ then the surface energy is given by:

$$\alpha_{ns} = \xi H_c^2 / 8\pi \quad (1.52)$$

where ξ is positive and

$$\xi = 8\lambda / 3\sqrt{2} \kappa = 1.89 \lambda / \kappa \quad (1.53)$$

If, however, κ is large, then α_{ns} is negative. By numerical solution it can further be shown that the surface energy is positive when:

$$\kappa < 1/\sqrt{2} \quad (1.54a)$$

$$\text{and negative when } \kappa > 1/\sqrt{2} \quad (1.54b)$$

Superconductors are thus classed as type I or type II depending whether they satisfy 1.54a or 1.54b. This classification is equivalent to that of Pippard. All further consideration of superconductivity will be concerned with type II superconductors.

1.3 Type II Superconductors

1.3a Critical Magnetic Fields and the Flux Line Lattice

The magnetic behaviour discussed in sections 1.1b and 1.1c of this chapter occurs only in type I superconductors, when the net surface energy is positive. Abrikosov (1957) showed that the magnetisation curve of a long needle-shaped crystal of type II material will not be of the form shown in figure 1.2 but of the form shown in figure 1.5a. Instead of complete expulsion of magnetic fields less than H_c , the transition from the completely superconducting phase to the completely normal phase takes place over a range of field strengths such that $H_{c_1} < H_e < H_{c_2}$. In this range the superconductor is described as being in the mixed state. H_c the "thermodynamic" critical field is then determined by equating the area under the magnetisation curve to $H_c^2/8\pi$.

Abrikosov (1957) solved the Ginzburg-Landau equations for H_c very near to H_c and, using a variational method, obtained solutions at lower fields giving a flux line lattice of the form shown in figure 1.5b. The solutions showed that a triangular lattice should be stable near H_{c_1} , transforming to a square lattice near H_{c_2} . Goodman (1961) discussed an alternative laminar structure, but more recent calculations by Cribier et al. (1964), Kleiner et al. (1964), Matricon (1964) and Goodman (1966) have shown the triangular lattice to be the stable form at all fields between H_{c_1} and H_{c_2} . Indeed, the electron

Figure 1.5a.

The magnetisation curve of an ideal Type II superconductor (Pb:8.33%In). The broken line is the magnetisation curve of a Type I material (Pb). (Livingston 1963)

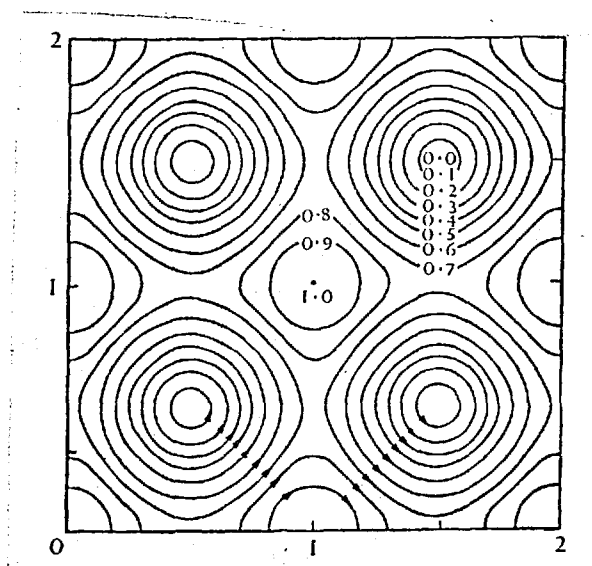
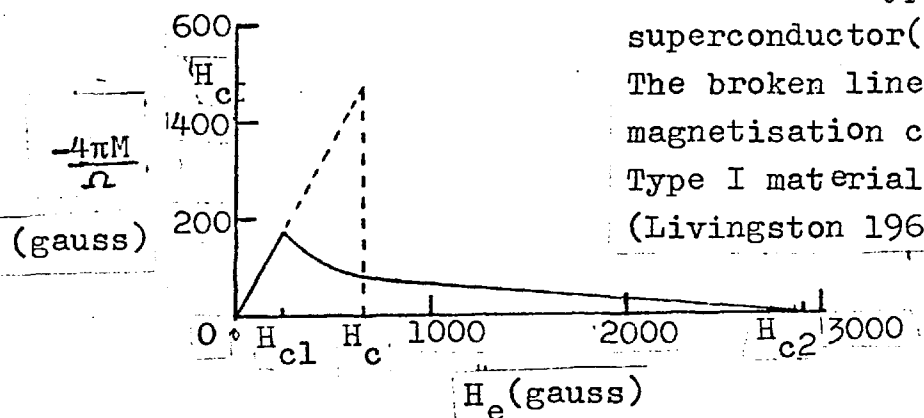


Figure 1.5b.

The Abrikosov flux line structure. (Abrikosov 1957)

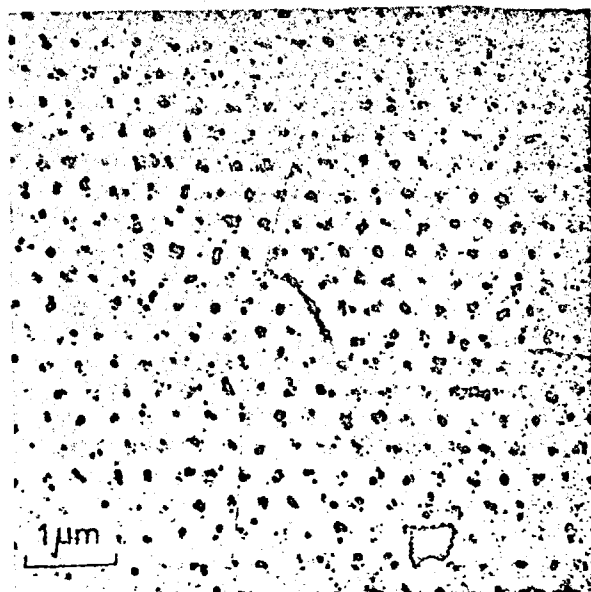


Figure 1.5c.

A perfect triangular lattice of flux lines on the surface of a Pb:4at% In rod at 1.1°K. (Essman and Träuble 1967)

micrographs of Essman and Träuble (1967, 1968), Sarma and Moon (1967) and Sarma (1968) actually show the triangular form (figure 1.5c).

The upper critical field is now defined by

$$H_{C_2} = \kappa/2 H_C \quad (1.55)$$

and the lower critical field H_{C_1} , below which a complete Meissner effect occurs, is defined as the lowest field for which it is possible for a flux line to penetrate the specimen. This can be shown to be:

$$H_{C_1} = \frac{\Phi_0}{4\pi\lambda^2} (0.081 + \ln\kappa) \quad (1.56)$$

where $\Phi_0 = 2\pi\hbar c/e^*$ is the fluxoid quantum.

A further critical field H_{C_3} associated with a surface sheath of depth $\approx \xi$ was shown to exist by St. James and de Gennes (1963). In a surface parallel to the applied field, H_{C_3} has a maximum value of $1.695 H_{C_2}$ and drops to H_{C_2} in a surface perpendicular field. A sheath is only observed for $\kappa > 0.42$ when $H_{C_3} = H_C$. For $\kappa < 0.42$, H_{C_3} is the lowest field to which the superconductor can be supercooled, i.e. kept in a normal state below H_{C_1} .

1.3b Non-Equilibrium Properties and Flux Pinning

In the Abrikosov fluxline model, although superconductivity can exist above H_{C_1} , an electric current will destroy it, because if the flux line distribution is uniform, the current density $\underline{J} = c \text{ curl } \underline{H}/4\pi$ will be on average zero. If the distribution of fluxoids is not uniform, the interaction of the lines will cause it to move towards a uniform distribution. Experimentally, however, it can be seen that the currents do not destroy superconductivity above H_{C_1} until they reach a finite, often very large, value. In

Nb_3Sn , for example, current densities of 1800,000 amp cm^{-2} have been observed (Cody and Cullen 1964).

Further, most experimental magnetisation curves are not reversible. In both type I and type II materials this can arise either from multiple-connectedness at the surface of the material or at cavities within the material such that when the field is reduced below H_c the magnetic flux is expelled from the superconductor but not from the cavity and a current, a result of the Meissner effect, will shield the superconductor from the trapped field. As the magnetisation of the sample is a result of both internal and external Meissner shielding currents, the demagnetisation curve will not follow that of the initial magnetisation, resulting in hysteresis and a remanent field as illustrated in figures 1.6a and 1.6b.

In type II materials hysteresis is also caused by a surface barrier effect. This is a consequence of the second Ginzburg-Landau equation, 1.49, which predicts that no supercurrent can flow normal to a specimen surface. To account for this, Bean and Livingston (1964) proposed the existence of image fluxoids outside the specimen, of opposite sign to the internal fluxoids. These image fluxoids exert an attractive force on the internal fluxoids which are prevented from moving into the bulk of the material.

In a type II superconductor, however, the most important cause of hysteresis is the pinning of flux lines in the material by structural defects. Anderson (1962) and Anderson and Kim (1964) considered these as point defects, while Friedel et al. (1963) treated them as cavities. In the Kim-Anderson model, equating the Lorentz force experienced by the fluxoid with the pinning force and taking into account the short range interaction between fluxoids, yields an expression

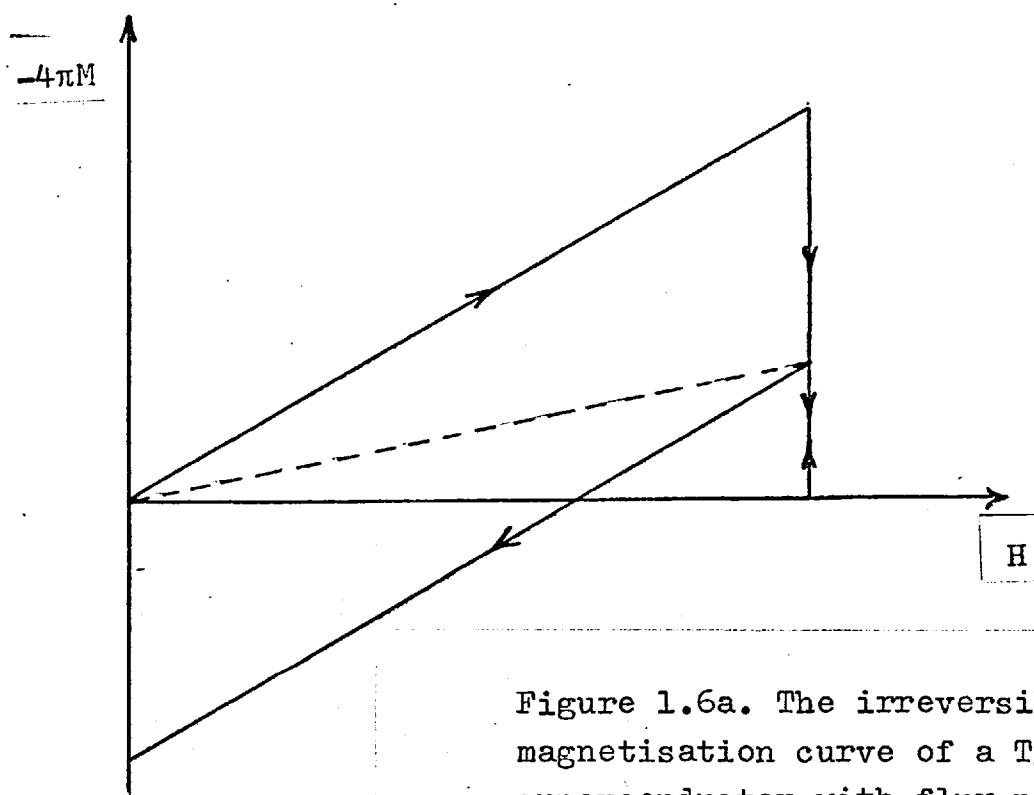


Figure 1.6a. The irreversible magnetisation curve of a Type I superconductor with flux pinning.

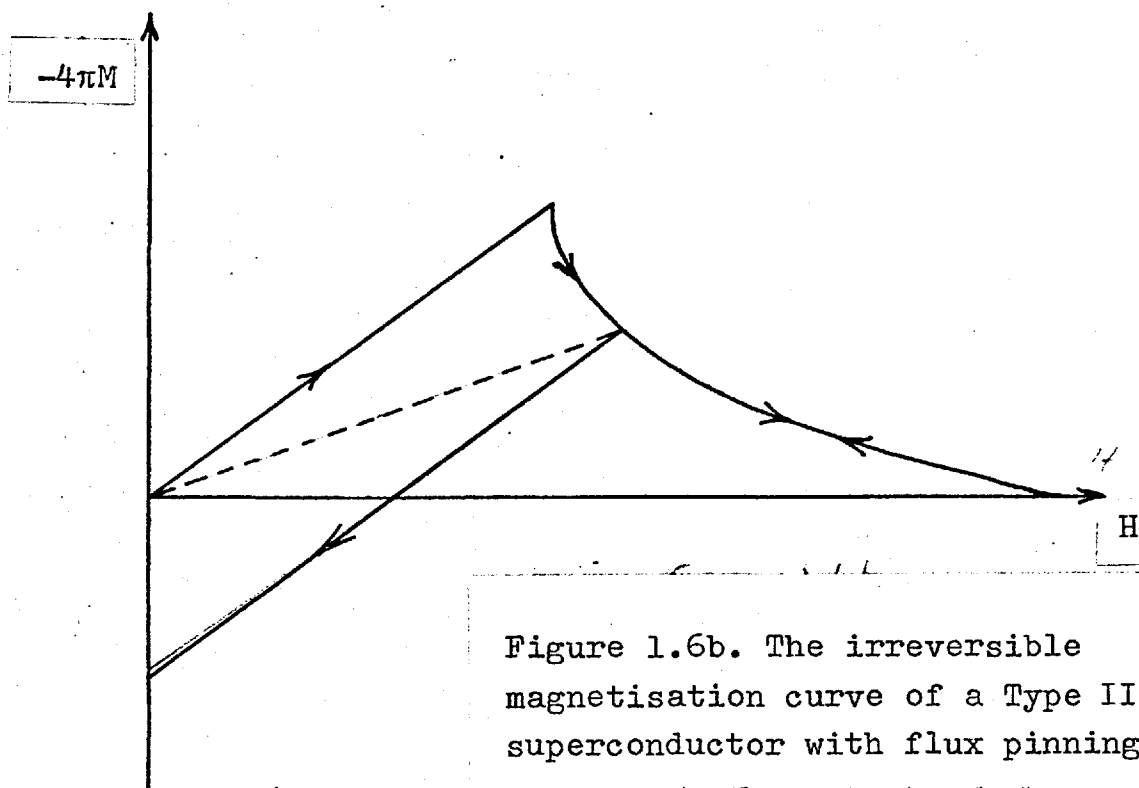


Figure 1.6b. The irreversible magnetisation curve of a Type II superconductor with flux pinning.

for the activation energy for a bundle of flux lines to jump a pinning centre:

$$E_b \approx \rho H_c^2 \xi_0^{-3} / 8\pi - J.B.\xi_0^3 L/c \quad (1.57)$$

where ρ is the fractional efficiency of the pinning centres and L the distance between them. These two parameters will vary from sample to sample, since ρ is dependent on the type of pinning centre and L on the metallurgical state of the material.

The nature and size of the pinning centres has been a subject for much discussion. Kramer and Bauer (1967) treated the single fluxoid/single dislocation interaction, drawing attention to the stress fields caused by the volume and elasticity differences between the normal and superconducting fractions of the material. These stress fields allow interaction with the stress fields of the defects. For single dislocations, however, the interaction energies are small and from this it has been deduced that it is dislocation tangles which pin rather than single dislocations (Narlikar and Dew-Hughes 1966). In the case of interactions with other defects, e.g. precipitates, inclusions, etc., Livingston (1968) has suggested that maximum pinning occurs when the defects have very different electronic properties from the superconductor, and, in agreement with Campbell et al. (1968), that to be effective, pinning centres must have a diameter greater than ξ .

At a certain field and temperature, the Lorentz force will just balance the pinning force and at this value the maximum internal current will be carried, the critical current J_c . From this critical state model it is possible to calculate the field distribution in a simple slabshaped sample as is shown in figure 1.7. Unfortunately it is not as easy to predict the critical current from the knowledge of the critical fields.

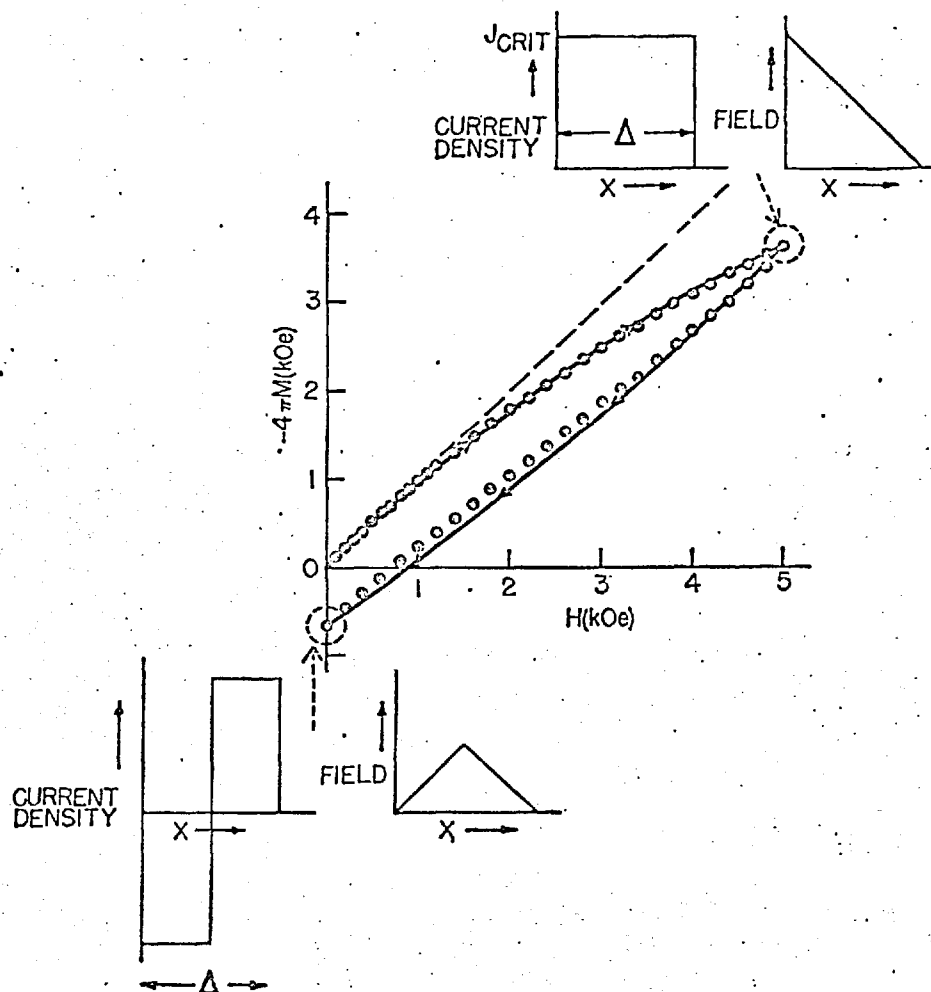


Figure 1.7. The magnetisation and demagnetisation curves of V_3Ga .

Dashed line-Expected result for complete flux expulsion.

Solid line -Theoretical prediction based on the model implied by the flux penetration diagrams.

Solid points-experimental results.

(Bean and Schmidt 1963)

1.4 Microscopic Theory of Superconductivity

All discussion up to this point has been on phenomenological theories of superconductivity, based on thermodynamic and electro-magnetic arguments, but not considering the basic mechanisms of superconductivity. The microscopic theory is an attempt to explain the phenomenon in fundamental terms.

1.4a The Isotope Effect

The first indication of the microscopic mechanism of superconductivity was the discovery by Maxwell (1950) and Reynolds et al. (1950) that the critical temperatures of the isotopes of mercury are related by:

$$T_c M^a = \text{constant} \quad (1.58)$$

where M is the isotopic mass and $a \approx \frac{1}{2}$. This relationship is illustrated in figure 1.8. The effect was rapidly shown to exist in a number of other elements (Lynton 1962, p. 75) but is not an essential property of all superconductors. Geballe et al. (1961) and Geballe and Matthias (1962) showed that for ruthenium and osmium the exponent a has a maximum value of 0.1, and this value appears to be a function of position in the periodic table (Matthias, 1957).

The existence of an isotope effect means that the phenomenon of superconductivity, an electronic effect, must be dependent on interactions between the lattice (i.e. phonons) and electrons.

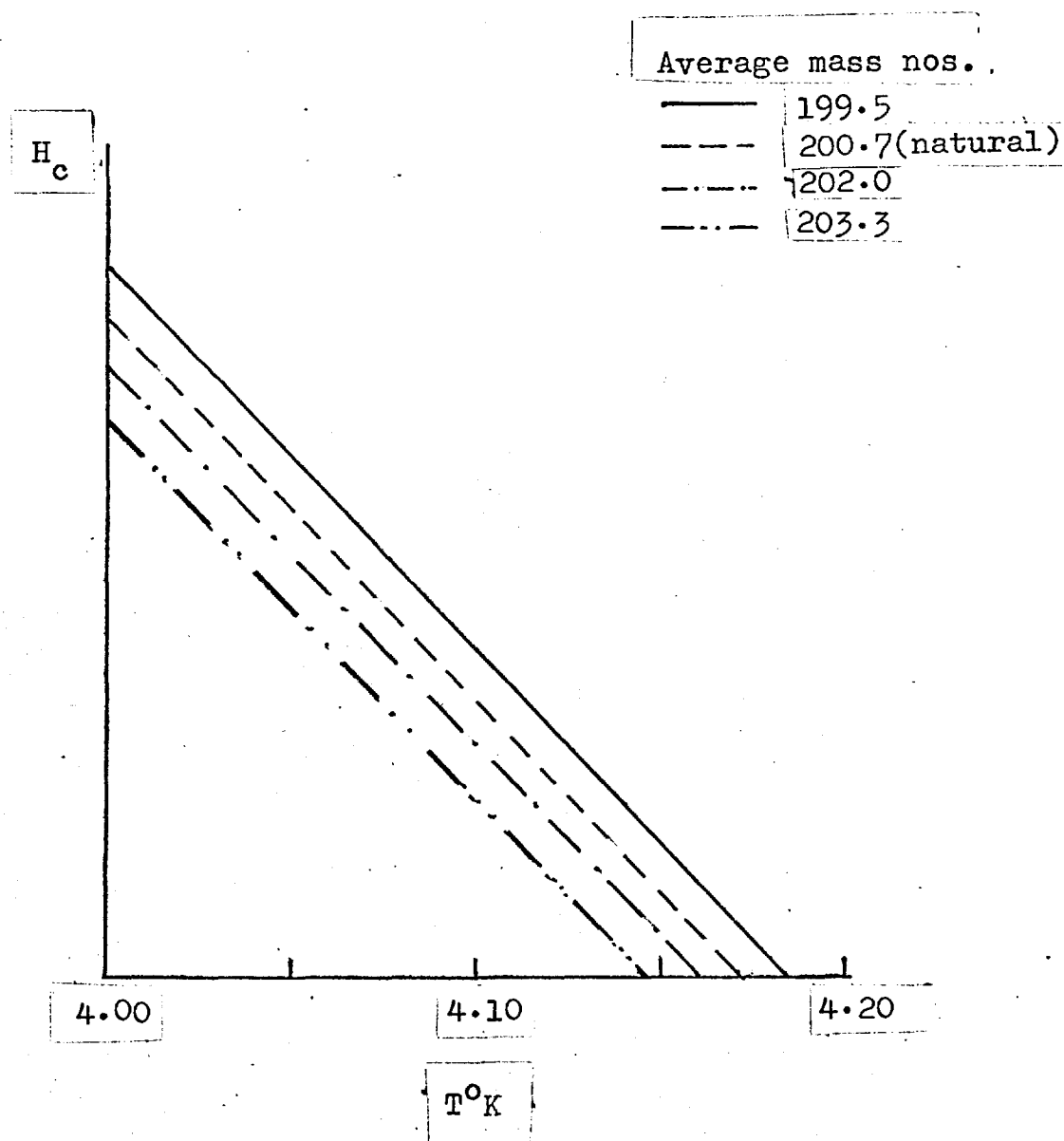


Figure 1.8. The Isotope Effect in mercury (Lynton 1962,p.74), showing the variation of critical field near T_c for different isotopes.

1.4b The Energy Gap

The existence of a gap in the single electron energy spectrum of a superconductor can be seen from five experimental results:-

- (i) Low temperature specific heat: An exponential dependence is found (Corak et al. 1956). In terms of Boltzmann statistics the simplest explanation of this is the existence of a gap.
- (ii) Low temperature thermal conductivity: An exponential temperature dependence is also found (Goodman 1953).
- (iii) Microwave absorption spectra: A sharp absorption edge is seen at $\omega = \omega_e$, so that the width of the energy gap $2\Delta = \hbar\omega_e$ (Glover and Tinkham 1957).
- (iv) Ultra-sonic absorption: Very high attenuation is observed below T_c (Morse and Bohm 1953).
- (v) Tunnelling Phenomena: The tunnelling current drops to zero for the finite non-zero voltage of Δ , a situation analogous to the work-function effect (Giaever 1960).

The existence of a gap such as that indicated by these results can be qualitatively seen in the two-fluid model. It has further been observed that for all elements the value of $2\Delta/k_B T_c$ is approximately equal to three (Lynton 1962 p. 92), where k_B is the Boltzmann constant.

1.4c The Electron-Phonon Interaction and Electron Pairing

Consideration of the isotope effect and the existence of an energy gap led to the microscopic theory of superconductivity. Fröhlich (1950) and Bardeen (1950) indicated that an electron moving through a lattice of positive ions will produce an oscillatory distortion which, because of the short time involved, can be treated as a virtual phonon. A second electron will be attracted by the positive charge produced and if the force is greater

than the coulomb force the net effect will be attractive. That the two electrons can be in a bound state was shown by Cooper (1956) and in 1957 Bardeen, Cooper and Schrieffer (1957) published a complete theory (BCS) assuming that the electron-phonon interaction is the mechanism involved and that all other interactions at 0°K are the same as for the ground state of the normal metal.

When two electrons with wave vectors $\underline{k}_1$ and $\underline{k}_2$ interact they are scattered by the phonon q into states $\underline{k}'_1$ and $\underline{k}'_2$ (figure 1.9a). As momentum must be conserved:

$$\underline{k}_1 + \underline{k}_2 = \underline{k}'_1 + \underline{k}'_2 = \underline{K} \quad (1.59)$$

Furthermore, as the superconducting characteristics of very different metals are similar, the interaction cannot depend on the detailed properties of individual substances. BCS therefore assumed that the interaction only takes place in a narrow shell, straddling the Fermi surface, of thickness 2ϵ where $|\epsilon| \ll \hbar\omega_q$, the average energy of the lattice. This means that to satisfy 1.59, the values of $\underline{k}_1$ and $\underline{k}_2$ are restricted to the shaded areas in figure 1.9b. There is thus a sharp maximum in the volume of phase space available at $\underline{K} = 0$, meaning that the lowest energy state occurs when electrons of opposite momentum are paired. From consideration of exchange terms it can be shown that the most energetically favourable condition is for pairing of electrons with opposite spin, forming quasi-bosons. The effect then of electronic interactions is only to scatter from one zero momentum state to another. The energy of this state is lower than that of a normal metal by an amount which at absolute zero is $H_0^2/8\pi$ per unit volume.

To excite a single unpaired electron from the condensed state reduces substantially the area of phase space available for pair interaction. The energy required, therefore, is not just the energy to break one pair bond, but a large multiple of this, which corresponds to the experimentally observed energy gap.

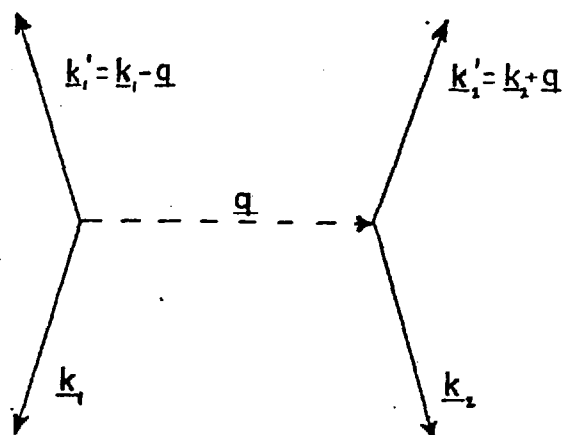


Figure 1.9a. The electron-electron interaction by means of a virtual phonon.

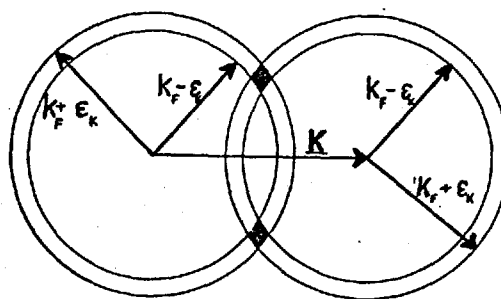


Figure 1.9b. The electron-electron interaction, showing the small volume of phase space available for the formation of Cooper pairs.

1.4d The Ground State Energy and the BCS Equation

If $V_{kk'}$, the matrix element which represents the difference between the electron-phonon interaction, by means of a phonon, and the coulomb interaction, is isotropic and, from the earlier assumptions, equal to V and the same for all electrons in the shell at the Fermi surface and zero elsewhere, and h_k is the probability that the states k and $-k$ are occupied by a pair of electrons, then the ground state energy $W(0)$ of the superconductor at $0^\circ K$ compared to that of a normal metal can be written as:

$$W(0) = \sum_k \epsilon_k h_k - V \sum_{kk'} \{h_k (1-h_{k'}) h_{k'} (1-h_k)\}^{\frac{1}{2}} \quad (1.60)$$

By minimising $W(0)$ with respect to h_k and defining:

$$\epsilon(0) = V \sum_k \{h_k (1-h_k)\}^{\frac{1}{2}} \quad (1.61)$$

$$E_k = \{\epsilon_k^2 + \epsilon^2(0)\}^{\frac{1}{2}} \quad (1.62)$$

one obtains an expression for h_k

$$h_k = \frac{1}{2} \left\{ 1 - \frac{\epsilon_k}{E_k} \right\} \quad (1.63)$$

Substituting 1.63 into 1.61 gives

$$\epsilon(0) = \frac{V}{2} \sum_k \frac{\epsilon(0)}{\{\epsilon_k^2 + \epsilon^2(0)\}^{\frac{1}{2}}} \quad (1.64)$$

Changing the sum to an integral of ϵ , assuming symmetry of states above and below the Fermi surface ($\epsilon = 0$) and introducing $N(0)$, the density of states at the Fermi surface, (1.64) becomes:

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \frac{d\epsilon}{\{\epsilon^2 + \epsilon^2(0)\}^{\frac{1}{2}}} \quad (1.65)$$

the upper limit of the integral being defined by the assumption that for $|\epsilon| > \hbar\omega_q$, $V = 0$. The solution of 1.65 is

$$\epsilon(0) = \hbar\omega_q / \sinh\left(\frac{1}{N(0)V}\right) \quad (1.66)$$

and substitution of 1.66 into 1.60 gives the ground state energy:

$$W(0) = \frac{-2N(0) (\hbar\omega_q)^2}{\exp(2/N(0)V) - 1} \quad (1.67)$$

To obtain the value of the energy gap at 0° K consider equation 1.60. The first term for the kinetic energy can be made arbitrarily small while the second is always finite. Thus, from 1.61 and 1.63 it can be shown that the energy gap is given by:

$$2\epsilon_0 = 2 \hbar\omega_q / \sinh(1/N(0)V) \quad (1.68)$$

To obtain the ground state energy at temperature T , an occupation probability for normal electrons is defined and, as before, the Gibbs Energy minimised, leading to an expression corresponding to 1.65.

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_q} \frac{d\epsilon}{\{\epsilon^2 + \epsilon^2(T)\}^{\frac{1}{2}}} \tanh\left(\frac{\{\epsilon^2 + \epsilon^2(T)\}^{\frac{1}{2}}}{2K_B T}\right) \quad (1.69)$$

The critical temperature is reached when all the pair states are broken, so that $\epsilon(T_c) = 0$ and 1.69 becomes:

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_q} \frac{d\epsilon}{\epsilon} \tanh\left(\frac{\epsilon}{2K_B T_c}\right) \quad (1.70)$$

which for $K_B T_c \ll \hbar\omega_q$ has a solution:

$$K_B T_c = 1.14 \hbar\omega_q \exp\{-1/N(0)V\} \quad (1.71)$$

This is the BCS equation and the existence of the isotope effect can be seen immediately from it as:

$$T_C \propto \hbar \omega_q \propto M^{\frac{1}{2}} \quad (1.72)$$

Combining 1.71 with 1.68 and taking the experimental value of $1/N(0)V \approx 3+4$, gives

$$2\varepsilon(0) = 3.52 K_B T_C \quad (1.73)$$

To illustrate the validity of this relationship, Mühlischlegel (1959) has tabulated the parameters concerned as functions of reduced temperature and the agreement with experiment is very close. As an alternative approach to the problem Thouless (1960) has produced a derivation of the BCS equation using perturbation theory, determining T_C as the point at which this breaks down. He finds that even for $K_B T_C / \hbar \omega_q \rightarrow \infty$, the energy gap at 0°K is still only $4.0 K_B T_C$. The most complete theory, however, has been produced by Bogoliubov (1958), who also uses perturbation theory, considering the phonon interaction explicitly in conjunction with "the cancellation of dangerous terms" a mathematical expression of the conservation of particles during the transformation, such that, when a pair of superconducting quasi-particles, "Bogoliubons", is produced, the correct number of electrons and phonons are used.

From the BCS equation G'orkov (1958) has derived the Ginzburg-Landau equations (1.48) and (1.49) using a Green's function method, an important step which identified the microscopic and phenomenological theories.

1.4e Weak and Strong Coupling

The limit of $K_B T_C \ll \hbar \omega_q$ is the weak coupling limit, where T_C , given by the BCS equation 1.71, is a strong function of the density of states at the Fermi surface, as equation 1.71 can be written:

$$\frac{T_C}{\theta_D} \approx \alpha' \exp(-1/N(0)V) \quad (1.74)$$

where θ_D is the Debye temperature.

In the strong coupling limit $K_B T_C \approx \hbar \omega_q$ and

MacMillan (1968), using the work of Eliashberg (1960) and Morel and Anderson (1962), has considered the electron-phonon and coulomb interactions in more detail and derived the expression:

$$\frac{T_c}{\theta_D} = 0.69 \exp \left[\frac{1.04 (1+\lambda)}{\lambda - \mu (1+0.62\lambda)} \right] \quad (1.75)$$

where λ is the electron-phonon coupling constant, approximately equal to $N(0)V$ and μ the coulomb coupling constant of Morel and Anderson (1962).

$$\mu = \frac{N(0) V_c}{1 + N(0) V_c \ln (E_B / \omega_0)} \quad (1.76)$$

where V_c is the average coulomb interaction, E_B the electronic band width and ω_0 the maximum phonon frequency. In the weak coupling limit $\lambda \ll 1$ and 1.75 reduces to the BCS equation.

For materials with a high T_c $\mu \ll \lambda$ and 1.75 can be written:

$$\frac{T_c}{\theta_D} = \alpha' \exp \frac{-(1+\lambda)}{\lambda} \quad (1.77)$$

$$\text{and } \lambda = N(0) \frac{I^2}{M\omega_q^2}$$

where I^2 is a term representing the change in crystal field arising from the ionic displacements in the electron phonon interaction.

1.5 Factors Influencing the Critical Temperature

1.5a Matthias's Empirical Rules

From studies of many superconductors Matthias (1957) produced a plot of T_c against the average number of valence electrons per atom (figure 1.10a). Morin

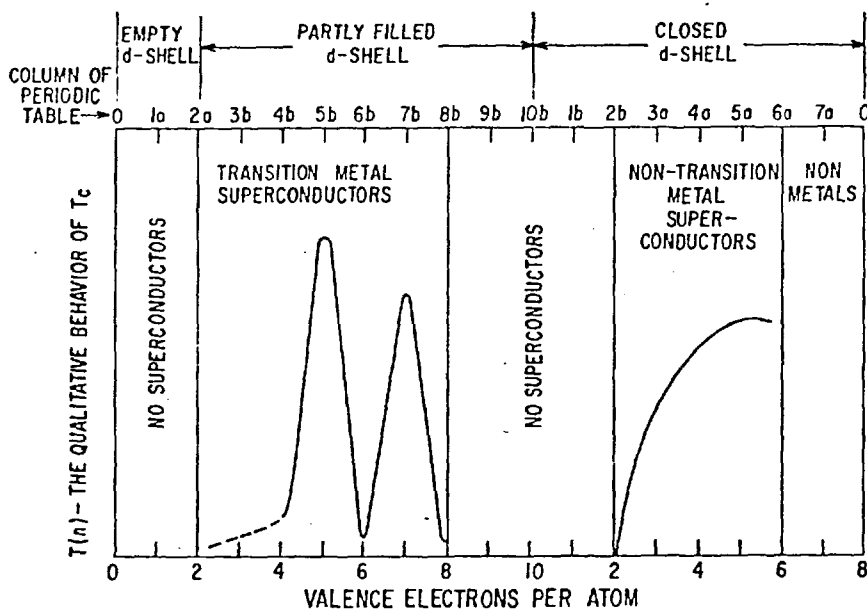


Figure 1.10a. The qualitative behaviour of T_c as a function of the average number of valence electrons per atom as proposed by Matthias(1957).

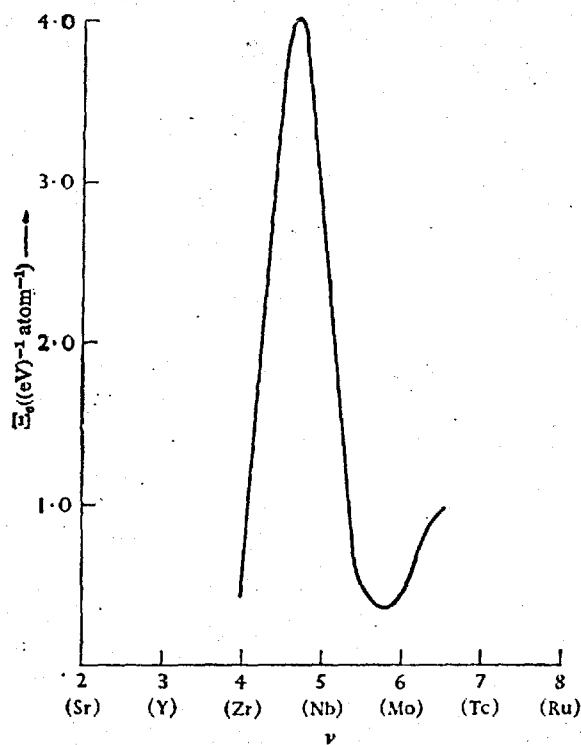


Figure 1.10b. The variation of the density of states E_0 as a function of mean valency. (Morin and Maita 1963)

and Maita (1963) have measured the variation in density of states for the transition metals as a function of the number of valence electrons (figure 1.10b) and peaks occur at the same values of 5 and 7 that occur in the Matthias plot (for alloys the peaks are at 4.7 and 6.5) and Pines (1958) has with partial success attempted to correlate the two variations on the basis of BCS theory.

1.5b Resonating Bond Theory

Pauling (1968) has given an interpretation of the Matthias plot in terms of his resonating bond theory (Pauling 1948, 1949). When a phonon moves through a lattice of positive and negative ions, the strain produced by the charge differences will either be relieved or increased at the peaks or in the troughs of the compressional waves. The superconducting current will then tend to move in the troughs if the strains are reduced in the troughs, where, to reduce the free energy, excess negative charge will be situated. This Pauling calls a trough superconductor. Similarly if the excess negative charge is associated with the peaks, one has a crest superconductor. From these assumptions are calculated ρ , the equivalent of λ in the BCS equation. By standardising to the experimental value of T_c for technetium, the curve in figure 1.11a is obtained, in which positive and negative values of ρ imply crest and trough superconductivity respectively. The resulting values of T_c are plotted in figure 1.11b, which can be compared with the Matthias plot, the gap between molybdenum and ruthenium arising from the change from crest to trough superconductivity.

1.5c The Effect of Atomic Order

Garland et al. (1968) have studied the effect of atomic disorder on the transition temperature. Disorder increases the average amplitude of the phonon spectrum, which leads to an increase in the electron phonon coupling constant and, hence, in T_c , but it also smears out the electronic band structure. Therefore in those materials where $N(0)$ and λ are small, disorder will enhance the

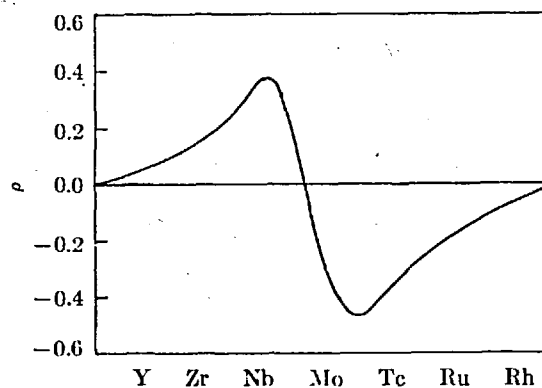


Figure 1.11a. The variation of the electron-phonon coupling constant ρ as a function of valence. (Pauling 1968)

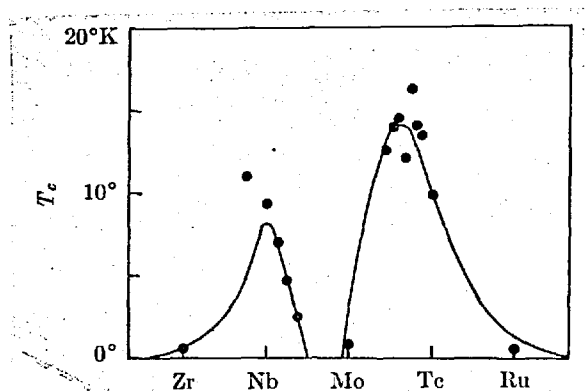


Figure 1.11b. The variation of the transition temperature T_c as a function of valence. (Pauling 1968)

transition temperature, while in those, particularly the β -W compounds where $N(O)$ is high, the effect of disorder will be to reduce T_c . The effects of order and composition in the β -W compounds will be considered in more detail later.

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Chapter Two

The Beta - Tungsten Materials

- Their Structure and Properties

"Even when the experts all agree, they may well be wrong".

- Bertrand Russell

2.1 Introduction

The Beta-Tungsten (β -W) structure is so-called because a β -phase of tungsten was once thought to exist. This was shown by Hägg and Schönberg (1954) to be tungsten oxide (WO_3), but the name has remained. The structure is also referred to as A.15 (Strukturbericht classification) and as the " Cr_3O " structure after one of the first compounds discovered to have the structure. The structure became of practical interest when it was discovered that the superconductors with the highest known critical temperatures had this structure. Representative values of these T_c 's are given in Table 2.1. In most of these alloys, a lattice softening occurs also at low temperatures and in a few instances this leads to a reversible phase transformation to a less symmetrical structure at temperatures a little above the superconducting critical temperature.

2.2 The Beta-Tungsten Structure

When fully ordered the β -W structure has the stoichiometric composition A_3B . The A atom is a transition element atom from groups IVA, VA or VIA, but the alloys with high transition temperatures all have niobium or vanadium as the A element. The B atom is either from the transition group VIII on one of the IIIB or IVB subgroup elements, usually with unfilled p levels.

The structure has the space group $\text{Pm}\bar{3}\text{n}$ (O_h^3) and the sites occupied by the B atoms are the body centred cubic sites in the unit cell, $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ while the A atoms occupy half the tetrahedral interstices which occur at $(0, \frac{1}{2}, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{3}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{3}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{3}{2}, 0)$. The structure of two unit cells is shown in figure 2.1 and it can be seen that by occupying only selected interstices, the A atoms form three mutually perpendicular rows of atom chains, continuous throughout the material. These chains are important in accounting for the physical properties and have the interesting

Table 2.1

Superconducting Critical Temperatures
of Beta-Tungsten Compounds.

Nb_3Al	17.1
Nb_3Au	11.5
Nb_3Ga	14.5
V_3Ga	16.8
Nb_3Sn	18.3
V_3Si	17.0

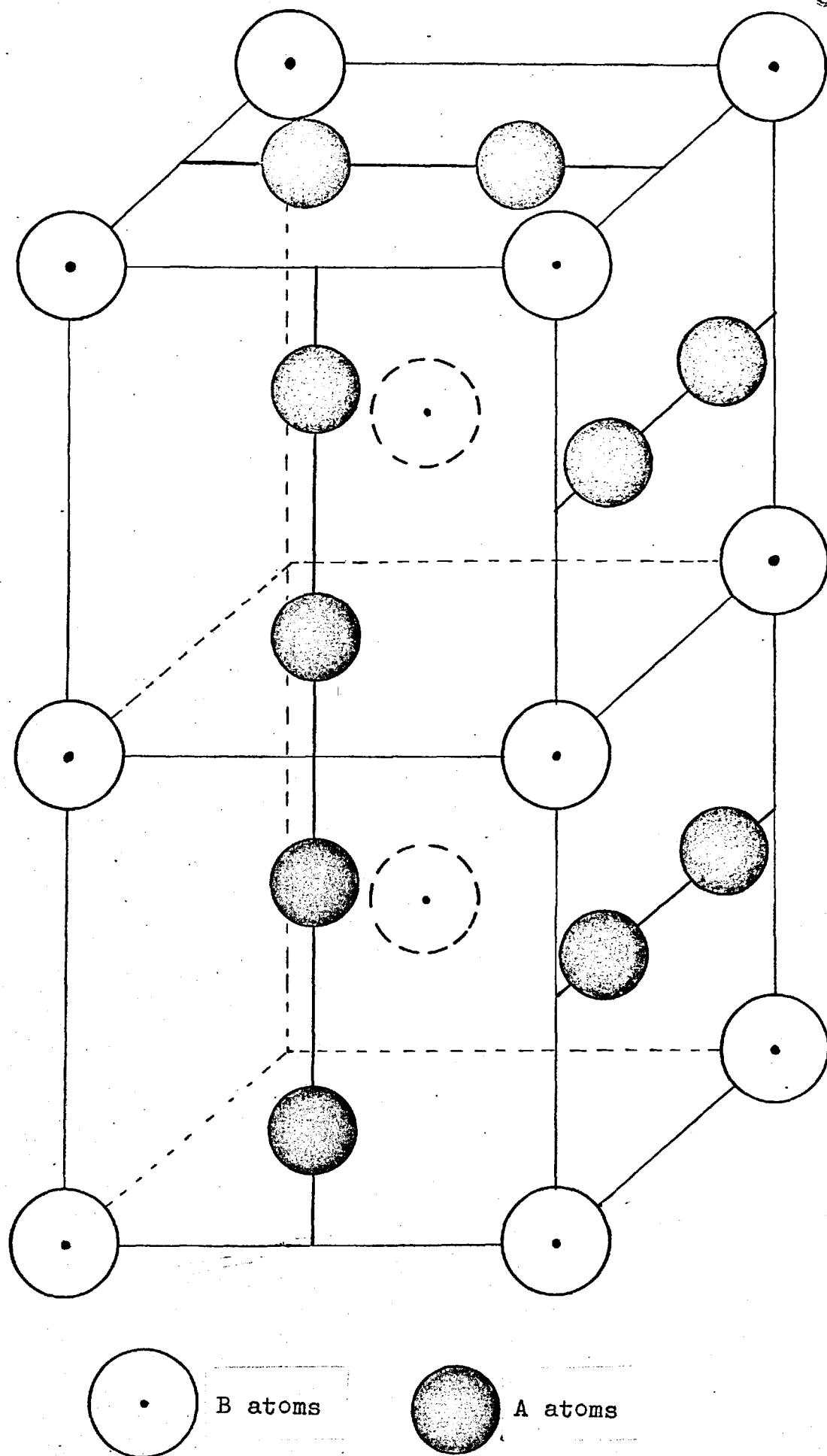


Figure 2.1. Two unit cells of the β -W structure. The atoms are shown on the front faces only, except for the body centre B atoms which are shown dashed.

feature that the interatomic spacing within them is less than the interatomic spacing in the structure of the respective transition element. For example, in Nb and V the interatomic spacings are 2.859 Å and 2.633 Å while in Nb₃Sn and V₃Si the Nb-Nb and V-V distances are 2.644 Å and 2.361 Å respectively, which represent decreases in atomic radius of 7.5% and 10.3%.

In this structure the B atoms have 12 nearest A atoms and can therefore be considered to have a coordination number (CN) of 12. The A atoms, on the other hand, have CN=14, made up of 10 A atoms and 4 B atoms. This aspect of the structure is considered in more detail in the next section.

2.2a Phenomenological Theories of the β-W Structure

Geller (1956) and Pauling (1957) have commented on the application of the resonant bond theory (Pauling 1947, 1949) to the β-W structure and Pauling (1957) has calculated the lattice parameters, a_0 , of many compounds of this structure using the equation

$$a_0 = 1.7888 \left(\frac{3}{2} R_A + \frac{1}{2} R_B \right) \quad (2.1)$$

where R_A and R_B are the metallic radii of the atoms A and B, the factors $\frac{3}{2}$ and $\frac{1}{2}$ represent the atomic ratio and 1.7888 is a geometrical factor. The calculated values agree well with experiment for stoichiometric compounds, but the author did not consider the variation of the lattice parameter in non-stoichiometric alloys across the composition width of the phase (see section 2.3), which, as shown later, is very important in the estimation of the physical properties.

One aspect of the structure that makes the resonant bonding approach approximate is that the ionic radii are not Pauling's normal C-N 12 radii. Frank and Kasper (1958, 1959) show that the structure can be treated

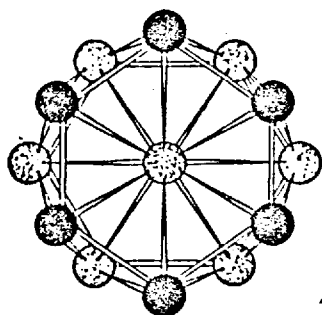


Figure 2.2a. The 'normal coordination polyhedron for CN 14 packing .The spheres above and below the central one are not shown.
(Frank and Kasper 1958)

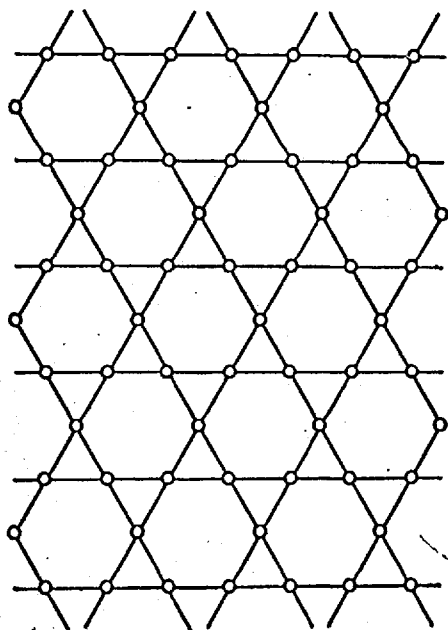


Figure 2.2b. The Kagome net 3.6.3.6. The numbers specify the sequence of the polygons around each vertex.
(Frank and Kasper 1958)

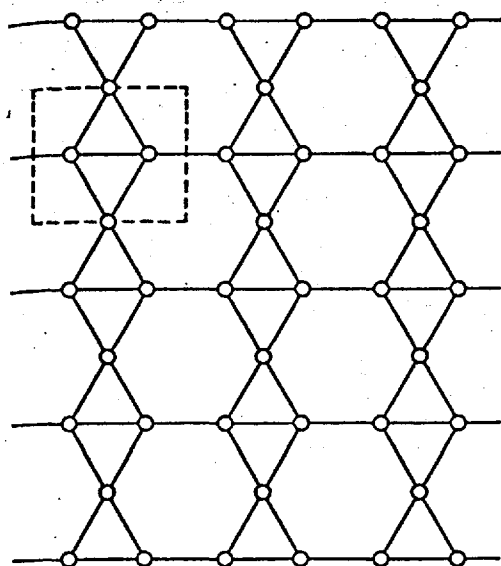


Figure 2.2 c. The net for the β -W structure.
(Frank and Kasper 1959)

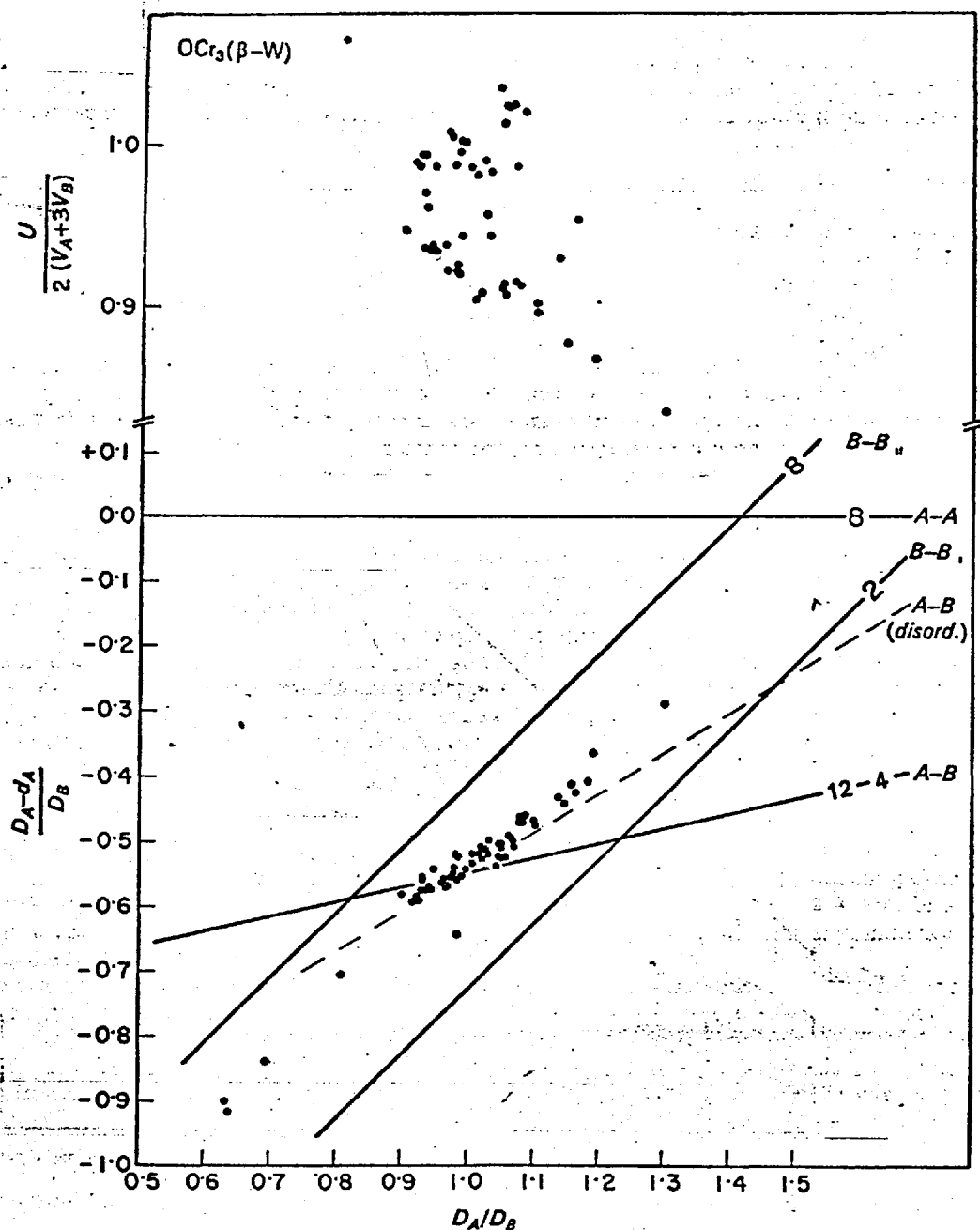


Figure 2.3. The nearest neighbour diagram for the β-W structure. The coordination for the contact lines is indicated. (Pearson 1968)

The contact lines are defined such that the following atoms are in contact in an AB₃ structure:

- A-A A atoms, B-B' B atoms (nearest neighbours).
- B-B'' B atoms (next nearest neighbours), A-B A and B atoms.

in terms of C-N 14 triangulated shells, which are somewhat distorted. The method is to consider the alloy in terms of solid sphere packing, or more correctly in terms of co-ordination polyhedra, and the co-ordinations which define a net of triangles on the surface of the sphere. The normal co-ordination polyhedron for C-N 14 is shown in figure 2.2a, and if these are combined in a certain way, one plane of the structure is the Kagome Net (figure 2.2b). This, slightly distorted so as to give a square cell, represents one plane of the β -W structure (figure 2.2c) and, in three dimensions, these are stacked alternately at 90° to the previous layer. An alternative approach is to consider the major skeleton, the skeleton made up of all the atoms with co-ordination number greater than 12. The major skeleton of the β -W structure is just made up of the chains of A atoms. To obtain the complete structure, hexagons of atoms normal to the bonds are drawn, as can be seen from considering the CN 14 geometry.

Pearson (1968), working from similar space-filling ideas of Laves (1956) has developed a quantitative method of analysing the effects of geometry and atomic size, using nearest neighbour diagrams. That for the β -W structure is shown in figure 2.3. The lines on the diagram are given by considering the various possible contacts A-A, A-B etc., which are considered as occurring when the interatomic distances, d_A , d_{AB} and d_B are equal to $2r_A = D_A$, $r_A + r_B = \frac{1}{2}(D_A + D_B)$ and $2r_B = D_B$ respectively where r_A and r_B are the atomic radii. The lower diagram shows a reduced strain parameter, $(D_A - d_A)/D_B$ plotted against the radius ratio r_A/r_B , and the upper diagram shows the volume as a function of radius ratio. From the positions of the experimental points on the diagrams, the relative importance of different factors in the formation of the structure can be determined, and it is clear from the clustering around the line representing the 12 - 4 A-B contacts and between the 8BB" and 2 BB' lines that the co-ordination factor is important in this structure, which clearly has 12 - 14 co-ordination, agreeing with Frank and

Kasper (1958, 1959). The very close packing, and similar compressive strain in the A atom chains is also very clear for this diagram, as is the tendency for the A and B atoms to be of the same size. That the alloys with high D_A/D_B ratio follow the A-B (disordered) line, may indicate partial disorder in these alloys.

2.3 The Equilibrium Diagrams of Systems containing β -W Phases

No known β -W phase forms congruently from the melt (Hansen 1958, Elliott 1965 and Shunk 1969) and therefore for the purposes of crystal growth as well as for the investigation of the compositional dependence of the physical properties, it is desirable to have as detailed a knowledge of the equilibrium diagrams of the systems of interest as possible. The four systems which will be considered, both here and throughout this thesis, are niobium-tin, niobium-aluminium, vanadium-silicon and vanadium-gallium, and in these only that part of the diagram concerned with β -W phase will be analysed.

2.3a The Niobium-Tin Diagram

The experimental work on the niobium-tin diagram has recently been reviewed by Madsen (1970). Some of the projected diagrams which he quotes are given in figures 2.4 and 2.5. From these Madsen deduces that the β -W phase forms peritectically at about 2130°C with a composition at the peritectic temperature of about 81.5 at % niobium. The diagrams quoted in figure 2.4 all show a range of homogeneity for the β -W compound down to room temperature. Many authors, e.g. Hanak et al. (1964), have established that Nb-Sn does have such a range of composition and it must be concluded therefore that diagrams showing just the stoichiometric composition are in error. The exact range and its variation with temperature are a matter of disagreement among the different authors, but Fowler (1963) deposited films of Nb_3Sn at 280°C , which implies that the phase is

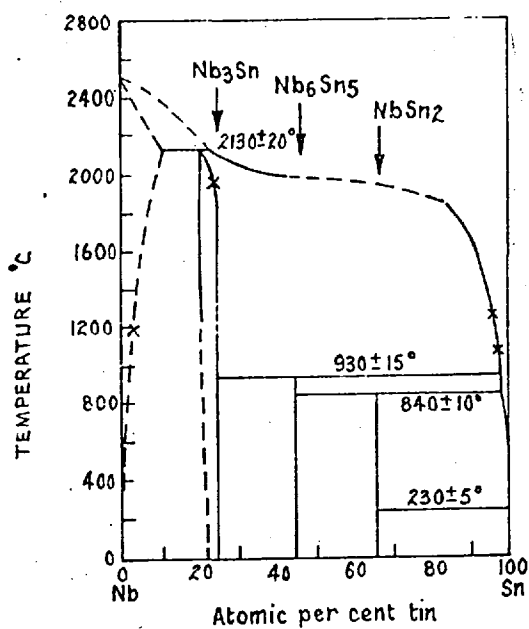


Figure 2.4a.

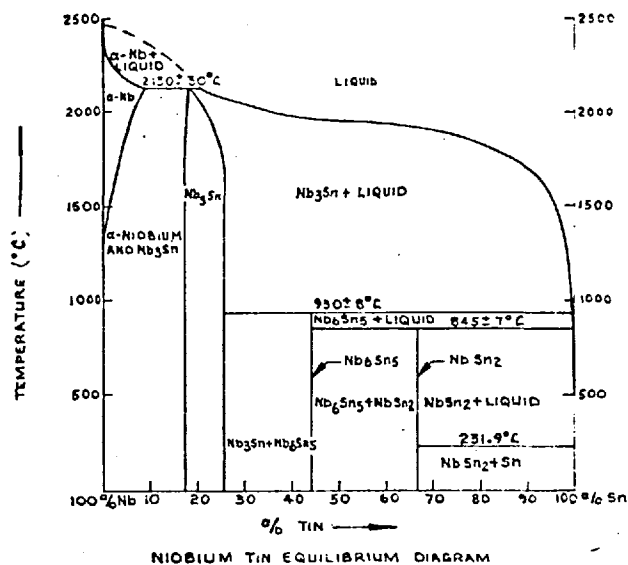


Figure 2.4b.

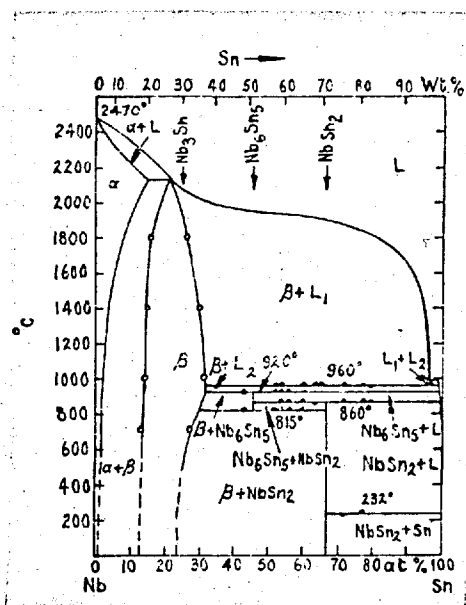


Figure 2.4c.

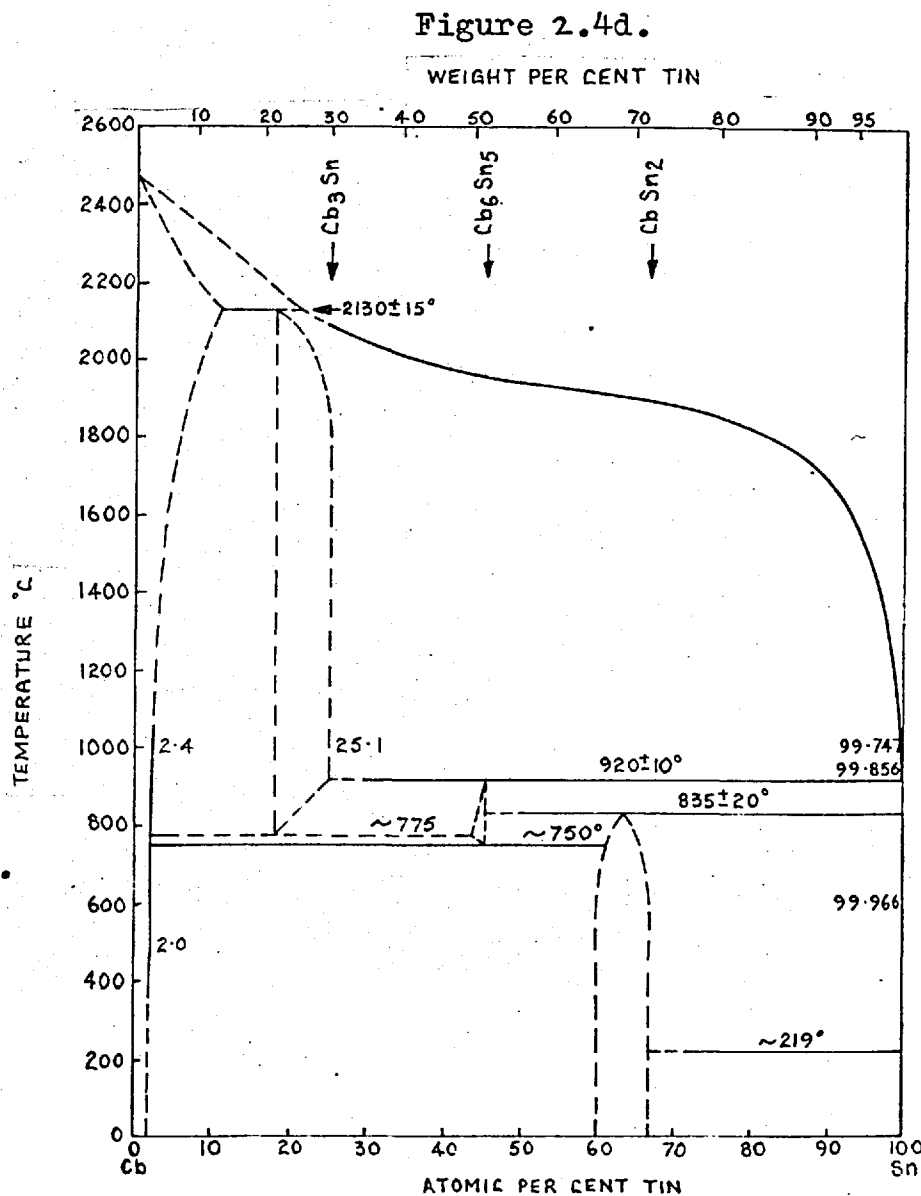
Proposed equilibrium
diagrams for the
Nb-Sn system.

(a) Van Vucht et al.
(1965)

(b) Charlesworth et al.
(1969)

(c) Svechnikov et al.
(1966)

(d) Shunk (1969)



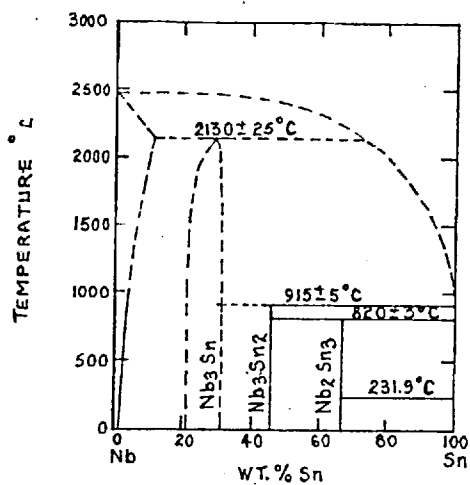


Figure 2.5a.

Proposed equilibrium
diagrams of the
Nb-Sn system.

(a) Ellis and Wilhelm (1964)

(b) Van Vucht (1964)

(c) Kuznetsova et al. (1967)

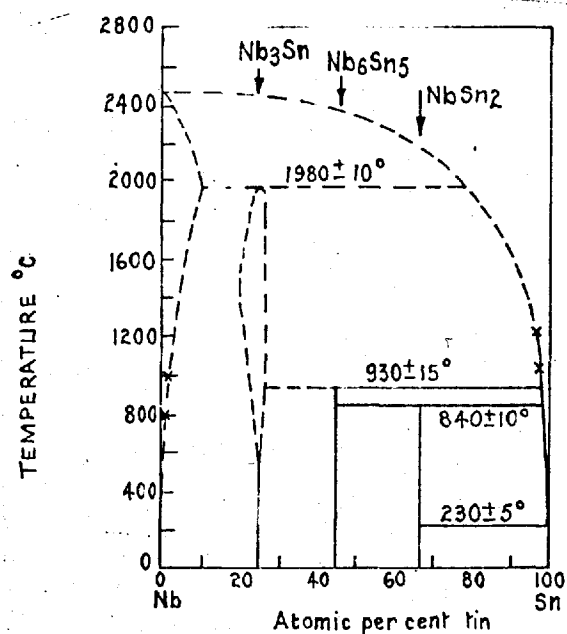


Figure 2.5b.

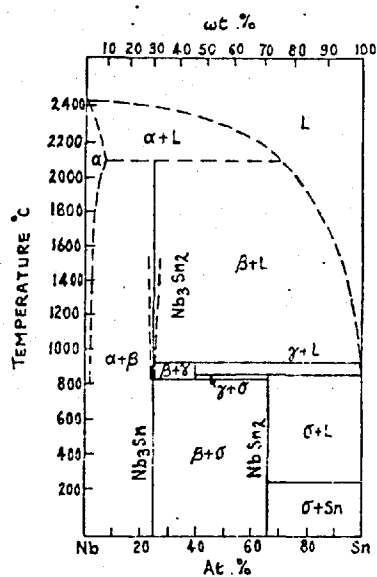


Figure 2.5c.

stable to room temperature and that Shunk (1969) is in error. The cooling rates necessary to check this would, however, be prohibitively slow. Although the phase does appear to be stable below 850°C , the diffusion rates slow down below this temperature, and this may have led to the interpretation that equilibrium had been reached at that temperature. The decomposition observed by Reed et al. (1962) is probably due to the narrowing of the range of composition towards the lower temperatures as is suggested by the diagram of Svetchnikov, Pan and Beletskii (1967).

The composition range of the Nb-Sn Al_5 compound is deduced by Madsen (1970) to be approximately 18 - 27 at.% Sn. This result is obtained by analysis of much published data summarised in figure 2.6, where many of the published compositions have been adjusted using the values of room temperature lattice parameters. These data are shown in figures 2.7. The straight line has been fitted using the data of Vieland (1964), Cullen (1964) and Pfister (1965).

Calculation of composition for β -W Nb-Sn is not always reliable, as the work of Sahm (1968) and Ziegler (1968) shows that if hydrogen is dissolved in the alloy then the lattice parameter is increased as indicated in figure 2.8a. Hydrogen may be introduced from etching solutions, so care has to be exercised when alloys are made by diffusion, and the excess Sn dissolved away with HCl in order that spurious results for the composition are not obtained. The specimens used by both Mailfert et al. (1967) and King et al. (1967) may have contained hydrogen which gave rise to the anomalously high lattice parameters before heat treatment.

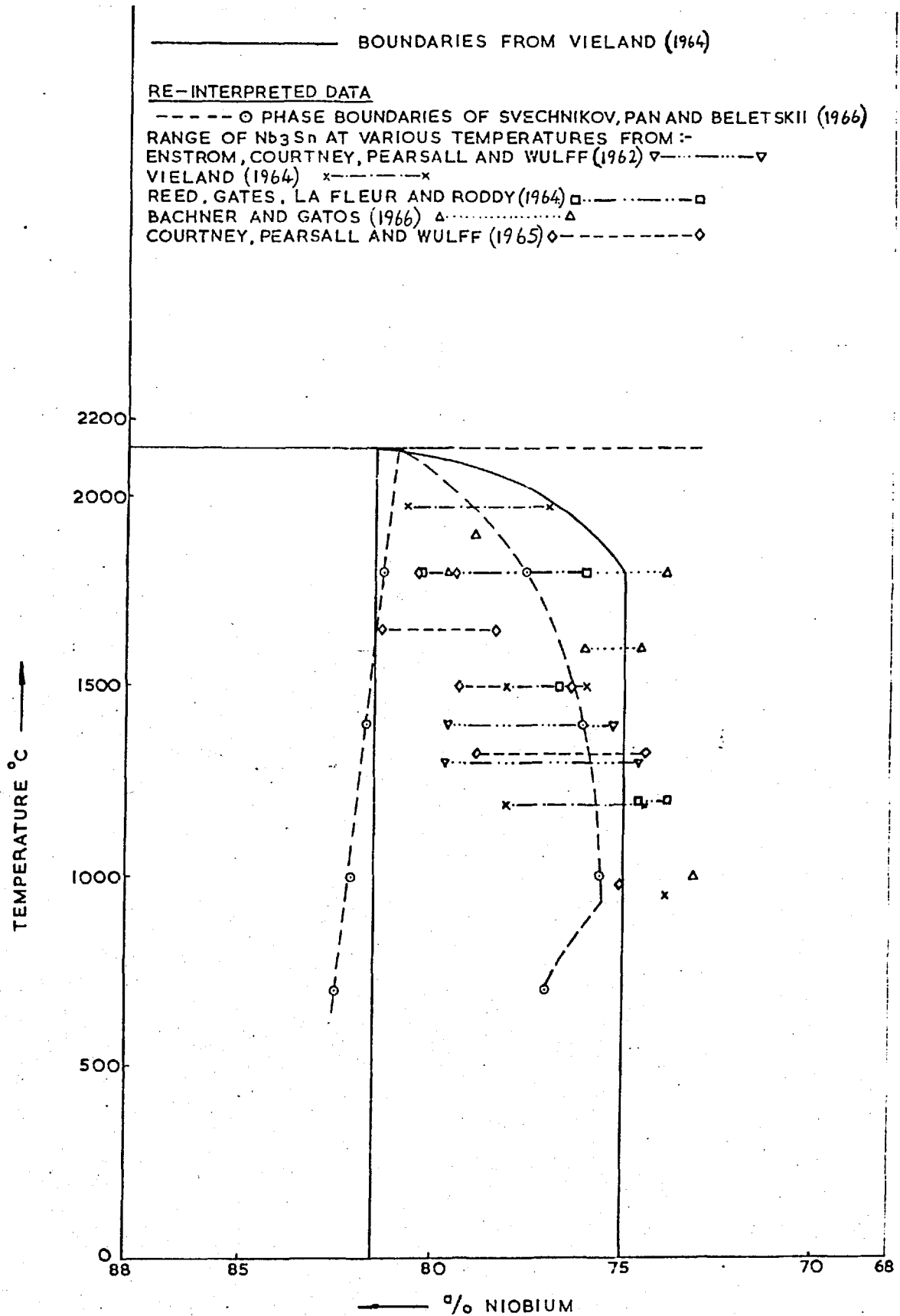


Figure 2.6. The boundaries of the β -W phase in the Nb-Sn system, as re-interpreted by Madsen (1970).

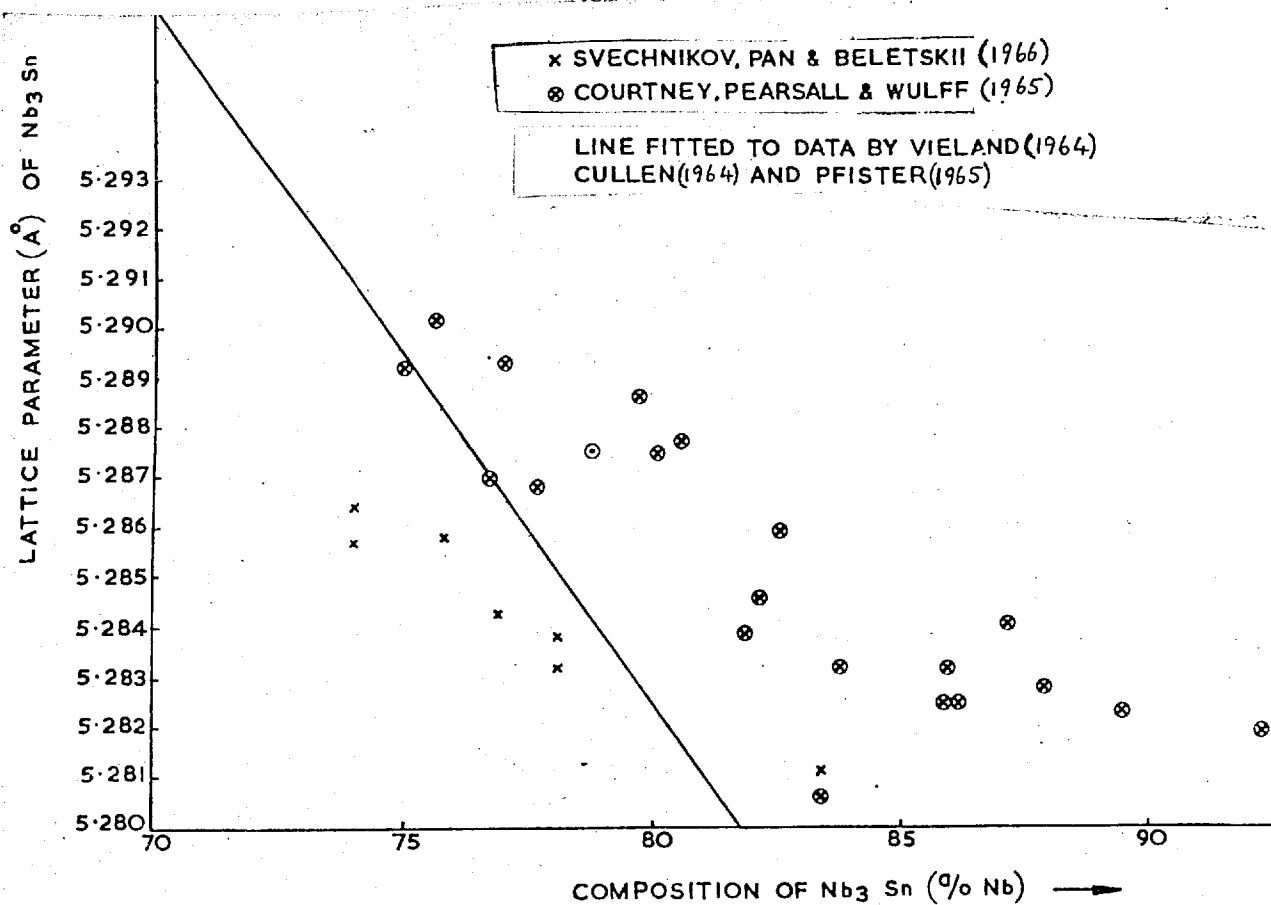
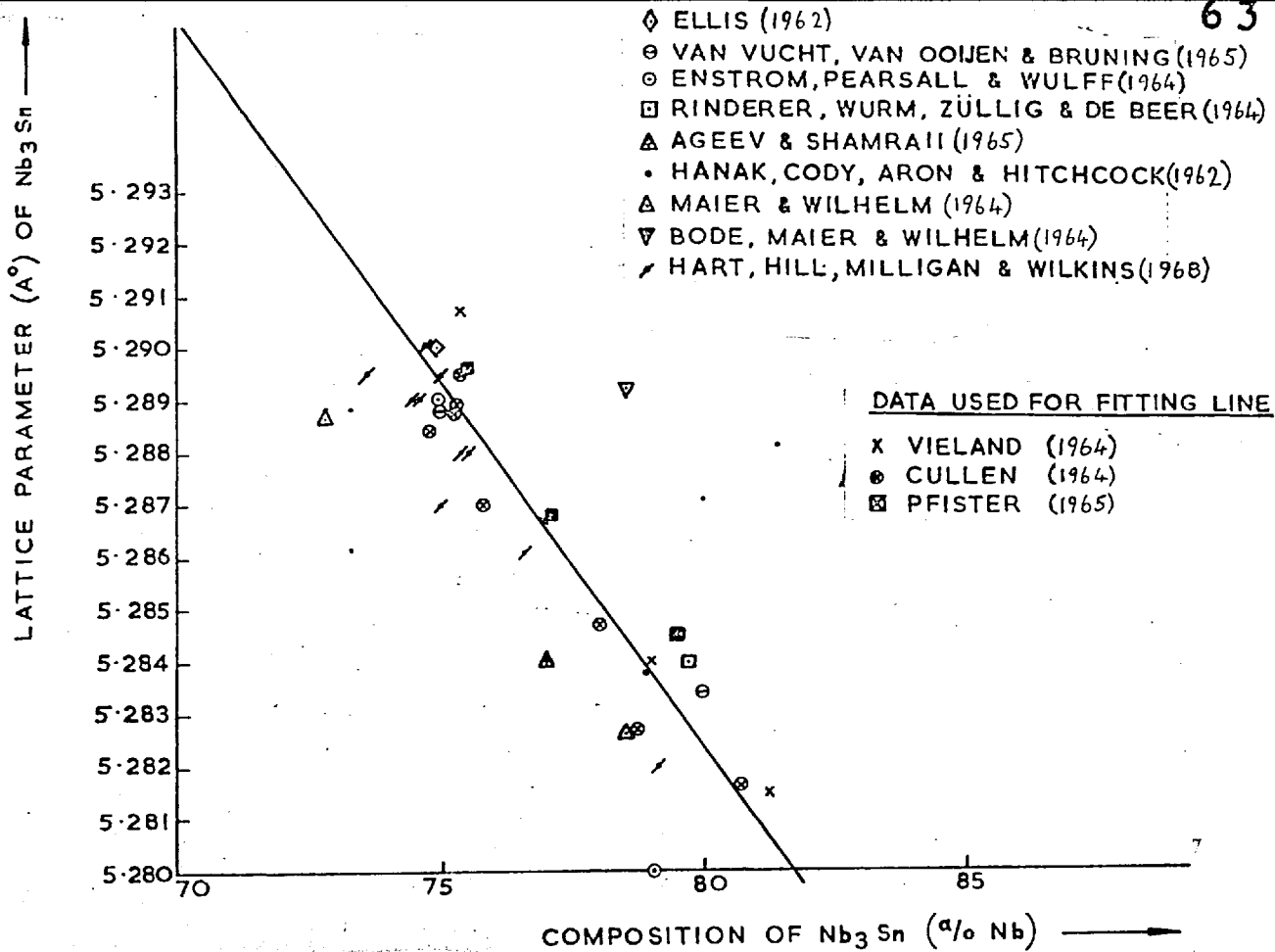


Figure 2.7. The dependence of the room temperature lattice parameter of the β -W phase of Nb-Sn upon composition (Madsen 1970).

2.3b The Niobium-Aluminium Diagram

Lundin and Yamamoto (1966) have considered the results of Savitskii (1959), Baron and Savitskii (1961), Nedumov and Rabezova (1961) and their own work to make an exhaustive study of the niobium-aluminium system. The diagram they deduce, including an enlarged inset of the niobium-rich end, is given in figure 2.8b. The Nb_3Al phase is shown as forming peritectically at 1960°C , agreeing approximately with all three Russian papers, who give the temperature as 2260°C , 2120°C and 2060°C respectively and with Richards (1962) who measured the peritectic temperature as 2050°C .

Lundin and Yamamoto (1966) give the range of composition of the Al_5 phase as 17 to 33 at % Al. This agrees approximately with Nedumov and Rabezova (1961) and with Kunz and Saur (1966) whose measurements of superconducting properties give an indication of the homogeneity range. All β -W alloys of this system, however, will be in a non-equilibrium state at room temperature, as the single phase regions occur at significantly different compositions at high and low temperatures. This may be one reason why single phase alloys are difficult to obtain. A plot of room temperature lattice parameter against composition is given in figure 2.9 and the wide scatter in the results is obvious. A reasonable line can be drawn to fit the data, however, if the results of Baron and Savitskii (1961) and those of Bachner and Gatos (1966) are ignored. In the former, case the alloys used by Gladyshevskii (1961) were the same as those used by Baron and Savitskii (1961) and the discrepancy in their results would imply that the low value of the later authors is either a misprint or the result of some experimental error. The compositions quoted by Bachner and Gatos (1966) are those before casting and it is highly probable that the true compositions have a lower aluminium content. In spite of this weight loss in casting their values of the

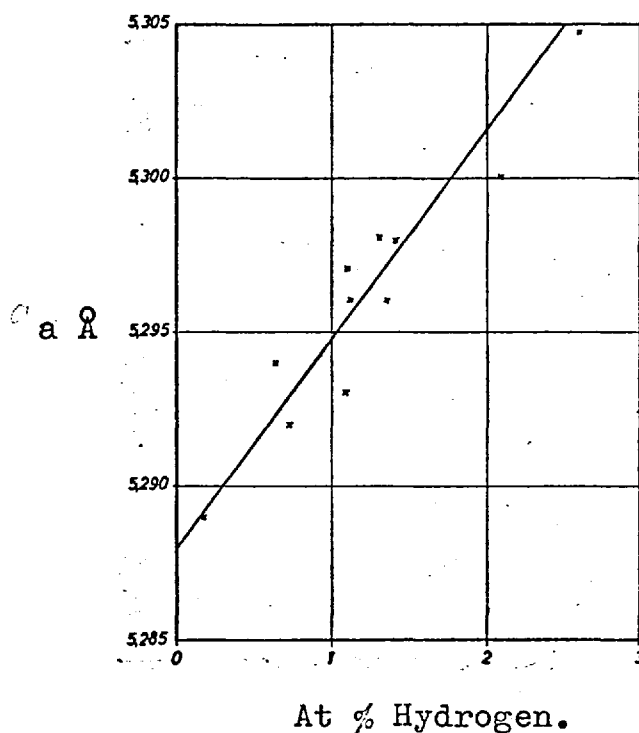


Figure 2.8a.

The lattice parameter of Nb_3Sn as a function of the amount of hydrogen in solution. (Ziegler 1968)

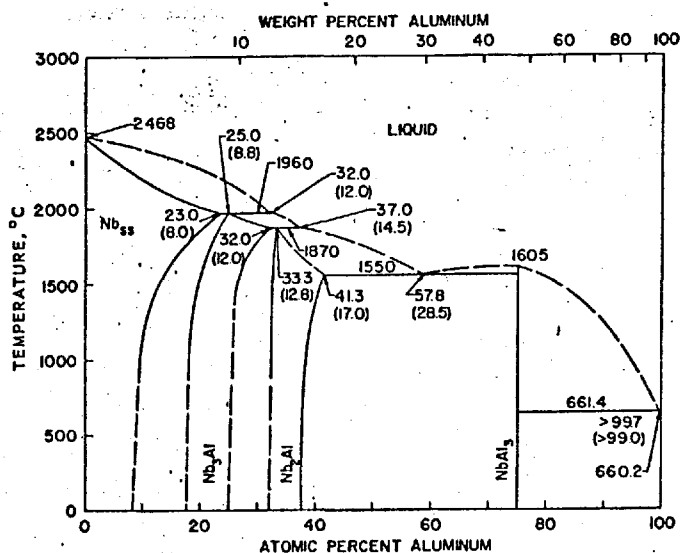
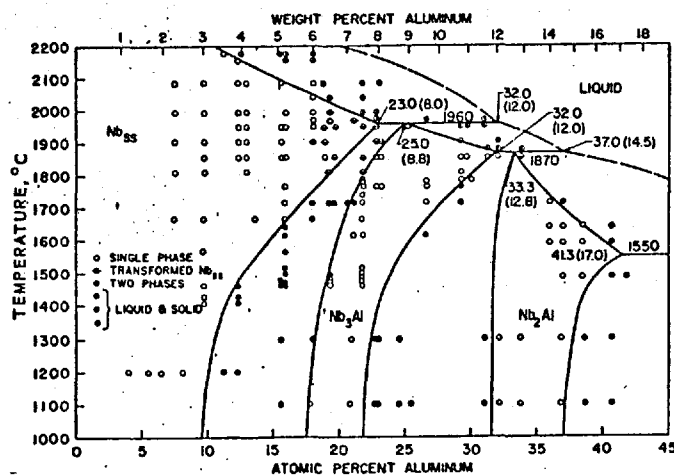


Figure 2.8b. The equilibrium diagram for the Nb-Al system as proposed by Lundin and Yamamoto (1966), with an enlarged inset of the Nb-rich end.



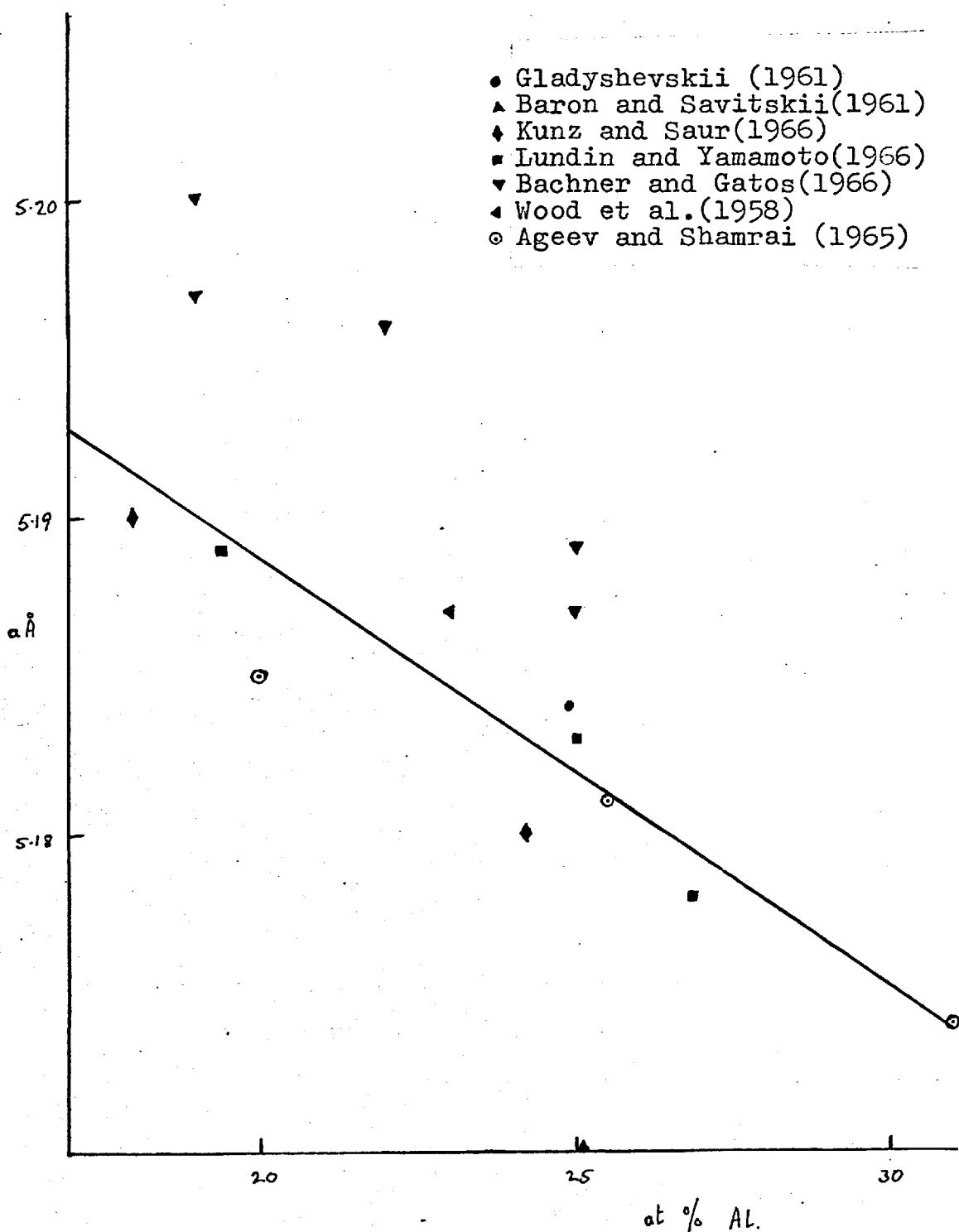


Figure 2.9. The dependence of lattice parameter upon the composition in the β -W phase of the Nb-Al system, taken from published data.

lattice parameters of alloys with low aluminium content seem anomalously high.

2.3c The Vanadium-Silicon Diagram

Only two studies have been made of the vanadium-silicon diagram in the region of 25 at. % Si. The resulting diagrams are shown in figure 2.10a (Efimov, 1963) and figure 2.10b (Bruning, 1967). There are certain discrepancies between the two. Efimov shows a much narrower range of composition at 1000°C than does Bruning and the former's eutectic and peritectic temperatures of 1840°C and 2030°C are both higher than Bruning's values which are 1780°C and 1970°C respectively.

That a range of homogeneity from about 18 at % to 25 at % Si exists can be clearly seen from the plot of room temperature lattice parameter against composition (figure 2.11). The data used to plot this graph are taken from many authors and the agreement between them is good. This indicates that the range shown by Bruning is the more likely to be correct, particularly as many of the alloys used in the lattice parameter plot were formed at temperatures below 1000°C . Whether the stoichiometric composition V_3Si falls inside this homogeneity range or not is difficult to determine with accuracy, but the indications are that it does not and this means that in strict terms the compound V_3Si does not exist, an important factor to be considered when discussing ordering and its atomic structure.

2.3d The Vanadium-Gallium Diagram

The early work of Savitskii et al. (1964) predicted the formation of the β -W phase in the V-Ga system, in a peritectic reaction, (figure 2.12a), while van Vucht et al. (1964) and Sazhin et al. (1968) both show the phase forming directly from the α -V solid solution (figure 2.12b and 2.12c).

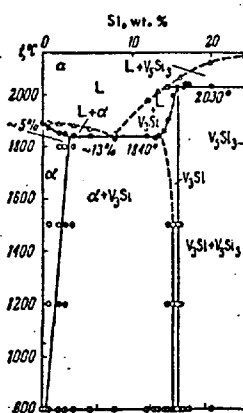


Figure 2.10a.

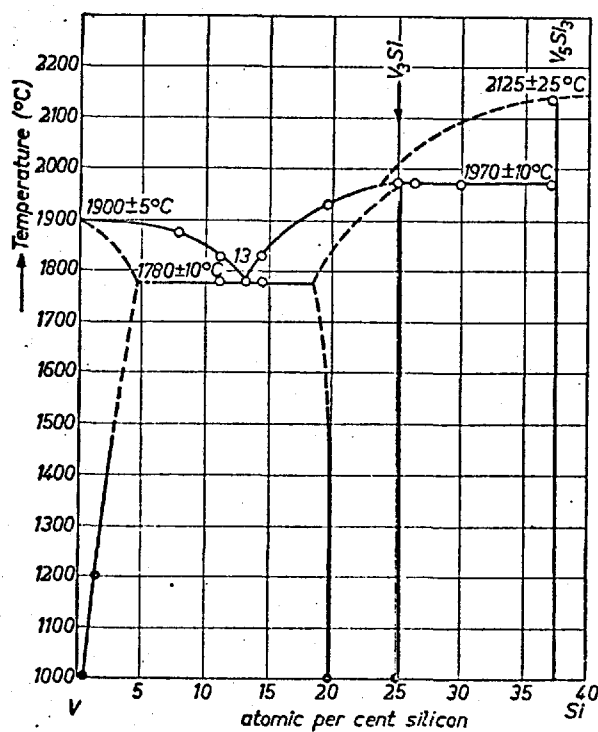


Figure 2.10b.

Equilibrium diagrams of the V-rich end of the V-Si system, as proposed by Efimov(1963) (a) and Bruning (1967) (b).

♦ Finlayson(1968)

▲ As cast

○ 100 hr. 1000°C

◻ 50 hr. 1200°C

Bruning(1967)

× Efimov (1963)

▽ As cast

▼ Furnace cooled

◊ Radiation cooled

■ Argon cooled

Rivlin

(Private

Communication)

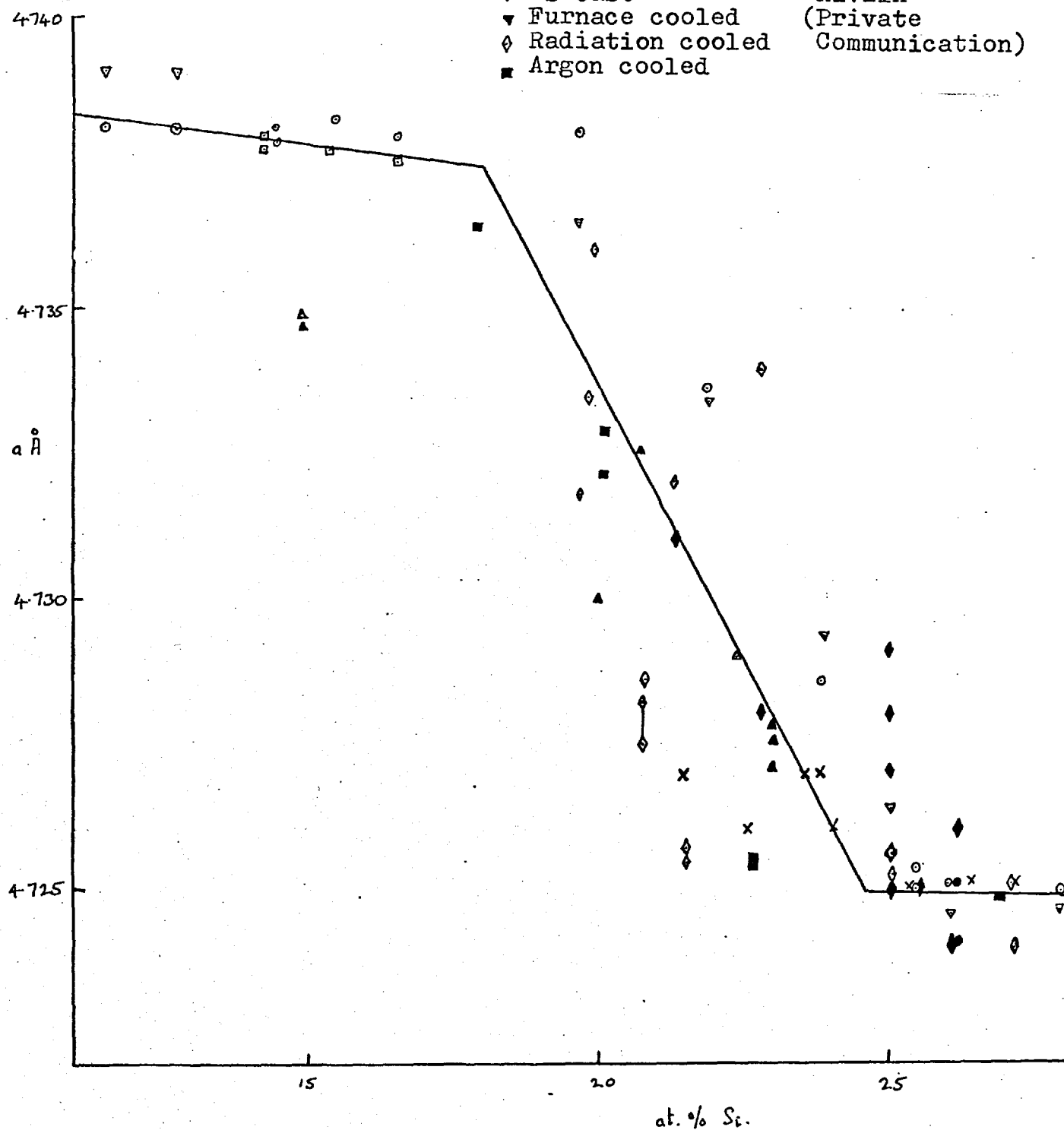


Figure 2.11. The dependence of lattice parameter upon composition in the β -W phase of the V-Si system, taken from published data.

Savitskii et al. (1966) and Savitskii (1967), however, show an additional high temperature phase β' , from which the Al₅ phase appears to form (figure 2.13a). This phase they describe as a partially ordered form of the α -V solid solution, having a structure related to the Cs-Cl type. However, as the range of composition of the phase does not reach the stoichiometric V-Ga, its formula is of the type $V(V_{0.5}Ga_{0.5})$ where the components in the brackets are disordered on one type of site. Levinstein et al. (1965) found a phase with the same composition and temperature limits as β' but they described it as γ , a hexagonal close packed solid solution of Ga in V. Moreover, Fischer and Probst (1965) were unable to obtain single phase V_3Ga by cooling from the melt. Although they attribute the second phase in their sampler to the α -V solid solution or to V_6Ga_5 , it may be that they had cooled through the β' (γ) phase and not reached equilibrium.

It seems probable that a high temperature phase does exist and as the papers by van Vucht et al. (1965) and Sazhin et al. (1968) do not have points in the region concerned, they do not contradict this view. As the X-ray intensity calculations of Savitskii et al. (1966) favour the Cs-Cl structure (figure 2.13b) and the powder pattern corresponds to this structure it would seem to be the more likely.

All the papers quoted except that of Fischer and Probst, which may differ for the reasons discussed above, agree that the range of homogeneity of the Al₅ phase is from about 20 at % to 35 at % Ga, or possibly higher, and the dependence of lattice parameter upon composition is shown in figure 2.14, which uses values from many authors including those quoted above. Levinstein et al. (1965) show a deviation from linearity in their plot, but the values of other authors show this to be fallacious and that in common with the other systems considered the relationship is essentially linear.

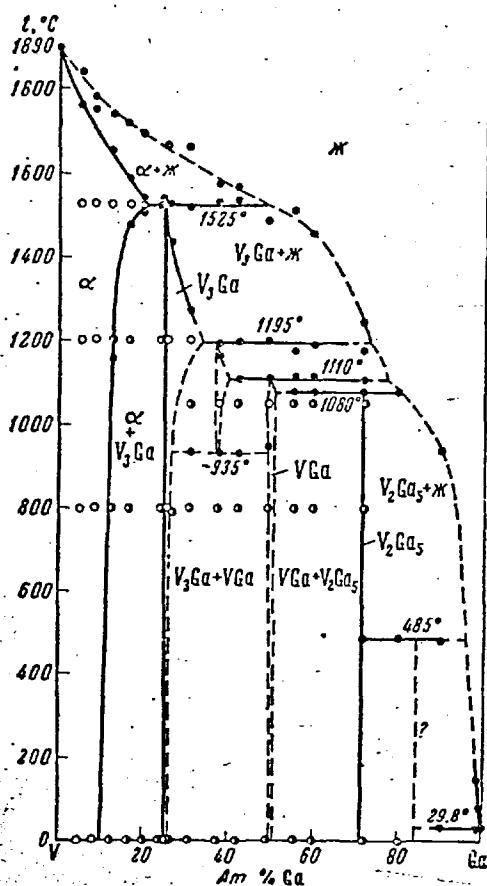


Figure 2.12a.

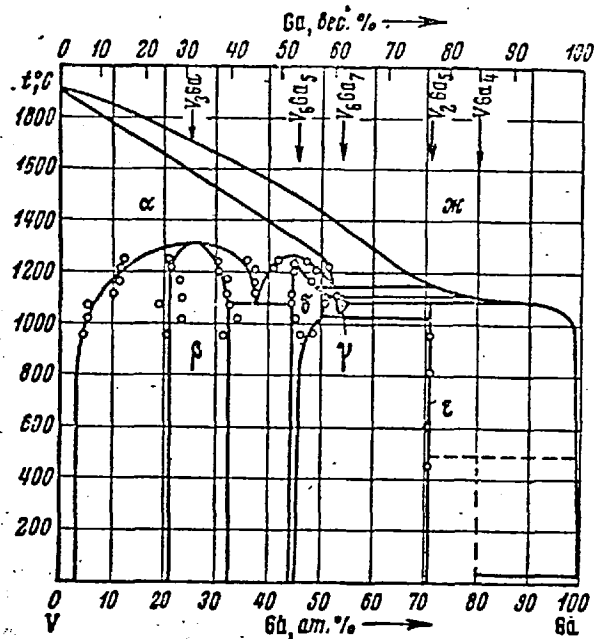
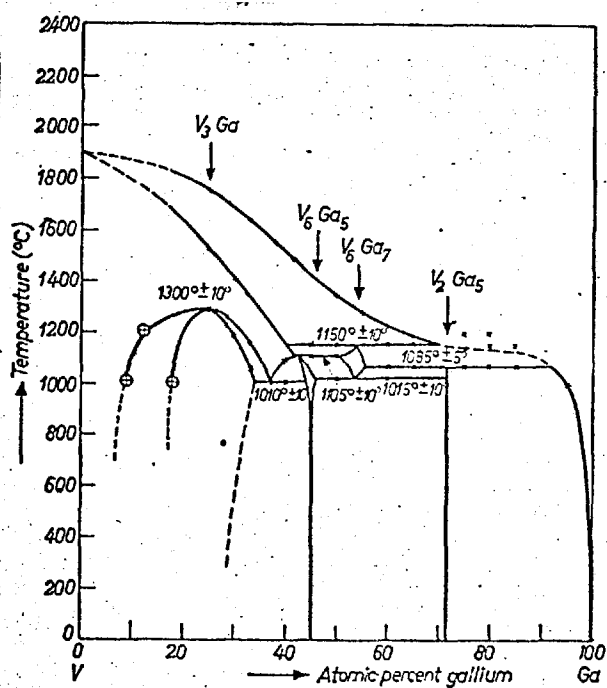


Figure 2.12c.

Equilibrium Diagrams of the V-Ga system as proposed by:-
 (a) Savitskii et al. (1964)
 (b) Van Vucht et al. (1964)
 (c) Sazhin et al. (1968)

Figure 2.12b.



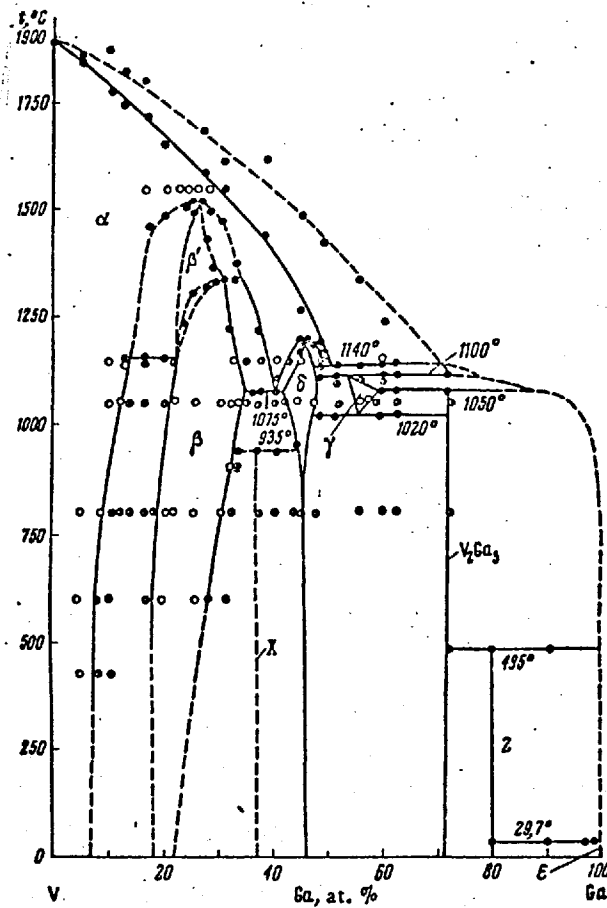


Figure 2.13a. The Equilibrium Diagram of V-Ga as proposed by Savitskii(1967).

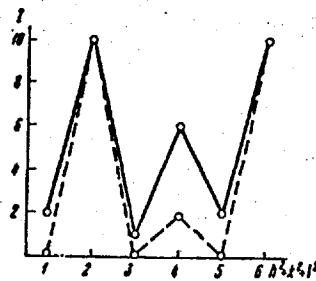


Figure 2.13b. Comparison of the calculated (dotted line) and the measured X-ray powder intensities for the high temperature 'Cs-Cl' phase of V-Ga. (Savitskii et al. 1966)

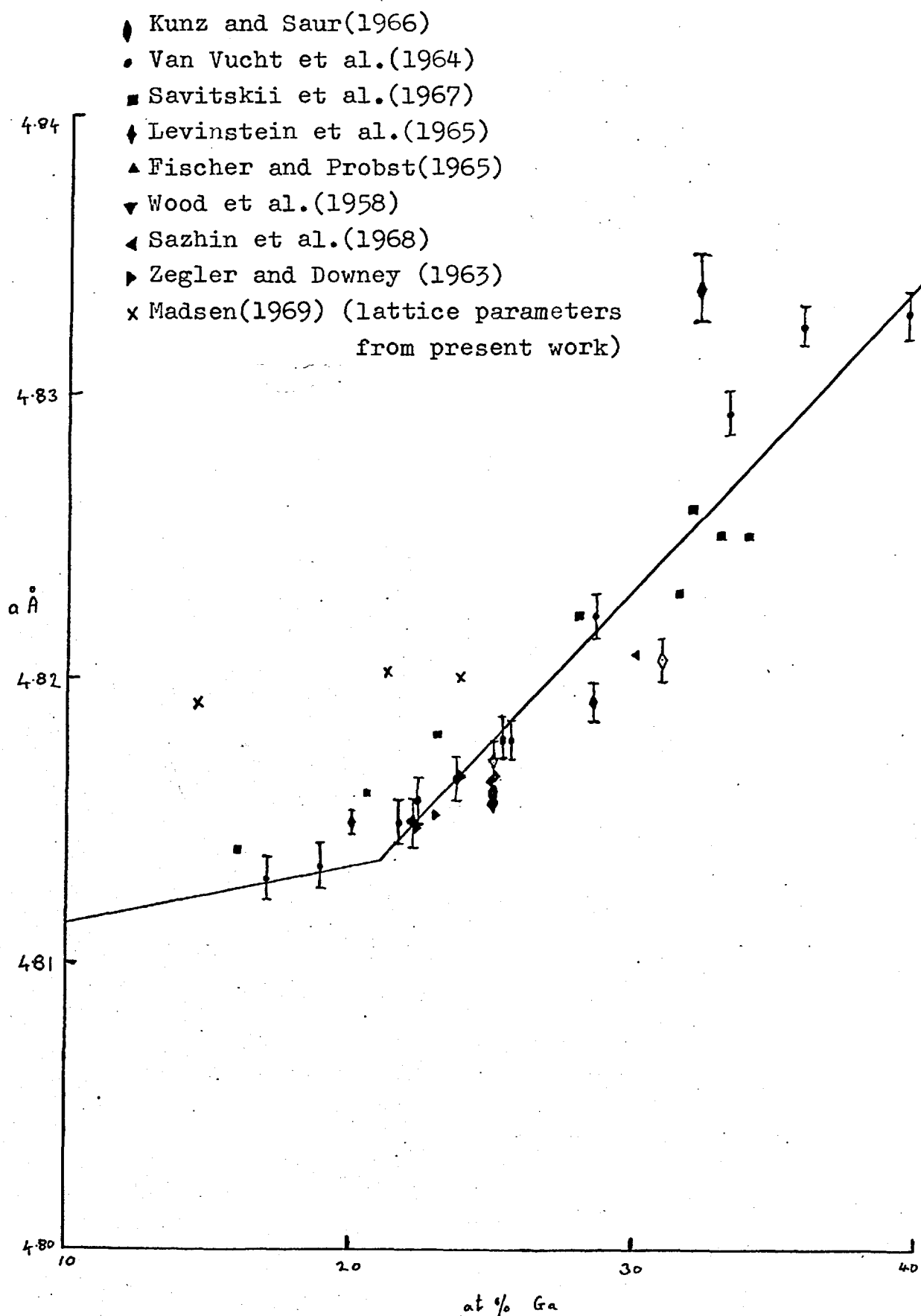


Figure 2.14. The dependence of lattice parameter upon composition in the β -W phase of the V-Ga system, taken from published data.

2.4 Order-disorder Studies

As the β -W compounds exist over a range of composition, two disordering mechanisms can be present, normal atom interchange and vacancy disorder. Only in the stoichiometric alloy can the structure be fully ordered in the Bragg-Williams sense. Van Reuth and Waterstraat (1968, 1969) from density measurements on several systems (not including V-Ga, Nb-Al or Nb-Sn) found that the density of vacancies is low enough for them to be ignored and hence they write the Bragg-Williams order parameter as:

$$S_A = \frac{r_\alpha - F_A}{1 - F_A} \quad (2.1)$$

$$S_B = \frac{r_\beta - F_B}{1 - F_B} \quad (2.2)$$

where r_α is the fraction of A sites occupied by a-atoms
 r_β is the fraction of B sites occupied by b-atoms
 F_A is the fraction of a-atoms in the phase
 F_B is the fraction of b-atoms in the phase.

With this modification, complete disorder leads to order parameters of zero, while at $S = 1$ the alloy will be as ordered as its composition will allow. A single order parameter S is defined such that $S = S_A/K_A = S_B/K_B$. For a non-stoichiometric alloy in its maximum ordered state, either K_A or K_B is equal to unity but not both. Their results are shown in figure 2.15a, with the results of Blaugher et al. (1969). The only result not shown in this figure is that from the latter paper for V_3Si , for which $S = 0.86$. The assumption of no vacancies in the structure is borne out by the good agreement between the densities calculated from the composition, assuming substitution disorder, as opposed to vacancy disorder, and the observed densities. Another feature of these results is that the value of S in the only systems studied over a range of composition, V-Pt and V-Ir, falls off on both sides of stoichiometry.

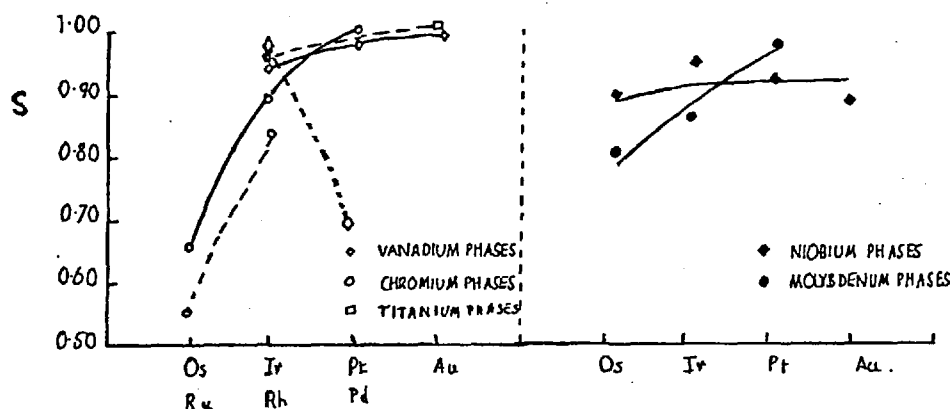


Figure 2.15a. Order in the β -W compounds as a function of the valency of the B atom (in an A_3B compound) (Van Reuth and Waterstraat 1968)

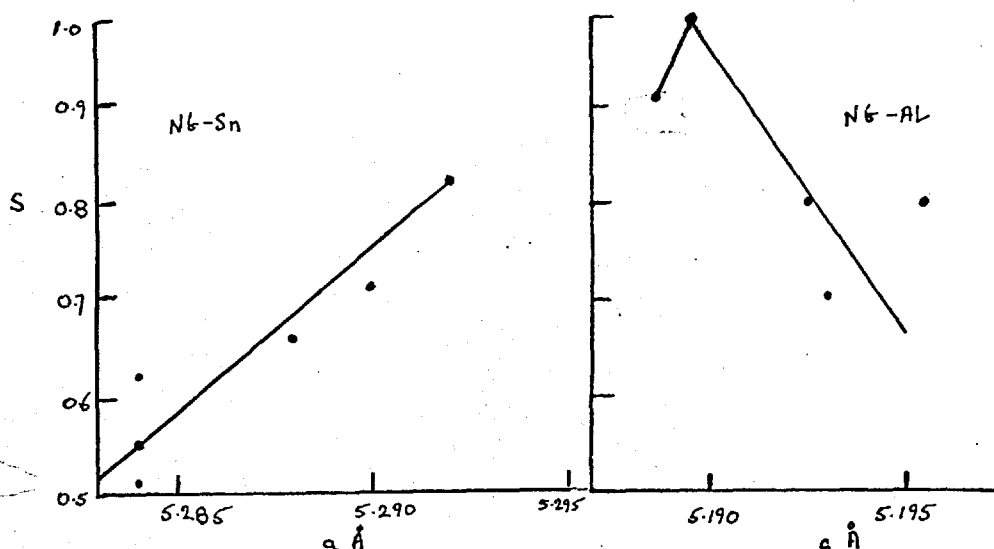


Figure 2.15b. The order parameter S as a function of lattice parameter in the β -W phases of Nb-Sn and Nb-Al. (Bachner and Gatos 1966)

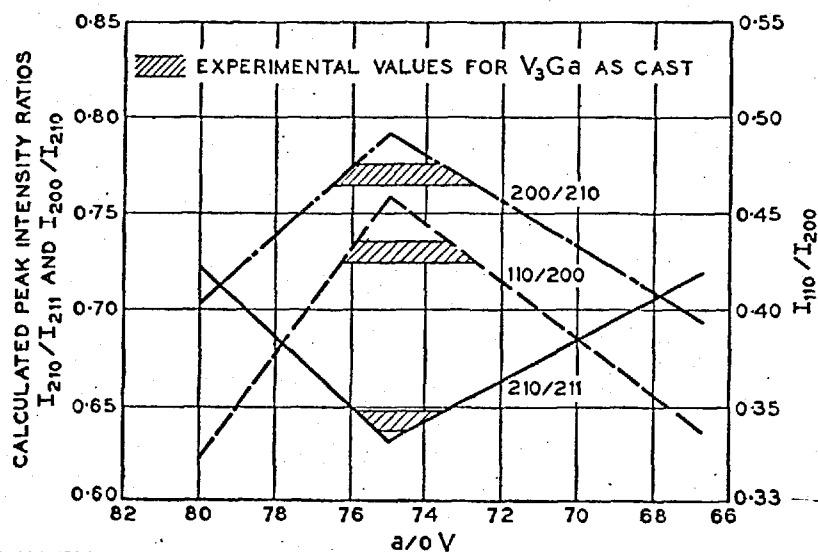


Figure 2.15c. Intensity ratios for V-Ga. The lines show the calculated values and the shaded areas the experimental values. (Levinstein et al. 1965)

Measurements of order in Nb-Sn compacts of various compositions by Enstrom et al. (1962) indicated complete order, but annealing Nb-Sn (25 at % Sn) at 1800° C was found by Reed et al. (1963) to lead to disorder, and also to a low T_C (see section 2.6b).

Vieland (1964) and Ageev and Shamrai (1965) found Nb-Sn sintered compacts and arc-melted samples to be ordered at several compositions. Pfister (1965), however, found a decrease in order with increasing niobium content in vapour deposited samples, consistent with a model where the excess niobium atoms replace tin atoms on the tin sites, but not with a model postulating vacancies in the tin lattice, while Courtney et al. (1965) and Bachner and Gatos (1966) found that with tin degradation and the consequent increase in niobium concentration, vacancies appeared on tin sites and, below a certain tin content, on niobium sites. From consideration of atomic sites the order is calculated in terms of a model assuming purely vacancy disorder (Bachner and Gatos 1966) so that the structure factor becomes:

$$F = X_A f_A (T_A + T_B) + 4X_B f_B T_B + S f_A (T_A/4 - 3T_B/4) \quad (2.3)$$

where X_A and X_B are the fractions of A and B atoms

f_A and f_B are atomic scattering factors of the A and B atoms

$$* \quad T_A = 2[(\cos 2\pi h/4)(\cos 2\pi l/2) + (\cos 2\pi k/4)(\cos 2\pi h/2) + (\cos 2\pi l/4)(\cos 2\pi k/2)]$$

$$T_B = 1 + \cos 2\pi(h/2 + k/2 + l/2)$$

S is the order parameter defined as $S = r_A - w_B$

where r_A and w_B are the fractions of A and B atoms on A sites.

This model will be developed further in chapter five. The results of this paper for Nb-Sn are shown in figure 2.15b, and the corresponding results for Nb-Al are shown in figure 2.15c..

* Note: In Bachner and Gatos (1966) this expression for T_A is incorrect as the square brackets have been omitted.

In the V-Ga system the only measurements of order have been made by Levinstein et al. (1965). They find that the stoichiometric alloy V_3Ga is ordered and they assume that in non-stoichiometric alloys there are no vacancies, the excess atoms going to the sites of the opposite type i.e. for excess Ga atoms, the Ga sites contain only Ga atoms and the V sites contain both V and Ga atoms. These results are given in figure 2.15d. No measurement of atomic ordering in any β -W phase above room temperature has been reported.

2.5 Lattice Softening and the Low Temperature Phase Transformation

Softening at low temperature in the V_3Si lattice was first reported by Testardi et al. (1965) and Testardi and Bateman (1967), in the Nb_3Al and V_3Ga lattices also by Testardi et al. (1967) and in the Nb_3Sn lattice by Keller and Hanak (1966, 1967), Testardi et al. (1967) and Rehwald (1968). The results of these papers are shown in figures 2.16 and 2.17a. The main feature of all the plots of $(c_{11} - c_{12})$, the stiffness parameter or shear modulus and of the velocity of sound, against temperature for V-Ga, V-Sn, Nb-Sn and Nb-Al is the drop at low temperatures, which implies lattice instability. In V_3Ge (also of the β -W structure) by comparison, there is a rise in both the shear modulus and the velocity of sound as can be seen in figures 2.17a and 2.17b.

At about the same time Batterman and Barrett (1964, 1965) reported a phase transformation in V_3Si to a tetragonal form with $c/a = 1.0024$ at about $20^\circ K$ and later Mailfert et al. (1962) observed the transformation in Nb_3Sn the tetragonality being of the opposite sign ($c/a = 0.9964$). Both these measurements of the transformation used Berg-Barrett topographs of single crystals and these crystals were grown by an HCl transport technique (Hanak 1963). These same crystals or similarly grown ones were those used for the lattice softening measurements of Rehwald (1968), Keller and Hanak (1965, 1966) while those

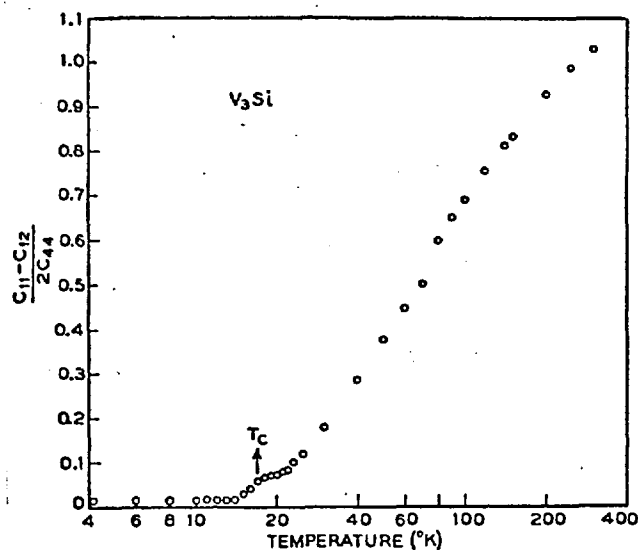


Figure 2.16a. The temperature dependence of the shear modulus in V_3Si . (Testardi et al. 1965)

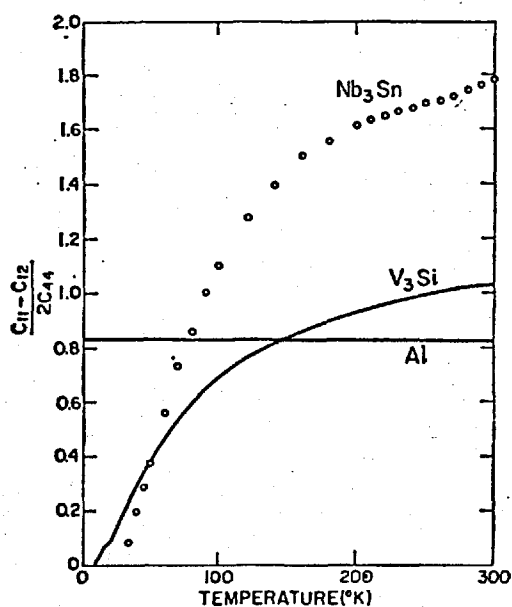


Figure 2.16b. The temperature dependence of the shear modulus for Nb_3Sn , V_3Si and Al . (Keller and Hanak 1967)

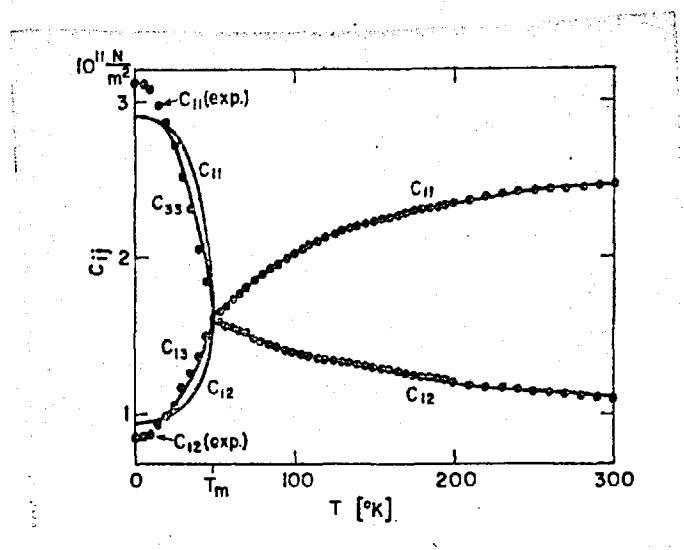


Figure 2.16c The elastic moduli c_{11} and c_{12} and the bulk modulus B as a function of temperature for Nb_3Sn . (Rehwald 1968)

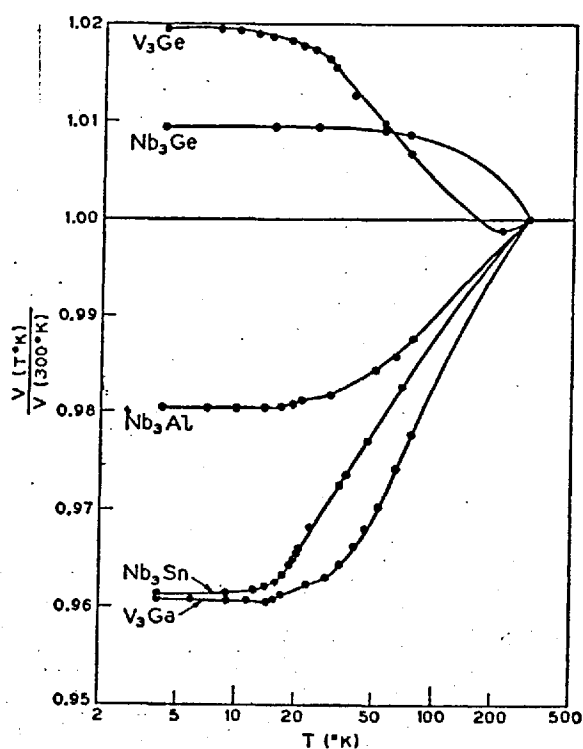


Figure 2.17a The temperature dependences of the sound velocities in β -W compounds. (Testardi et al. 1967)

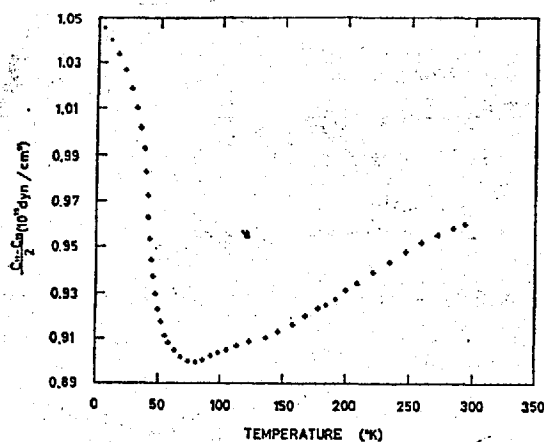


Figure 2.17b. The temperature dependence of the shear modulus in V_3Ge . (Rosen et al. 1969)

of Testardi and co-workers were grown by the zone refinement technique of Greiner and Mason (1964). Gorringer and Valdré (1965, 1966), using crystals supplied by Batterman, observed the transformation using an electron microscope.

King and Pollock (1967), however, could not observe the transformation optically in V_3Si , while apparently observing one by X-ray diffraction on a powdered sample (though see section 4.4), and, indeed, Batterman and Barrett (1965) found that not all single crystals cut from the same bar transformed. In Nb_3Sn , however, both Mailfert et al. (1967) and King et al. (1967) found heat treatment to be necessary to drive off either excess tin or hydrogen before a transformation could be observed. That the amount of lattice softening also varies from sample to sample can be seen in the results of Vance and Finlayson (1968) and Testardi and Bateman (1967) (figure 2.18 a & b). The results of Bonnerot et al. (1969) for the specific heat also of V-Si also show a compositional variation (figure 2.18c). King (1968) has investigated the dependence of the transformation on composition in Nb-Sn and produced the phase diagram in figure 2.19. The changes in Young's modulus with temperature measured by Finlayson (1968) replotted as a function of lattice parameter in figure 2.20, indicate that a similar diagram may exist for V-Si. Figure 2.20 also shows Finlayson's results for the effect of a magnetic field on lattice softening.

Testardi et al. (1970) report that (from a stoichiometric melt) the first samples to freeze have low resistance ratios and little second phase and are unlikely to transform. Subsequent regions to freeze show an increasing resistance ratio, and amount of second phase and become more likely to exhibit a structural transformation at $T_m \approx 17^\circ K$. The last to freeze have the largest resistance ratio, the greatest amount of second phase and almost certainly transform at $T_m \approx 22^\circ K$. This may imply

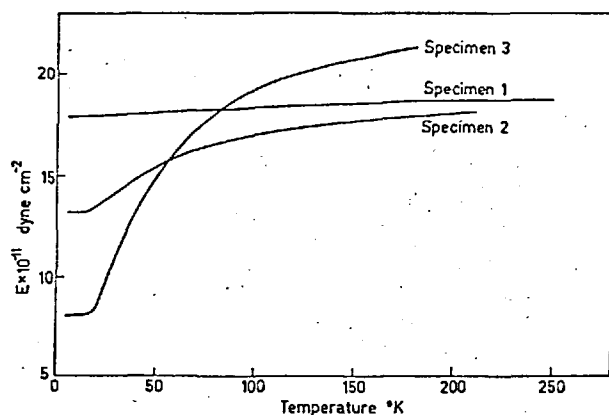


Figure 2.18a. The temperature dependence of Young's modulus for three different V-Si samples. (Vance and Finlayson 1968)

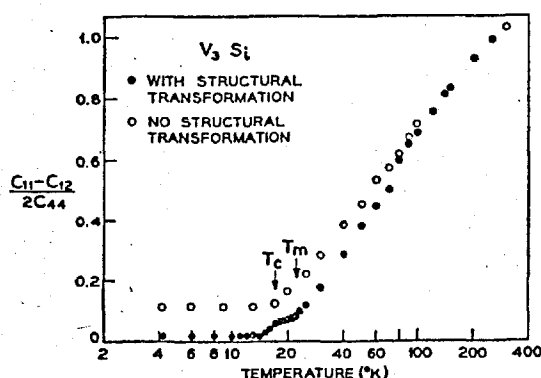


Figure 2.18b. The temperature dependence of the shear modulus of a V-Si sample with and one without a structural transformation. (Testardi and Bateman 1967)

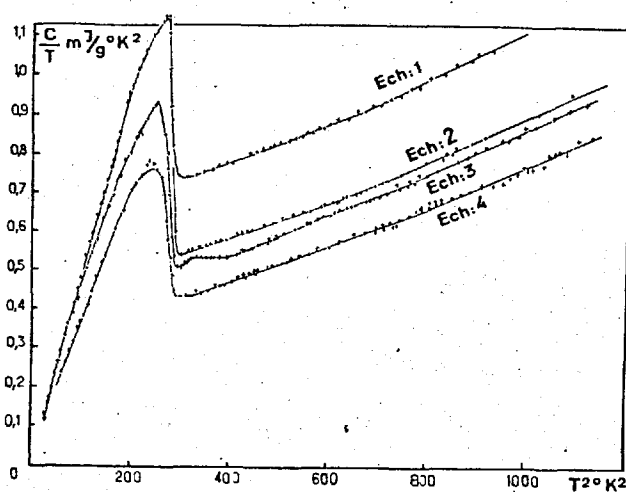


Figure 2.18c. The variation of the ratio of specific heat to temperature as a function of temperature squared. (Bonnerot et al. 1969)

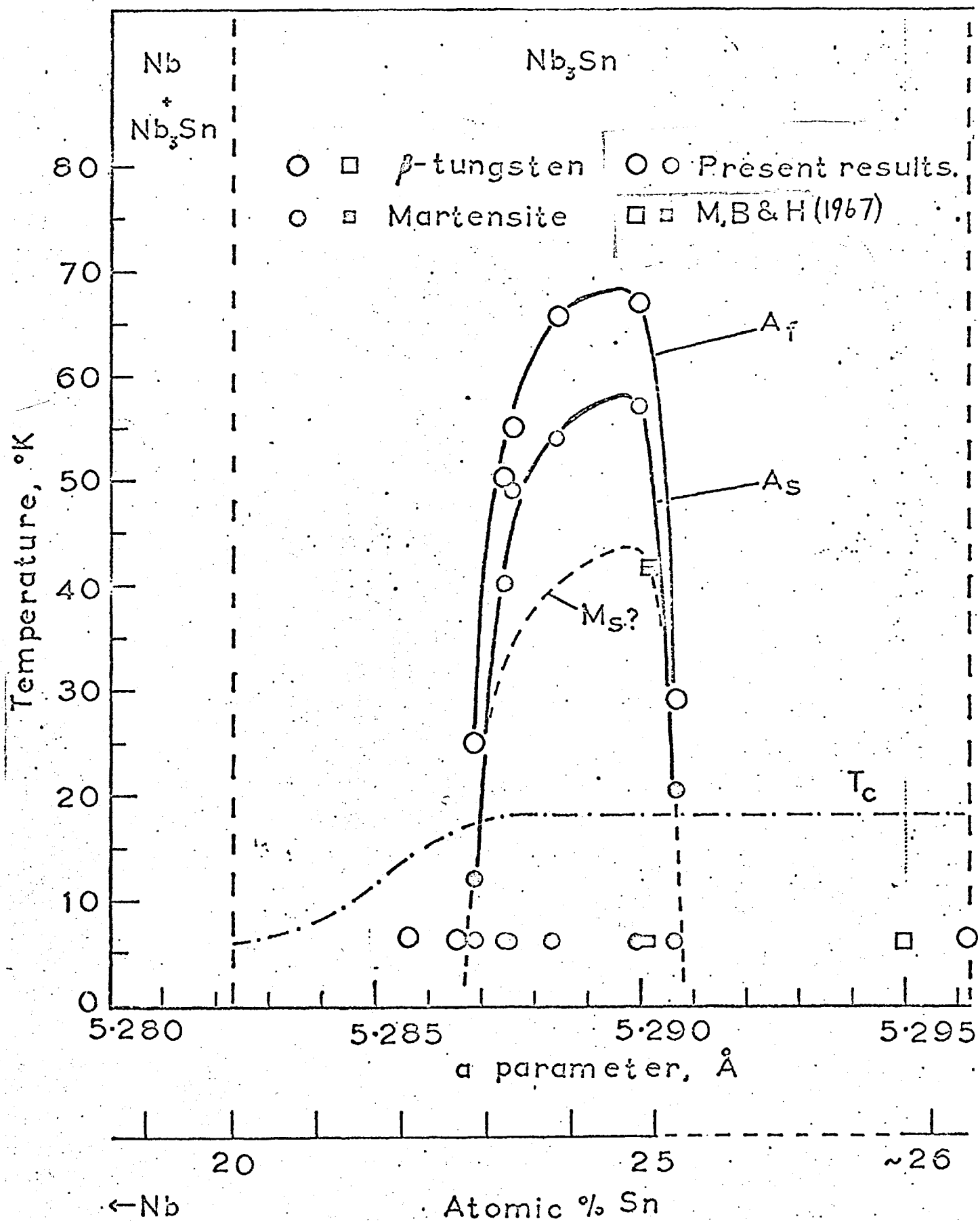


Figure 2.19. The low temperature phase diagram of Nb-Sn.
(King 1968)

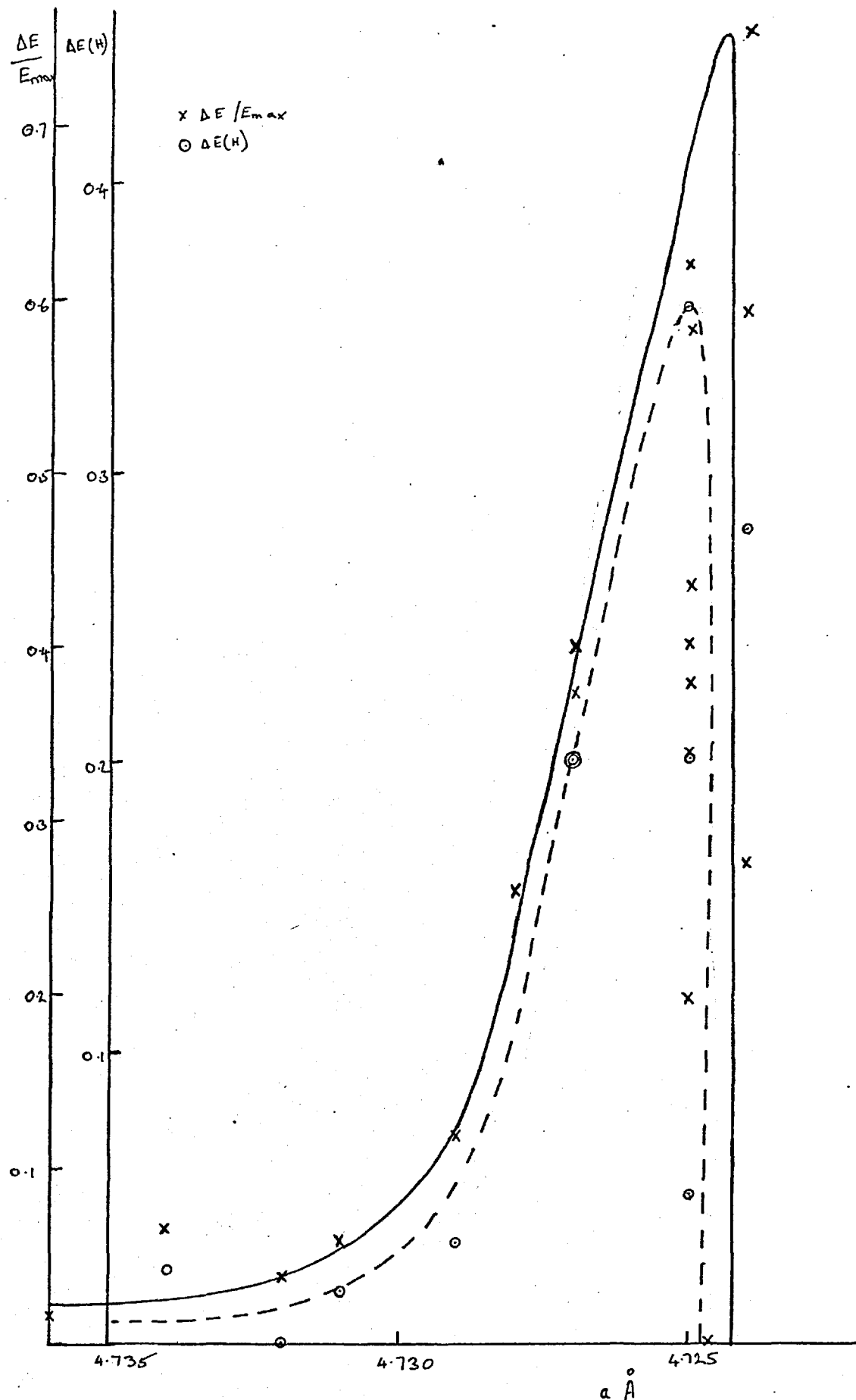


Figure 2.201 The variation in the lattice softening $\Delta E/E_{\max}$ as a function of lattice parameter in V-Si. Also shown is the increase in lattice softening on applying a magnetic field of 50 kG, $\Delta E(H)$. (Finlayson 1968)

a slight change in composition between the first and last crystals or the amount of second phase may be important in controlling the transformation.

The phase transformation has been observed in the V-Si and Nb-Sn by other methods also. Indeed the measurements of Shull (1964) using neutron diffraction were the first indications of a transformation. Patel and Batterman (1966) measured the lattice softening directly and concluded that a stress along the [100] direction, if large enough, could suppress the transformation completely. The temperature of the transformation is, however, unaltered by stress. The specific heat measurement of Kunzler et al. (1966) confirm this, while the extent of the specific heat anomaly decreases with stress (figure 2.21 a and b).

The thermodynamic order of the transformation has been the subject of much debate. Mailfert et al. (1967) observed no volume change at the transformation and implied that the phase change was of the second order. King et al. (1967), however, observed a 0.28% increase in volume in the tetragonal state and concluded that the change was first order, in support of the theories of Labbe and Friedel (1967) and Cohen et al. (1967), (see sections 2.7b and 2.7c). A recent paper by Vieland et al. (1971), moreover, confirms that the transformation in Nb_3Sn is first order, from measurements both of sound-velocity and by X-ray diffraction. Vieland et al. (1971) also show that the transformation takes place over a narrow temperature range with a spontaneous tetragonality at the transition (figure 2.22a), and that the shear modulus does not actually go to zero at the transformation temperature (figure 2.22b). Vieland (1971) has also measured the Debye-Waller factor of Nb_3Sn using X-ray methods and finds a certain disagreement with the values found by Shier and Taylor (1968) using the Mossbauer effect (figure 2.22c). A further anomaly was pointed out by Vieland and Wicklund (1968), in that specific heat measurements at the transformation indicate the transition to be second order, and

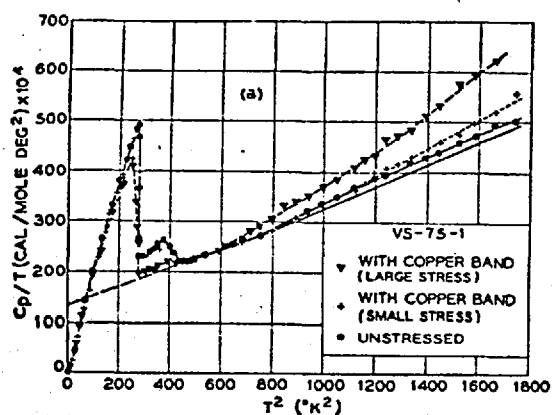


Figure 2.21a.

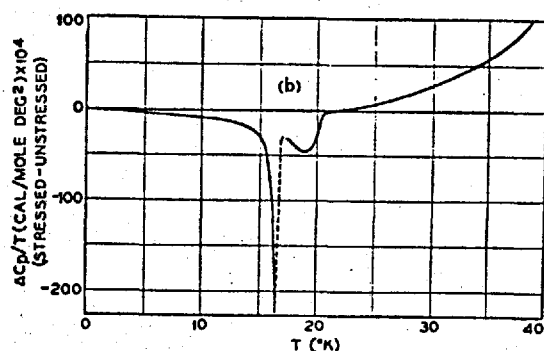


Figure 2.21b.

Figure 2.21a shows the differences in the specific heat curve with different stresses applied to a V_3Si crystal. Figure 2.21b shows the difference between the specific heats in the stressed and the unstressed states. (Kunzler et al. 1966)

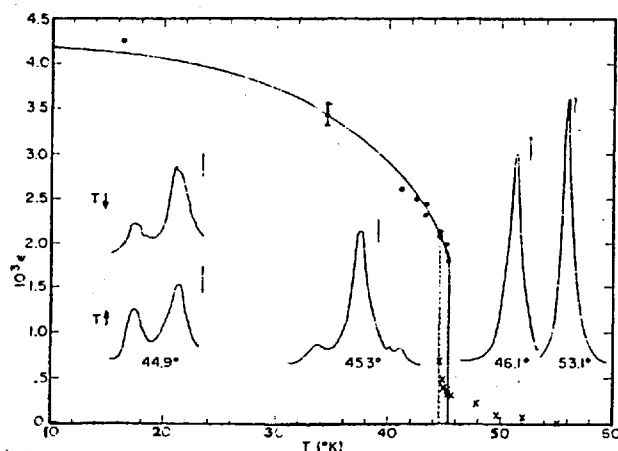


Figure 2.22a. The tetragonality of the Nb-Sn martensitic phase as a function of temperature. Also shown are the X-ray diffraction profiles of the 14,0,0 peak. (Vieland et al. 1971)

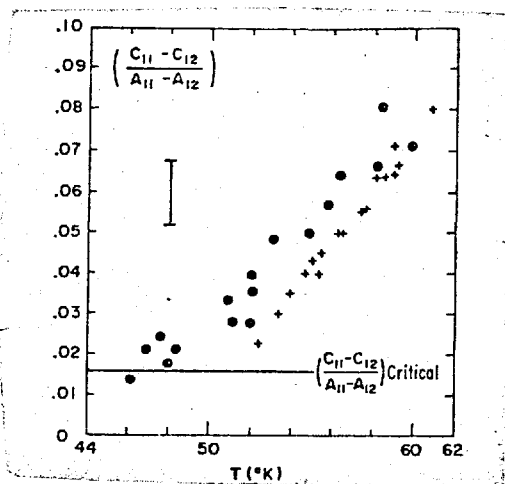


Figure 2.22b. The shear modulus as a function of temperature for Nb-Sn. The horizontal line represents the minimum value of the soft mode at the transition. (Vieland et al. 1971)

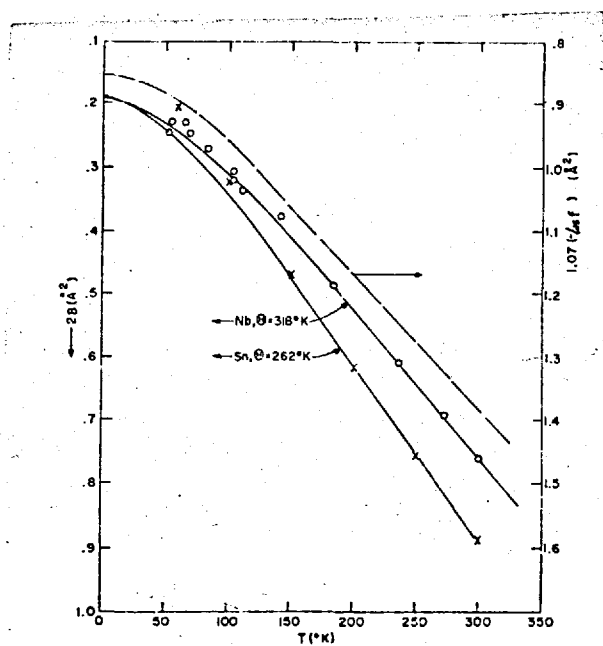


Figure 2.22c. The Debye-Waller factor $2B$ as a function of temperature. The solid lines are the theoretical B-T relationships, the dashed line the results of Shier and Taylor (1968). The circles are B_{Nb} and the crosses B_{Sn} . (Vieland 1971)

that the X-ray, acoustic and direct specific heat measurements appeared to be irreconcilable within the available theoretical framework. Rothwarf (1970) may provide an explanation of these anomalies. He suggests that in the transition metals the electron-electron interaction involved in both superconductivity and the structural transition is the result of acoustic plasmons, rather than, or as well as, phonons. These acoustic plasmons, suggested by Fröhlich (1968) are collective modes of the screened inner-band electrons. According to this theory, (considered in more detail in section 2.8) the different methods of measuring the physical properties will lead to different results because what is being measured is different for each method.

A transformation has been reported in V-Ga by Nembach et al. (1970). This was in a thin film electron microscope specimen, the β -W phase being formed by interdiffusion of Ga and V. The temperature of the transformation was about 50°K but the composition of the β -W phase was unknown. No bulk transformation of V-Ga has been reported in the literature and Gossard (1966) reports the absence of distortion of the n.m.r. spectrum for V-Ga. Similarly in the Nb-Al system no transformation has been observed and Willens et al. (1969) report that they did not observe a transformation. Their sample, however, is referred to simply as Nb_3Al , with no composition, or room temperature lattice parameter to characterise the composition, reported and thus it cannot be inferred from this result that there is no transformation in the Nb-Al system. Certainly lattice softening has been reported in both V-Ga and Nb-Al systems by Testardi et al. (1967a) as can be seen in figure 2.17a.

2.6 Superconducting Properties

2.6a Introduction

When Nb_3Sn was shown by Matthias et al. (1954) to have a critical temperature of 18.05°K , this was the start of work on the superconducting properties of the β -W structure compounds. The subsequent discovery by Kunzler et al. (1961) that the phase also carried a high critical current indicated that Nb_3Sn could be of use for manufacturing high field superconducting magnets. The properties of other compounds with the same structure were also measured and it was realised that it was the structure which gave rise to these exceptional properties. Indeed, Geballe et al. (1967) found that a ternary alloy $\text{Nb}_3(\text{Al-Ge})$ had a T_c of 20.05°K .

2.6b Critical Temperature

It was shown by Hanak et al. (1964) that the critical temperature of the Nb-Sn β -W phase was a function of composition and subsequent papers by Bode et al. (1964, 1967) for example, having confirmed this. A plot of transition temperature against composition (or lattice parameter, the relation between the two taken from figure 2.8a) is given in figure 2.23a.

The critical temperature in the other 3 systems under consideration, Nb-Al, V-Ga and V-Si, has been shown to be a function of composition by various authors, and the results plotted as for Nb-Sn are shown in figures 2.23b, 2.24a and b respectively. There are also results available for the dependence of critical temperature on formation temperature, annealing temperature and annealing time and it is clear that there are other ways of plotting composition dependence. It has been suggested that atomic order also has an effect on the critical temperature (e.g. Hanak et al. 1962, Reed et al. 1963), but the results of Bachner and Gatos (1966) indicate that it is difficult to separate effects of non-stoichiometry from those of disorder. Indeed the dependence on composition may be partly a result of the two sorts of disorder described in section 2.4.

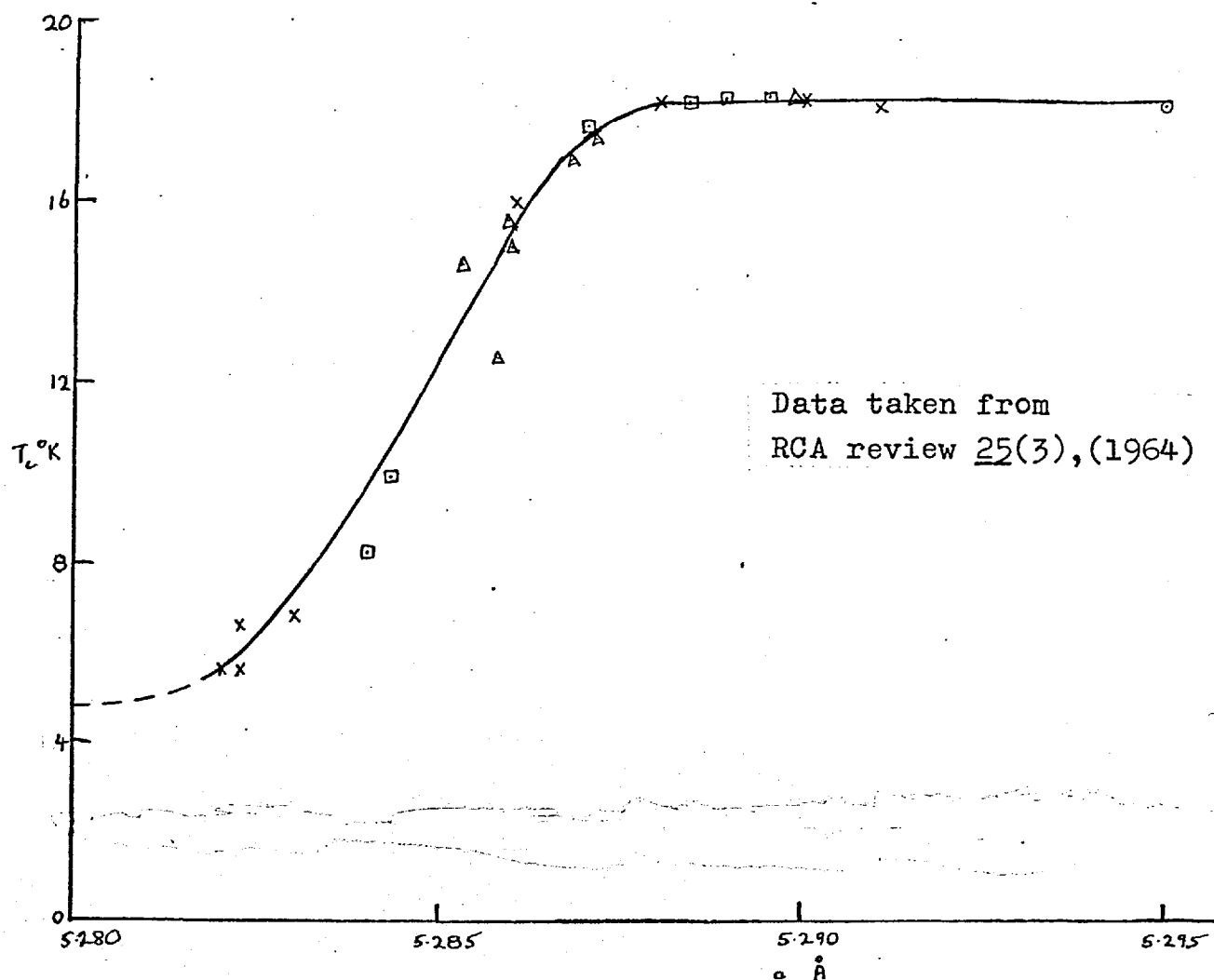


Figure 2.23a. The dependence of the critical temperature of Nb-Sn upon lattice parameter.

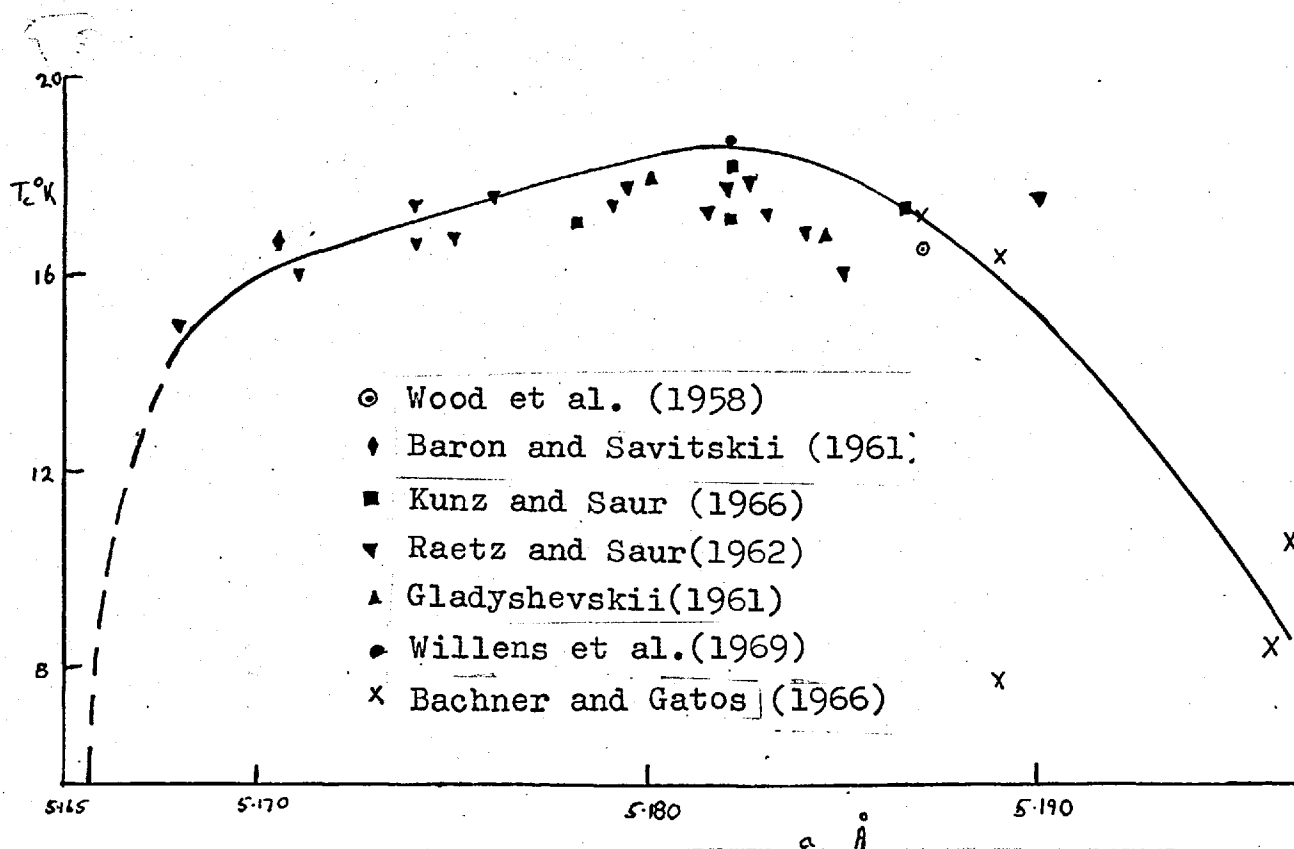


Figure 2.23b. The dependence of the critical temperature of Nb-Al upon lattice parameter.

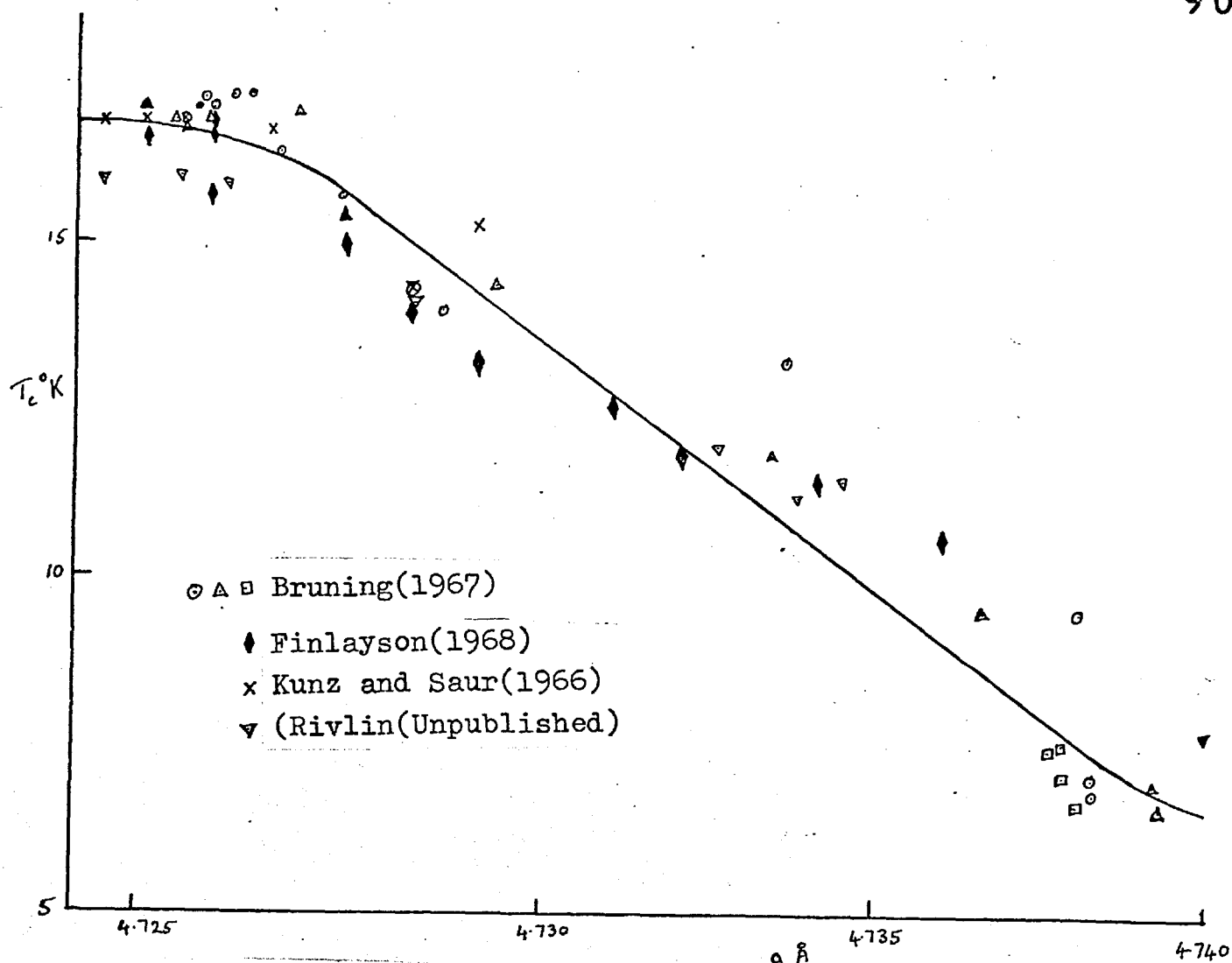


Figure 2.24a. The dependence of the critical temperature of V-Si upon lattice parameter.

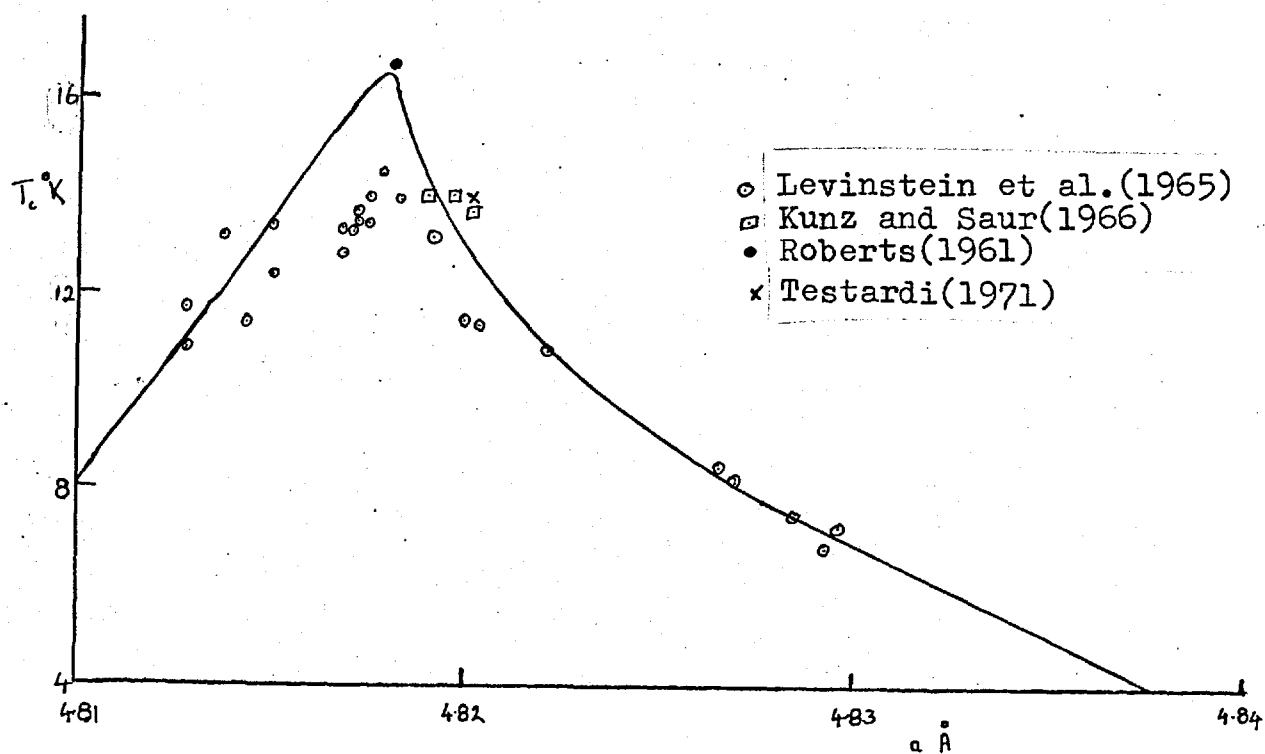


Figure 2.24b. The dependence of the critical temperature of V-Ga upon lattice parameter.

The B.C.S. equation (equation 1.71) gives T_c as:

$$T_c = 1.14 \theta_D \exp (-1/N(0)V) \quad (2.4)$$

A change in composition will, therefore, affect all the parameters θ_D , $N(0)$ and V , apart from affecting the degree of order and there has been much discussion as to the relative importance of the electronic and phonon band widths. This will be discussed in more detail in sections 2.8 and 2.9 when the band structure of the β -W compounds is discussed.

2.6c Critical Field and Critical Current

The upper critical field H_{c2} and the critical current J_c in type II superconductors are very structure sensitive and the work of Hanak and Enstrom (1966) indicates that grain boundaries act as pinning centres. An increase in J_c has also been observed after the irradiation of Nb_3Sn (Cullen and Novak 1966) and Hart et al. (1969) show a direct relationship between the oxygen content and the critical current density (figure 2.25a).

A good measure of the pinning force is the magnetic hysteresis or remanent flux of a sample and the measurements of Potapov (1967, 1969) in Nb-Sn and Finlayson (1968) in V-Si show that these factors are composition dependent (figures 2.25b and 2.25c). Potapov attributes the variation to the variation of grain boundary area with composition and Finlayson to the amount of second phase in the β -W structure matrix. The lower critical field H_{c1} is also a function of pinning because of its dependence on κ (see section 1.3). which is structure sensitive and the results of Meyer (1968) show a variation in H_{c1} with composition (figure 2.26a), another indication of the variation of the pinning force with composition. The reason for this composition

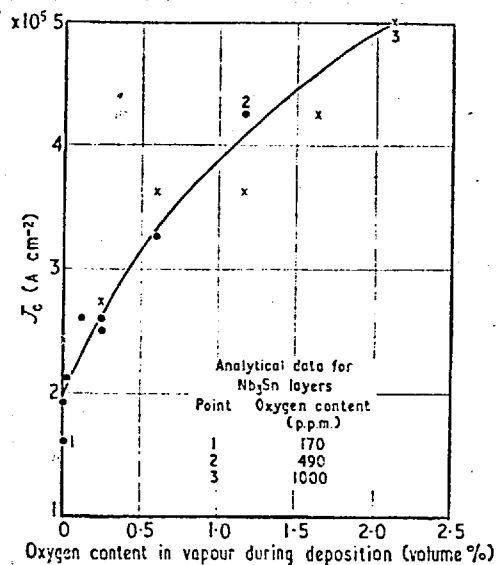


Figure 2.25a. Critical current density J_c as a function of oxygen content in Nb₃Sn at 46 kG and 4.2°K. (Hart et al. 1969)

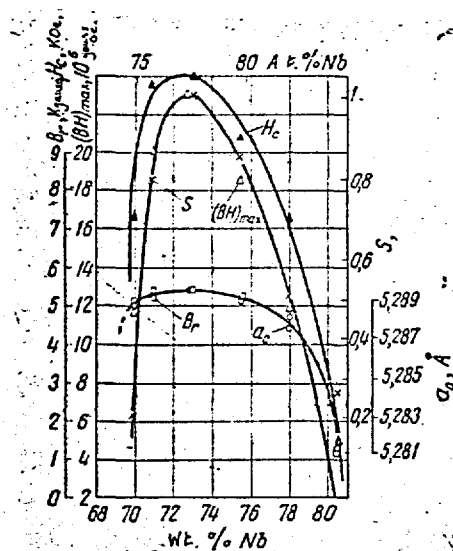


Figure 2.25b. The variations on remanent flux B_r , hysteresis BH_{max} , area of grain boundaries S and lattice parameter a_0 as functions of composition in Nb-Sn. (Potapov 1969)

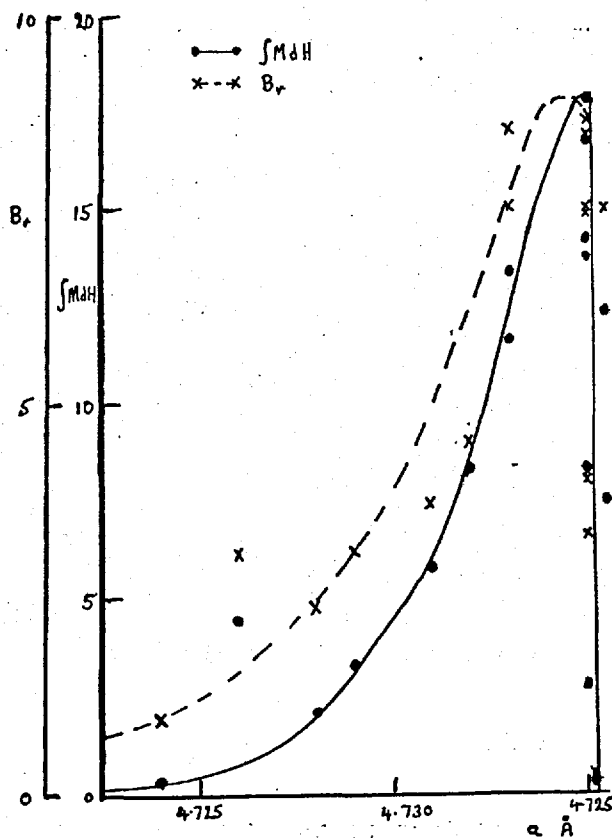


Figure 2.25c. The variations in remanent flux B_r and magnetic hysteresis $\int MdH$ with lattice parameter in V-Si. (Finlayson 1968)

dependence is not clear and a high concentration of pinning centres in a sample does not necessarily indicate that a phase transformation has taken place in the sample, though the results of Livingston (1966) on In-Tl alloys (figure 2.26b) show that cubic-tetragonal phase boundaries can act as strong pinning centres.

Measurements of the magnetisation curves of V-Ga and Nb-Al have been made by Foner et al. (1970) and their results are in figure 2.26c. It is clear from the two curves for V-Ga that this system also has the composition dependence of the magnetic properties and the values of Levinstein et al. (1965) (figure 2.26d) show this clearly. Also shown in figure 2.26c are the authors' measurements on $\text{Nb}_{79}(\text{Al}_{73}\text{Ge}_{27})_{21}$ and the high value of H_{c2} observed for this alloy may indicate pinning at phase or grain boundaries or both, for Howlett (1969) has reported that the ternary alloys tend to be multiphase, with more than one phase of the β -W structure, all with slightly differing compositions. The high values of critical current and field for the ternary alloys have also been observed by Yasukochi et al. (1970).

2.7 The Electronic Structure

2.7a Early Approaches

To explain the strong temperature dependence of the electronic susceptibility, the large electronic specific heat in V_3X compounds and Knight shift measurements Clogston and Jaccarino (1961) suggested a one-electron model in which the density of states $\rho(E)$ has a sharp maximum on, or near, the Fermi level. Weger (1964) developed this model and suggested that the density of states is essentially one-dimensional. The 3d states of the V atom electrons, forming, if the tight-binding approximation is used, three degenerate bands, such that the Fermi surface appears as illustrated in

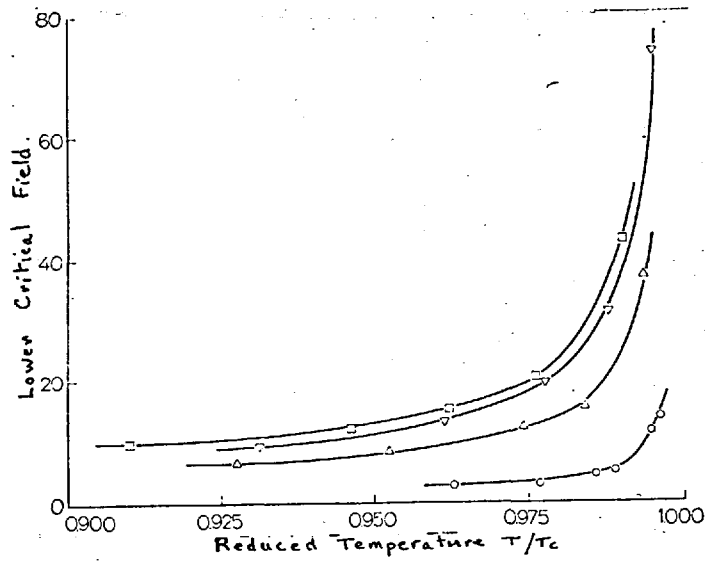


Figure 2.26a. The variation in the lower critical field with temperature for four different specimens. (Meyer 1968)

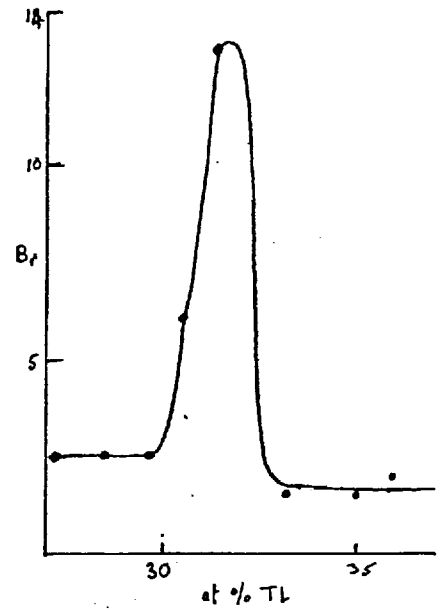


Figure 2.26b. The variation in remanent flux as a function of composition in In-Tl. (Livingston 1966)

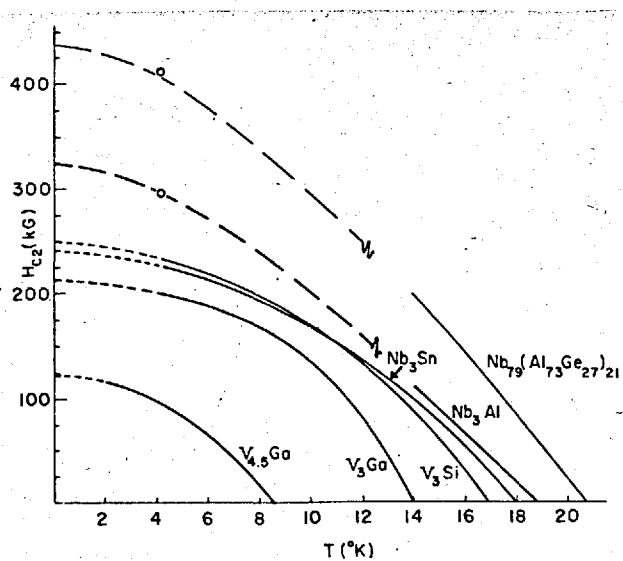


Figure 2.26c. The variation of upper critical field as a function of temperature in different β -W compounds. (Foner et al. 1970)

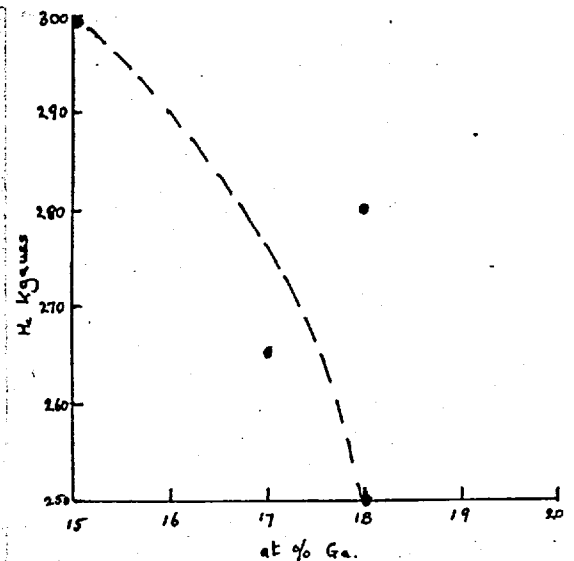


Figure 2.26d. The variation in critical field as a function of composition in V-Ga. (Levinstein et al. 1965)

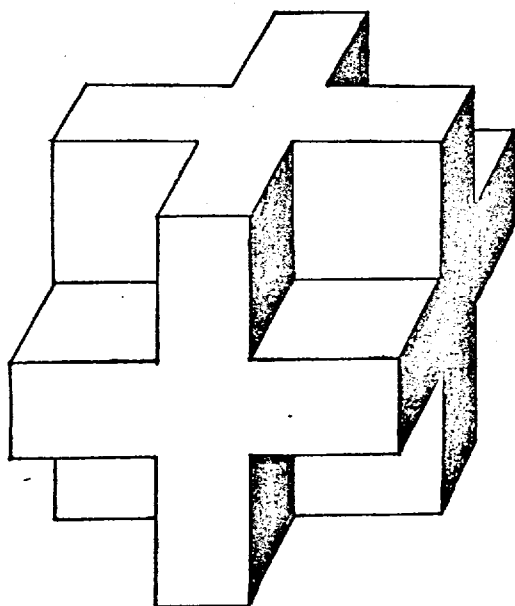


Figure 2.27a. The Fermi surface of the 3d electrons in V_3Si . (Weger 1964)

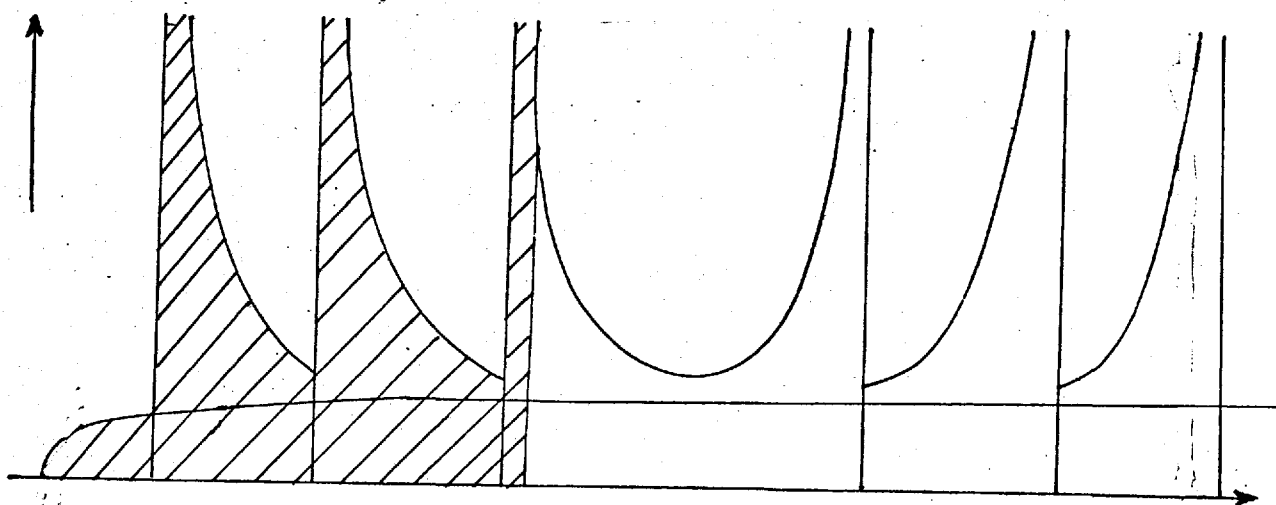


Figure 2.27b. The density of states of the compounds with the β -W structure. (Labbe and Friedel 1966)

figure 2.27a. This one-dimensional model has been taken and used to develop two similar theories by Labbé, Friedel and Barišić, and Cody, Cullen and Halloran. These will be considered in the following sections.

2.7b The Labbé-Friedel-Barišić Model

The basis of this theory is given by Labbé (1968) and Labbé and Friedel (1966). Because the atoms in the $\langle 100 \rangle$ chains are so close, the nearest-neighbour interactions are much stronger than any others, and the chains can be considered separately. There are thus three degenerate 3d bands. These, however, split into three sub-bands as a result of the crystal field, a kind of Jahn-Teller effect. The resultant density of states appears as illustrated in figure 2.27b. The specific heat measurement of Morin and Maita (1963) and the Knight shift measurements of Clogston (1964) indicate that the Fermi level must lie at one of the peaks.

On the basis of this model many of the low temperature properties have been calculated. By expanding the free energy as a power series in temperature, Labbé and Friedel (1966) calculated the distortion in the tetragonal state and the temperature of the phase transformation. Labbé (1968) deduced from this the relationships between the shear modulus $M = \frac{1}{2}(C_{11} - C_{12})$, the temperature at which it goes to zero T_m and Q the number of electrons (or holes) per vanadium (or niobium) atom in the sub-band. These relationships are illustrated in figure 2.28. There is qualitative agreement between the dependence of T_m on Q for Nb_3Sn in figure 2.28b and the compositional dependence of the martensitic transformation found by King (1968) (figure 2.19). Labbé also shows that the transformation must take place in the normal state as the distribution function in the superconducting state is no longer the Fermi function. The values of T_c given in figure 2.28.

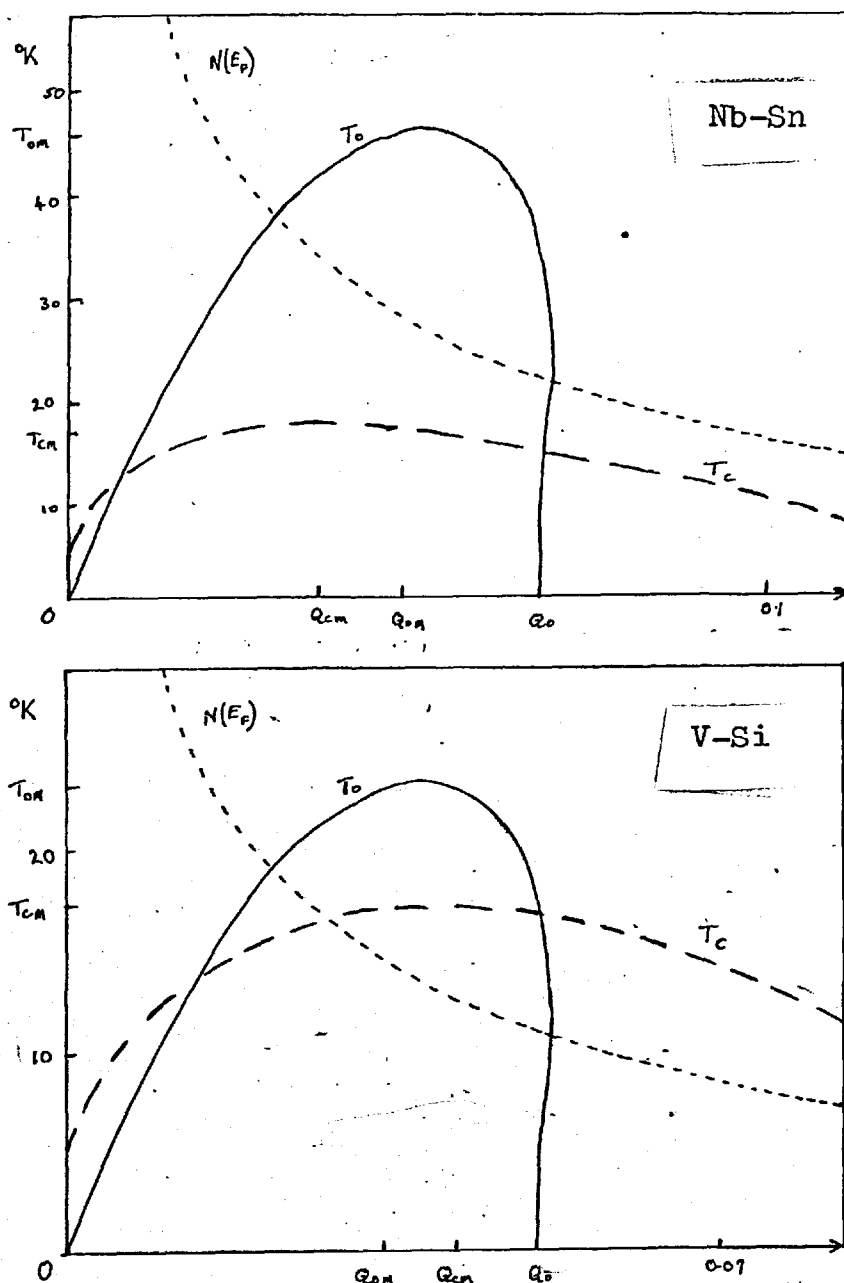


Figure 2.28a. The dependence of T_m and T_c on the small number Q of electrons in the d sub-band in V-Si and Nb-Sn. (Labbé 1967)

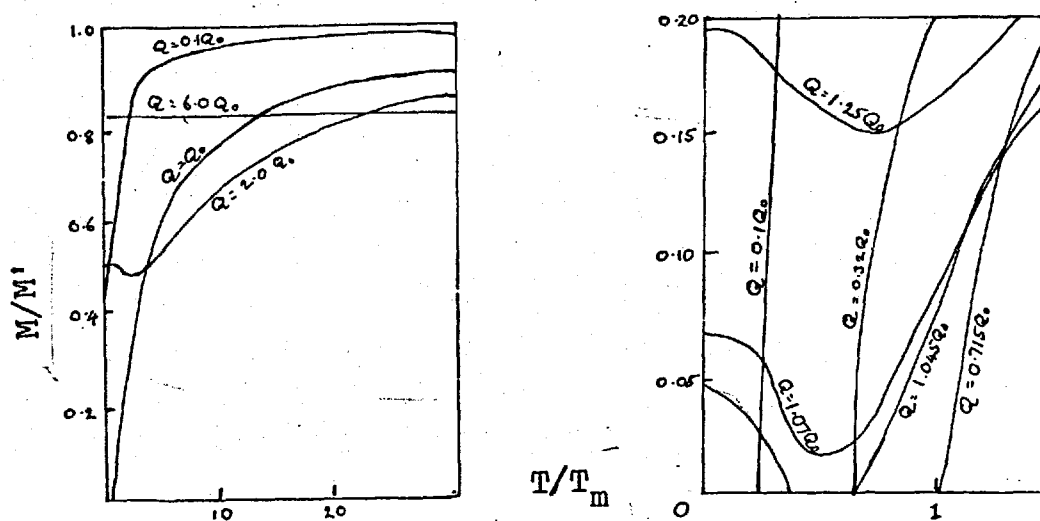


Figure 2.28b. The variation of the shear modulus $M=(c_{11}-c_{12})/2$ as a function of temperature for various values of Q . M' is a lattice contribution. (Labbé 1967)

are those calculated by Labbe et al. (1967), where they assumed that the lack of isotope effect observed in Nb_3Sn (Garland 1963) implied that the narrow range of the electronic spectrum imposes the energy-range limitation in the electron pairing interaction. This is the opposite of the more usual situation where the narrowness of the phonon spectrum produces the limitation (see section 1.4c).

The paramagnetic susceptibility in the normal state and the Knight shift in the cubic and tetragonal phases have also been calculated using this model (Labbe 1967) and the agreement with the results of Clogston et al. (1964, 1962) and Gossard (1966) is reasonable.

2.7c The Cohen-Cody Model

The model of Cohen et al. (1967) takes the sub-band structure but emphasises the aspect of the sharp drop in the density of states near the Fermi level. The position of the Fermi level is found by equating the total number of occupied states at temperature T to that at $T = 0^\circ \text{K}$. The temperature dependence of C_n , $C_n - C_{n_0}$, the electronic susceptibility and the resistivity are calculated in terms of the motion of the Fermi level at the sharp drop in the density of states. The agreement with the experimental data of Woodward and Cody (1964), Keller and Hanak (1967) and Clogston et al. (1964b; 1962) is good (figure 2.29 a-c).

In a further paper (Cody et al. 1968), the tetragonal distortion and the specific heat as functions of T/T_m are calculated, the correspondence with the experimental data of Mailfert et al. (1967) and the authors own work being good (figure 2.29d).

The theory, as that of Labbe et al. predicts a first order phase transformation, while Anderson and Blount (1965) and Birman (1966) suggest that the transition may be second order, arising from a change in internal symmetry, similar to the appearance of a polar axis in a ferro-electric e.g. in BaTiO_3 (Guttman 1950).

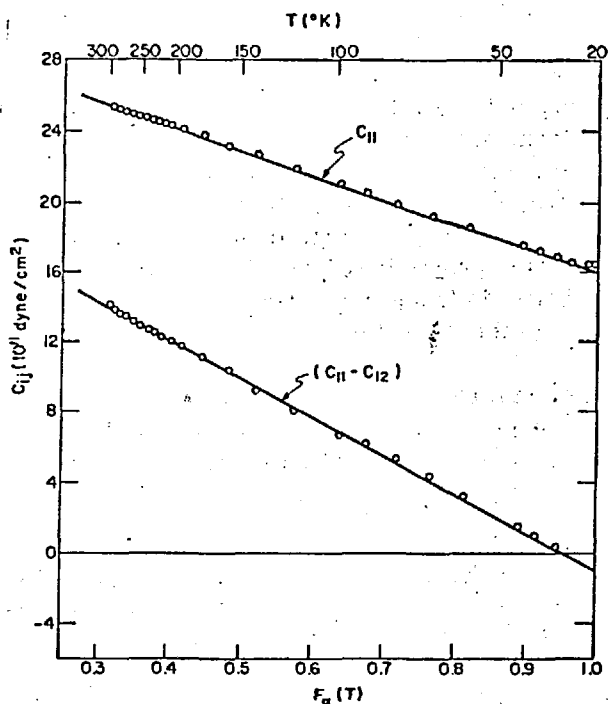


Figure 2.29a.

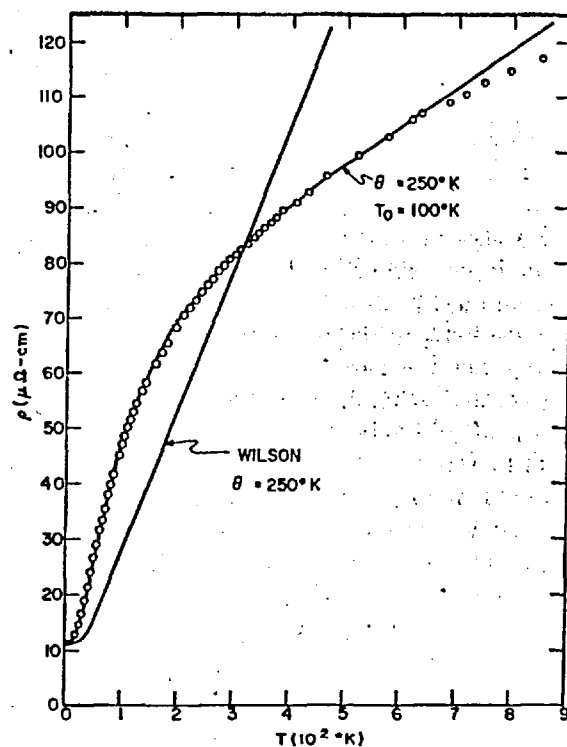


Figure 2.29b

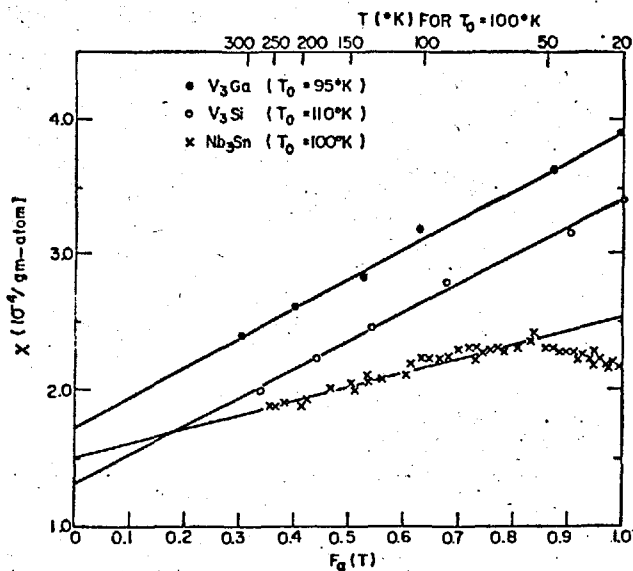


Figure 2.29c

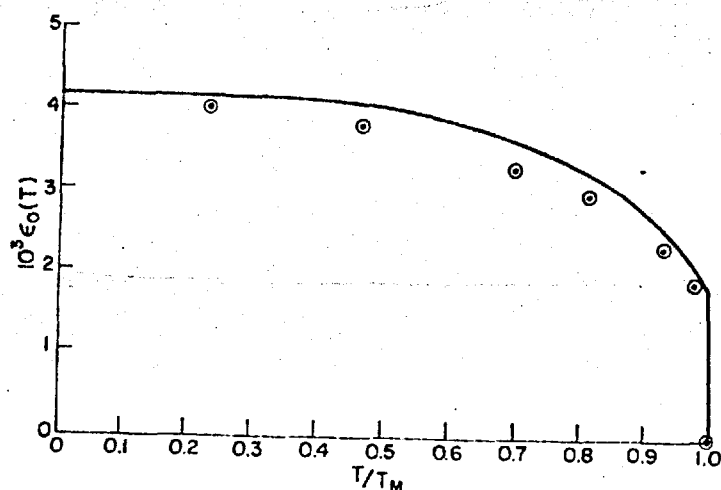


Figure 2.29d.

Comparisons of the predictions of the electronic properties of the β -W materials from the theory of Cohen et al. (1967)

- (a) elastic constants
- (b) resistivity
- (c) susceptibility
- (d) tetragonal strain in the martensite as functions of temperature.

The experimental evidence seems to show that the transformation is first order but with a much smaller latent heat than that predicted by either theory (Vieland and Wicklund 1969).

A similar band structure is derived by Mattheis (1965) using the augmented plane wave method, but this method is not very suitable for the β -W structure as it assumes that the electronic distribution at the atom has radial symmetry, which is not the case in this structure, which is highly anisotropic. One point that does appear from these calculations is that the band structure is changed very little by changing the B atom (in an $A_3 B$ alloy).

2.7d Further Developments of the Band Structure

Kats (1969) accepts the Labbé density of states and uses the small number of electrons in the d-band as the important factor in a Green's function method to derive similar qualitative results to Labbé et al. for T_C and T_m , the transformation temperature. He points out, however, that these results cannot be quantitative for two reasons, one for which he allows, though ignored by Labbé et al. (1970) in their calculation of T_C and a second which is fundamental in that it is not possible to sum over all the electron-phonon interactions, or Cooper diagrams. Further, Vieland (1970) using the experimental results of Reed et al. (1963), Bachner et al. (1967) and Hagner and Sauer (1962) on $Nb_3Sn_{1-x}Sb_x$ finds that T_m , the transformation temperature, and, presumably the band parameters and the filling of the d-band, do not vary with differing proportions of Sn and Sb, while T_C decreases linearly with increasing Sb content. The direction of the tetragonality, however, does alter with the Sn content, the alloys near Nb_3Sn having tetragonality of the same sign as the binary alloy while those with $x = 0.15$ have the opposite tetragonality. Alloys with $x = 0.05$ appear to have transformations of both signs!

Weger (1970) analyses the band structure in more detail and points out that for two of the d sub-bands the next-nearest neighbour, or interchain, interaction is more important than the nearest neighbour, or intra-chain, interaction, while at some high symmetry points in reciprocal space the interchain interaction vanishes altogether, enhancing the one-dimensionality of the situation. The combination of these factors leads to the quasi-one dimensional situation given by Weger (1964) in his earlier paper (figure 2.27a). With the special symmetry of the environment of the linear chains, splitting of doubly degenerate bands may occur giving singularities in the density of states. In a distorted crystal, non-degenerate bands may also split giving rise to the lattice instability. Weger (1970) also points out that the Cohen et al. (1967) model, which accounts for the most properties, is essentially two-dimensional including discontinuities but not singularities in the density of states and that magnetic properties and non-magnetic properties arising from the effective and the bare densities of states respectively will vary differently, as indeed appears to be the case in Nb_3Al (Willens et al. 1969).

A further important point made by Weger (1970) is that the good superconducting properties and the lattice instability are probably intimately connected, as originally suggested by Fröhlich (1954) and by Pauling (1969) in his resonating bond theory of the electron - phonon interaction. This point is underlined by Rothwarf (1971) who attributes the structural transformation to the coupling of the plasmon and phonon modes such that at lower temperature the plasmons have more energy and drive the lattice into a new mode of oscillation. This may be related to the composition dependence of the transformation, which can be seen by comparing figures 2.30a and b. Figure 2.30a shows the lattice contribution to the specific heat as measured by Bonnerot et al. (1969)

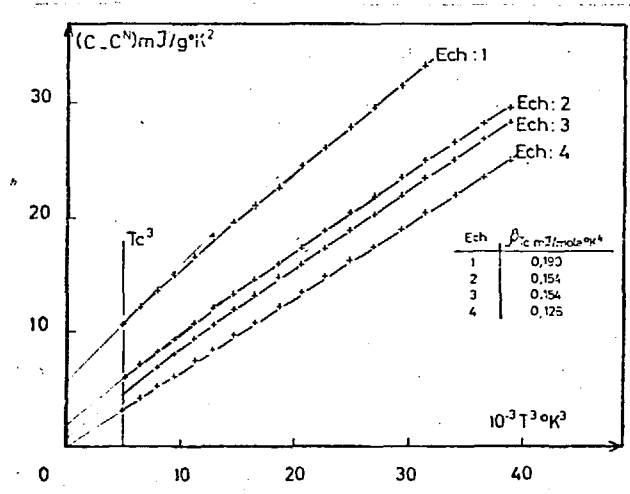


Figure 2.30a.
The lattice contribution to
the specific heat for four
different V-Si alloys.
(Bonnerot et al. 1969)

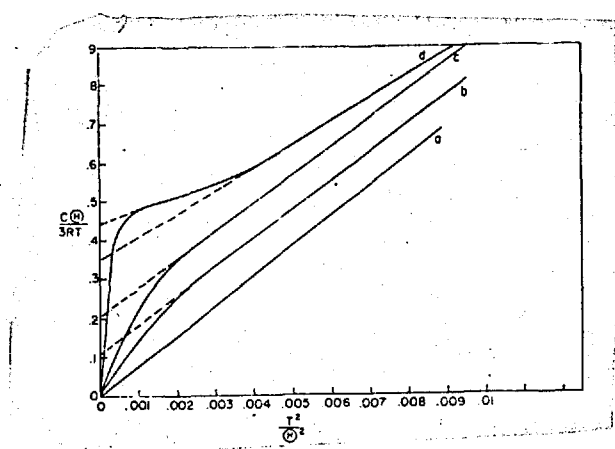


Figure 2.30b.
The lattice contribution to
the specific heat as calculated
from the consideration of
acoustic plasmons.
(Rothwarf 1970)

and figure 2.30b shows the calculated variation with different numbers of plasmon modes.

2.8 The Occurrence of Superconductivity

As pointed out by Kats (1969), for the reasons stated in the last section, it is not possible to calculate critical temperatures exactly. However, Blaugher et al. (1969) and Hein et al. (1969) have analysed experimental results in terms of the following equation (1.75), (McMillan 1968).

$$T_c = \frac{\theta_D}{1.45} \exp \left[- \frac{1.04(1+\lambda)}{\lambda - \mu (1+0.62\lambda)} \right] \quad (2.5)$$

By this method, they consider the relative importance of λ, θ_D and, with knowledge of γ , the electronic specific heat coefficient of $N(0)$, in determining T_c . Figure 2.31a shows a plot of λ against $N_{bs}(0)$ where $N_{bs}(0)$ is the basic density of states and it can be seen that the A atom is important in determining T_c , the two lines approximating the behaviour of compounds which have 3d and 4d transition metals as the A atom. This is reflected in the plot of T_c against the number of valence electrons per atom (figure 2.31b). However, from specific heat measurements one would expect the 3d compounds to have higher T_c 's than the 4d compounds, while the reverse is the actual case. This leads Hein et al. (1969) to infer that it is the phonon density of states, rather than the electronic density of states which principally determines the strength of the electron-phonon interaction in Al5 compounds, while Blaugher et al. (1969) suggest that the phonon density of states itself may be a sensitive function of atomic order as well as the electron density of states as proposed by Garland et al. (1968), (see section 1.5c).

If, however, it is the acoustic plasmons which determine the strength of the superconducting interaction

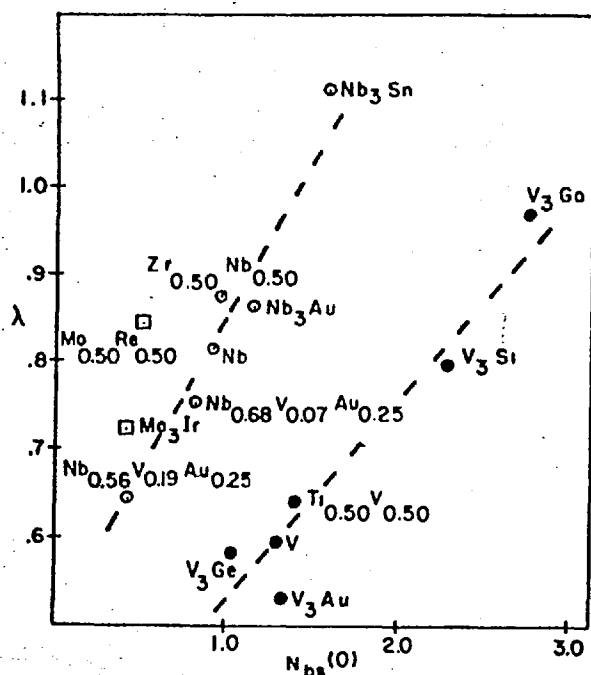
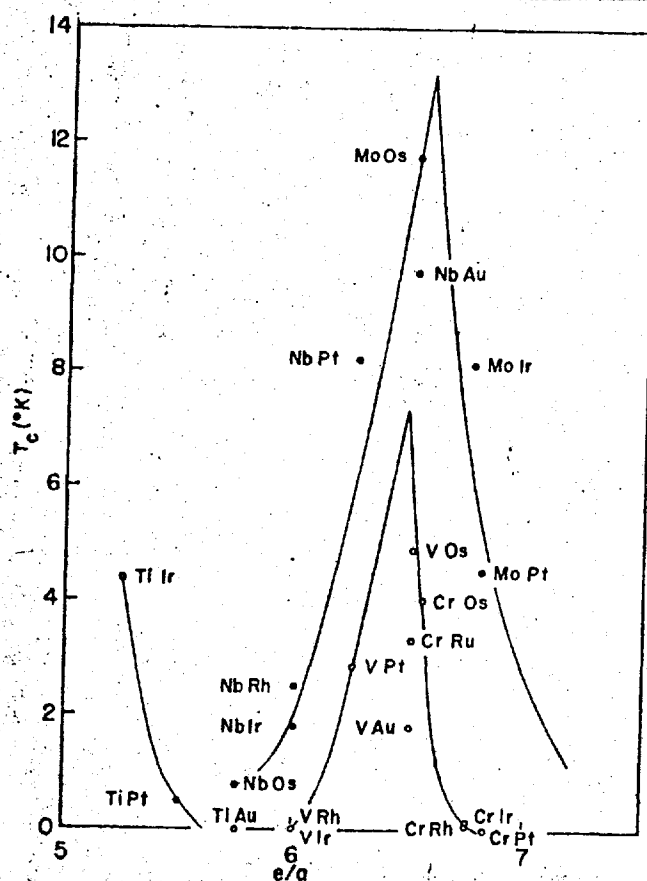


Figure 2.31a. The electron-phonon coupling constant for a number of β -W compounds as a function of the band structure density of states $N_{bs}(0)$.



(Blaugher et al. 1969)

Figure 2.31b. The critical temperature T_c as a function of the electron to atom ratio for β -W compounds. (Hein et al 1968)

as suggested by Rothwarf (1970) then the interaction will be a sensitive function of pressure, impurity content, composition and order, for when the d-band density of states at the Fermi surface is high, the parameter controlling T_c is $\epsilon_0(q_m)$, the contribution to the longitudinal dielectric constant arising mainly from band to band electronic transitions, where q_m is the maximum wave number of the acoustic plasmons determining the number of modes, or degrees of freedom, associated with the acoustic plasmons. This factor $\epsilon_0(q_m)$ appears from Rothwarf's calculations to be highly sensitive to structural variables.

Testardi et al. (1971) suggest that the compositional variation of T_c is due to strain in the lattice and also calculate the change in T_c for V_3Si due to the structural transformation, which appears to agree with experiment.

2.9 Summary

It seems clear from the published results that both the superconducting properties and the magnitude of the lattice instability in a particular alloy depend critically on its composition. It also seems probable from the theoretical work that these properties arise from the unusual density of states of the β -W structure and that their variation with composition is a function of the position of the Fermi surface. However, neither the exact mechanism of this dependence nor the part played by atomic disorder is at all clear.

Further problems are, firstly, the absence of a phase transformation in alloys, in which theory, based on previous results, predicts a transformation; secondly, the role, if any, of second phase in alloys and, lastly, the role, if any, of impurities in the A.15 phase itself.

The exact mechanism of the interaction from which the superconductivity and the lattice instability arise is also in doubt and may be by means of either phonons or acoustic plasmons.

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Chapter Three

Experimental Techniques

"Life can only be understood
backwards, but it must be lived forwards".

- Søren Kierkegaard

3.1 Sources and Preparation of Materials

The materials used in the present work came from a variety of sources. Some were kindly supplied by other laboratories and others were prepared as part of the project. A complete list of the alloys used, their sources and the methods of preparation is given in Table 4.1. In certain cases the method of preparation is unknown and this is indicated by a question mark.

Of those materials prepared in the course of the project, some were prepared by R.F. induction heating under purified argon, using the method of Stirling and Warren (1963), as adapted by McDonnell et al. (1967), and others by arc melting. Attempts to make vanadium-gallium by interdiffusion proved unsuccessful because the vapour pressure of the gallium proved to be too great for the silica capsules which were used. The analyses and sources of the constituents of the alloys prepared in the present work are given in Table 3.1.

All samples were heat treated and, except where otherwise specified, in sealed silica capsules in an alumina horizontal tube furnace, heated by "Crusilite" silicon carbide elements and controlled by a Eurotherm PID/SCR 25 controller. Other heat treatments were performed in an Edwards vacuum furnace. The temperatures in both furnaces were measured by a Pt : Pt 13% Rh thermocouple with the cold junction at 0°C, in an ice and water mixture, using a Croydon Precision Instruments Potentiometer Type P.4.

3.2 Metallography

For metallographic examination the samples were mounted in metallurgical mounting plastic and polished using graded silicon carbide papers and finally with alumina powder on a damp polishing cloth. This produced a more scratch-free surface than using diamond paste, presumably because of the brittleness of compounds with

Table 3.1.

Specifications of Materials
Used in Alloy Preparation.

Si (Johnson and Matthey)

Cu	1ppm
Mg	1ppm

Al(Johnson and Matthey)

Mg	20ppm
Zn	8ppm
Fe	3ppm
Cd	2ppm
Si	2ppm
Cu	1ppm
Ag	1ppm

Nb(Johnson and Matthey)

Si	50ppm
Fe	20ppm
Mg	1ppm
Ta	0.02% (X-ray Spectroscopy)

V(Union Carbide)

C	0.059%
O ₂	0.09 %
N ₂	0.043%

β -W structure. The samples were then etched in a solution of 5% HF, 30% HNO₃, and 65% H₂O. (Gorringe and Valdre, 1966). The micrographs were then taken using an Olympus Pen 35 mm. camera mounted on a Nachet metallurgical microscope.

3.3 Measurement of Room Temperature Lattice Parameters

The measurement of accurate room temperature lattice parameters was important as these values were used to characterise the composition of the alloys, with which most of the other properties were related. Powder patterns were obtained using a Philips 2 radian (180 mm. circumference) Debye-Scherrer camera, mounted against the line source of a Philips vertical tube X-ray generator, with a copper target. In many cases it was necessary to place an aluminium foil over the film to improve the peak to background ratio. The films were measured using a Hilger and Watts vernier film measuring device. It was found by repeated measurement that reading accuracy could be reproduced to ± 0.005 cm.

Using the wavelengths of the copper $K\alpha_1$ (1.54051Å) and $K\alpha_2$ (1.54433Å) lines for resolvable doublets and the weighted mean of these (1.54178Å) for unresolved doublets, all three taken from the International Tables for X-Ray Crystallography (1959), the lattice parameters were calculated by the computer programme D.S.L.P. (Appendix 4a).

The basic method of the computer programme is that of Vogel and Kempter (1961), based on those of Hess (1951) and Cohen (1935), with indexing checks taken from the methods of Hoff et al. (1964, 1965) and Farrar (1966). A shrinkage correction is first calculated using the mean of each pair of lines to define the $2\theta = 0$ and $2\theta = 180^\circ$ positions. During this operation an accuracy check is made and any line which lies outside three standard deviations of the mean is thenceforth ignored in the calculations. The Bragg angles θ are then calculated and an indexing check carried out by comparing the values of $(\sin^2\theta/\sqrt{N})$ for each line (where $N = h^2 + k^2 + l^2$ and hkl

are the Laué indices) with a mean value and re-indexing those lines which do not fall within specified limits.

To calculate the accurate lattice parameter a_0 , the Bragg equation is written in the form,

$$\frac{\lambda}{2d} = \sin(\theta + \Delta\theta) = \cos \frac{1}{2}(\phi + \Delta\phi) \quad (3.1)$$

where $\phi = (180^\circ - 2\theta)$ is the experimentally measured angle and $\Delta\phi$ is the correction, arising from systematic errors, which causes the Bragg equation to be satisfied, (d is the inter-planar spacing). This equation can be expanded by Taylor's theorem and written in terms of a residual function F as:

$$F = A_0\alpha + K_0\delta - \gamma \quad (3.2)$$

where $A_0 = 1/a_0^2$, a_0 = lattice parameter,

$\alpha = \frac{1}{2}\lambda^2(h^2 + k^2 + l^2)$, λ = wave length

hkl = Laue indices, K_0 = "drift" constant

$\gamma = 1 + \cos\phi = 2\sin^2\theta$

$\delta = \sin^2 2\theta \left(\frac{1}{\sin\theta} + \frac{1}{\theta} \right)$, the extrapolation function for Debye-Scherrer Geometry.

K_0 corresponds to the gradient of the extrapolation plot obtained using the graphical method. Using the least squares method of Deming (1943), with the approximate value of a_0 taken from the highest angle reflection and the initial value of $K_0 = 0$, the function $\sum wF^2$ is minimised, where the sum is taken over all observations; w is an observation weight derived by Vogel and Kempter (1959) and Kempter (1959) (given by Beu (1967)) using the method of maximum likelihood:

$$w = 1/\left[K_0 \left(4 \cos^3\theta - 8 \sin^2\theta \cos\theta + \frac{2 \sin 4\theta}{\theta} - \frac{\sin^2 2\theta}{\theta^2} \right) - 2 \sin 2\theta \right]^2 \quad (3.3)$$

From this minimisation, corrections to the values of A_0 and K_0 are found and the calculation reiterated until

it converges. When the lattice parameter has been derived the Bragg angles are calculated and compared with the measured angles. If the agreement is not within specified limits, the relevant lines are re-indexed or discarded and the calculation repeated.

3.4 X-Ray Measurements at High Temperatures

Order-disorder effects and lattice expansion effects were measured with a Unicam S.150 High Temperature Camera designed by Goldschmidt (1955, 1961), mounted on a Hilger and Watts Y.33 Generator.

3.4a The High Temperature Camera

The Goldschmidt Camera is shown in figure 3.1. The camera had been unused for several years before the present work, and serious vacuum leaks were found in two places; the compression joint through which the thermocouple leads pass and the compression joints holding the circular aluminium windows, through which the incident and straight-through beams pass. The first of these leaks was cured by redesigning the thermocouple exit from the vacuum chamber and replacing the compression seal with a ceramic lead-through mounted in an O-ring seal. This involved removing the vertical and rotational oscillation motors, which were only needed for measuring the temperature variation across the furnace gap (section 3.4c). The second leak, arising from unevenness in the surfaces involved, was cured by packing the joint with a layer of Apiezon sealing compound. The main window of the camera was also renewed before starting the experiments.

The camera was evacuated with an Edwards type 102 diffusion pump backed with an Edwards 2SC 20A two stage rotary pump and the vacuum was measured using a Pirani gauge. When the vacuum was better than 1μ Hg., this was regarded as adequate, as the powder specimen was sealed within a separate capsule as described in section 3.4b.

Key

A- focussing furnace

D- thermocouple

F- pumping line

G- aluminium window

H- specimen rotation motor.

K- leaded glass.

N- collimator

Other letters refer to water and electrical connections etc.

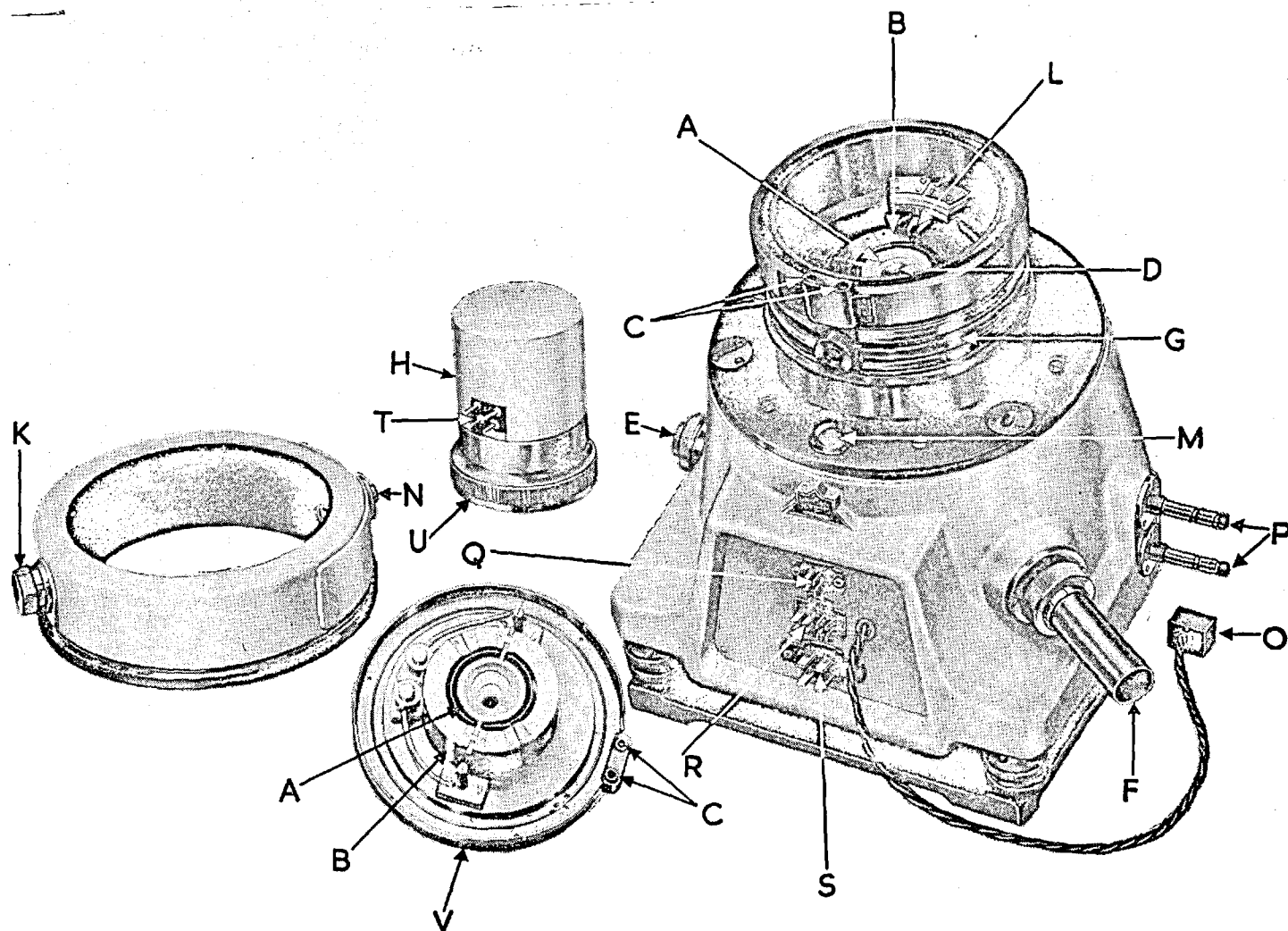


Figure 3.1.

The Goldschmidt High Temperature Camera

The specimen was aligned by adjusting the capillary in the camera top while viewing through a telescope and then the camera alignment was checked by centring the image of the capillary on the leaded glass screen of the film holder with the adjustments illustrated in figure 3.2a.

3.4b Specimen Preparation

As all the materials being studied were alloys of niobium or vanadium, both of which oxidise readily at high temperatures, it was necessary to ensure that the specimens were maintained under vacuum at all times. The design of the standard specimen mount (figure 3.2b) is such that if the capillary is left open and then mounted in the alumina tube, the fixing cement can block the end of the capillary, thus preventing effective evacuation. If the tube remains clear, it is then likely that the powder will be sucked out of the capillary if the evacuation is sudden.

To avoid either of these situations, the specimens were sealed in the capillaries under vacuum. To this end the apparatus, shown schematically in figure 3.3, was constructed. The detailed use of this device is described in Appendix 1, but the main principles are as follows. The capillary is mounted in a copper foil using "Araldite" epoxy resin and the foil is sealed to the underside of the bell-jar base plate in a compression seal. The specimen powder is placed in a small hopper, which can be opened when the bell-jar has been completely evacuated, so that the powder can fall freely into the capillary. The capillary, which extends outside the bell-jar, is then sealed with an oxy-gas flame. The powder itself was prepared by grinding the alloys with a pestle and mortar and sieving through 350 mesh. With the brittle compounds being studied, stress-relieving proved unnecessary, which was an advantage as this treatment could have altered

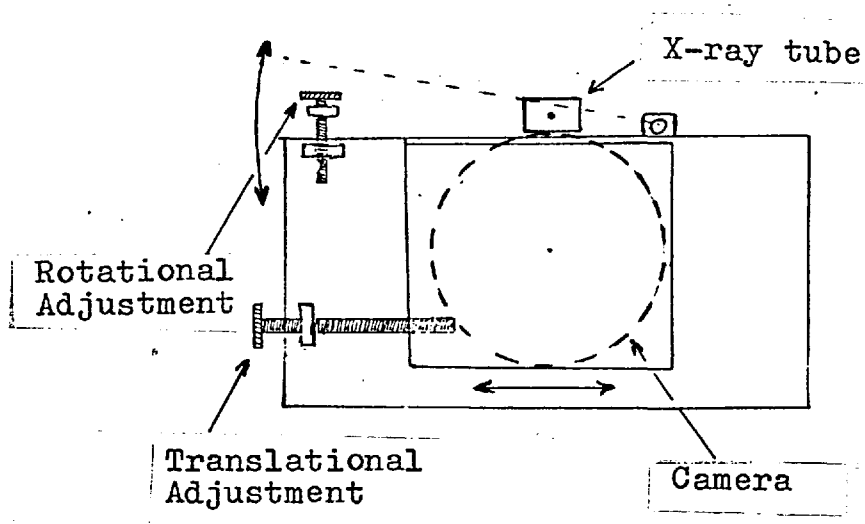


Figure 3.2a. Alignment of the Goldschmidt camera.

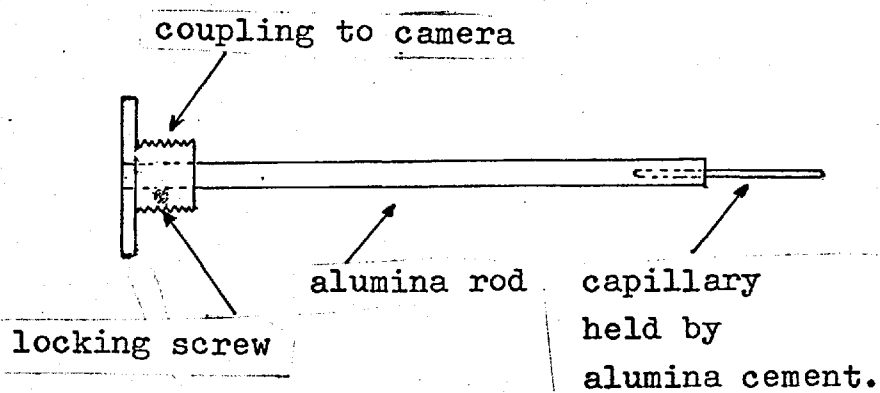


Figure 3.2b. The specimen mount for the high temperature camera.

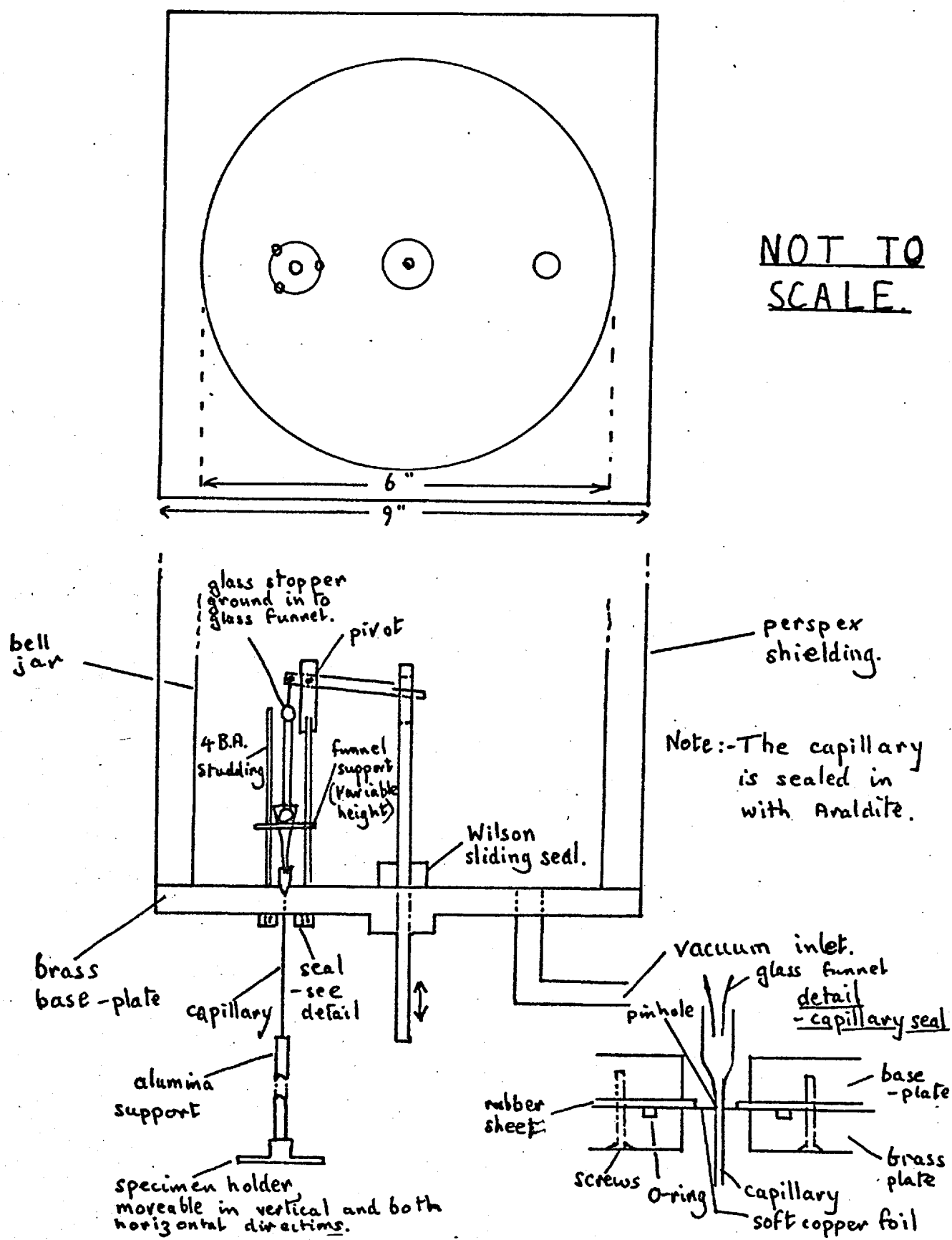


Figure 3.3. Apparatus for loading capillaries under vacuum.

the degree of order in the sample.

To reduce exposure times, which were, none the less, long (between 6 and 20 hours), capillaries of 0.5 mm. diameter were used in place of the usual type of 0.3 mm. diameter. The capillaries were of quartz to withstand the high temperatures. In some of the alloys there may have been slight interaction between the powder and the silica causing brittleness as breakage sometimes occurred on cooling. This may, however, have been due to simple thermal stress in the capillaries.

3.4c Choice of Radiation

The original intention was to use copper but as the camera was used with a demountable Hilger and Watts Y.33 microfocus X-ray tube, it was a simple matter to change anodes to obtain other radiations. With copper radiation the peak to background ratio on the films was so low, that it was difficult to distinguish the powder pattern even at room temperature, and as the temperature was raised the pattern became completely indistinguishable. This low peak to background ratio could have been due to any of four factors:-

1. High absorption in the sample, giving fluorescence.
2. Lack of collimation inside the furnace.
3. Absorption in the aluminium window of the camera.
4. The long specimen to film distance.

Since precision room temperature lattice parameters were obtained using the Philips 2 radian Debye-Scherrer camera with copper radiation, fine collimators and an aluminium foil over the film it was considered that the first two factors listed above were the most important. This was confirmed by the unusually long exposure times required to obtain films with good contrast. An attempt was made to improve the collimation in the Goldschmidt camera by making a narrow set of collimating

slits and some small improvement was observed but any further improvement would have involved a redesign of the furnace itself, which would have seriously affected the temperature distribution and thus increased the temperature gradients across the specimen (section 3.4c).

The collimation problems will, of course, be present whatever the radiation used, but it was found that molybdenum radiation gave satisfactory low angle lines at all temperatures, mainly because the absorption, and hence the fluorescence, is less than for copper radiation. The high angle lines were still indistinguishable and although it was possible to obtain reasonable resolution by exposing for much longer times (≈ 40 hours) and cutting the development time by a factor of two, this would have meant that fewer specimens would have been examined in the time available and that the film was not being used under the recommended optimum conditions. The problem of high angle lines was, therefore, overcome by ignoring it and using low angle lines for both order-disorder and thermal expansion measurements (section 3.4f).

3.4d Knife Edge Calibration

The film on a 19 cm. camera is in two sections, and, therefore, the Straumanis method of correcting for film shrinkage and measuring the diffracted angles cannot be used and the camera knife edges must be calibrated as an internal reference. Bradley and Jay (1932) recommend three ways of doing this:-

1. To use an optical goniometer.
2. To use calipers.
3. The method of mixtures, when a substance of a known lattice parameter is mixed with material under investigation.

Method 2 and a modification of method 3 were used in the present work. To use the method of mixtures at high temperatures could lead to reactions between the two substances, which is not desirable, although it can be

allowed for in terms of lattice expansion, but to introduce this further unknown is unnecessary. As the film holder remains essentially at constant temperature, one calibration is adequate. A sample of the silicon powder used in the International Union of Crystallography precision lattice parameter project (Parrish 1960) was exposed to copper radiation and, from the film obtained, the knife edge positions and the camera radius were calculated using a least squares method. If S_θ is the line position on the film, θ the Bragg angle, c the circumference of the camera and S_0 then

$$S_\theta = \frac{2c}{360} \theta + S_0 \quad (3.4)$$

The values of S_θ and θ for each line were measured and calculated from the Bragg equation respectively and equation (3.4) fitted to the data, giving values of c and S_0 . This was done for both sides of the camera and from these values and the measured knife edge shadows on the film the angular positions of the latter were calculated as:

Right:	9.67°	and	169.92°	Circumference = 59.645 cm.
Left:	9.72°	and	169.99°	Circumference = 59.694 cm.

It can be seen that the values of the camera circumference appear to be different for the two halves of the camera. While this may be so, the difference is more likely to arise from a difference in film shrinkage, so that as long as the values of c and S_0 are used together the results will be self-consistent. The calculation also assumes that the absorption of X-rays in the silicon is negligible, and recalculation of the lattice parameter using the knife-edge values shows this to be not unreasonable.

Lattice parameter assumed	=	$5.43054 \text{ \AA}$
Lattice parameter recalculated	=	$5.43045 \pm 0.0001 \text{ \AA}$

The lattice parameter was calculated using the computer programme H.T.L.P. (see next section) and the least squares fit using computer programme LSF (see Appendix 4b).

3.4e Temperature Calibration

The temperature of the furnace was measured using a Pt : Pt 13% Rh. thermocouple connected to compensating leads with the cold junction at 0°C (in an ice and water mixture). The thermocouple was situated at a position immediately below the specimen and did not measure the exact temperature of the specimen. The temperature distribution across the furnace gap was measured using the vertical oscillation motor (before it was removed) such that in a period of 36 seconds the thermocouple tracked across the furnace gap and back (figure 3.4a). The resulting variation at various temperatures is shown in figures 3.4b and c. As a considerable variation can be seen across the gap it was essential to have a fixed thermocouple accurately calibrated. This was a second reason for redesigning the thermocouple feed through.

With the new thermocouple mount in place, a series of measurements of the lattice parameters of tungsten powder, also used in the I.U.Cr. precision lattice parameter project (Parrish, 1960), and nickel (Matthey 'Specpure': 2 ppm. Fe, 2 ppm. trace elements) at different temperatures were calculated using the computer programme H.T.L.P. (Appendix 4c). which uses the same method as D.S.L.P. to calculate the values of the lattice parameter from the Bragg angles, which are computed from the measurements from the films exposed in the 19 cm. camera. The thermal expansion curves of tungsten and nickel shown in figure 3.5a are plotted from published data, a best line being drawn in the cases of disagreement. The horizontal lines represent the measured lattice parameters in the present work. The resultant calibration curve for the experimental arrangement used is given in figure 3.5b with the standard curve plotted from data supplied by Johnson & Matthey Ltd. The agreement is fair except at low temperatures where heat transfer by radiation is low and temperature gradients become greater.

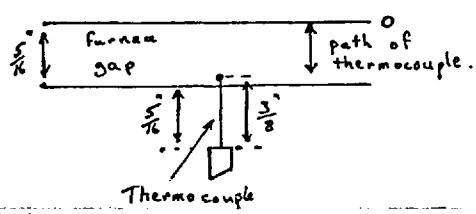


Figure 3.4a.
Path of the thermocouple
in measuring temperature
gradients.

Figure 3.4b.
Variation in the
thermocouple reading
at different
temperatures.

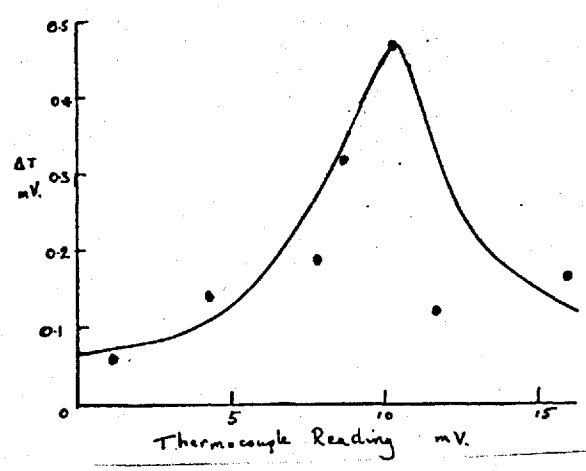
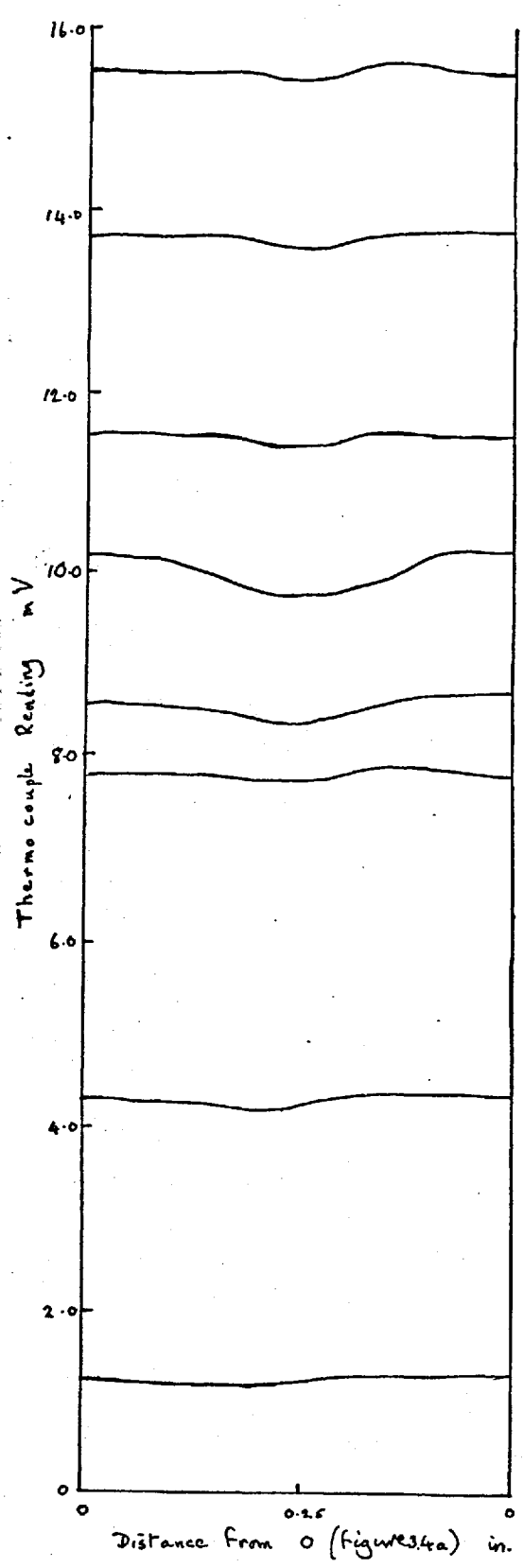


Figure 3.4c.
Variation of temperature
across the furnace gap as
a function of temperature.



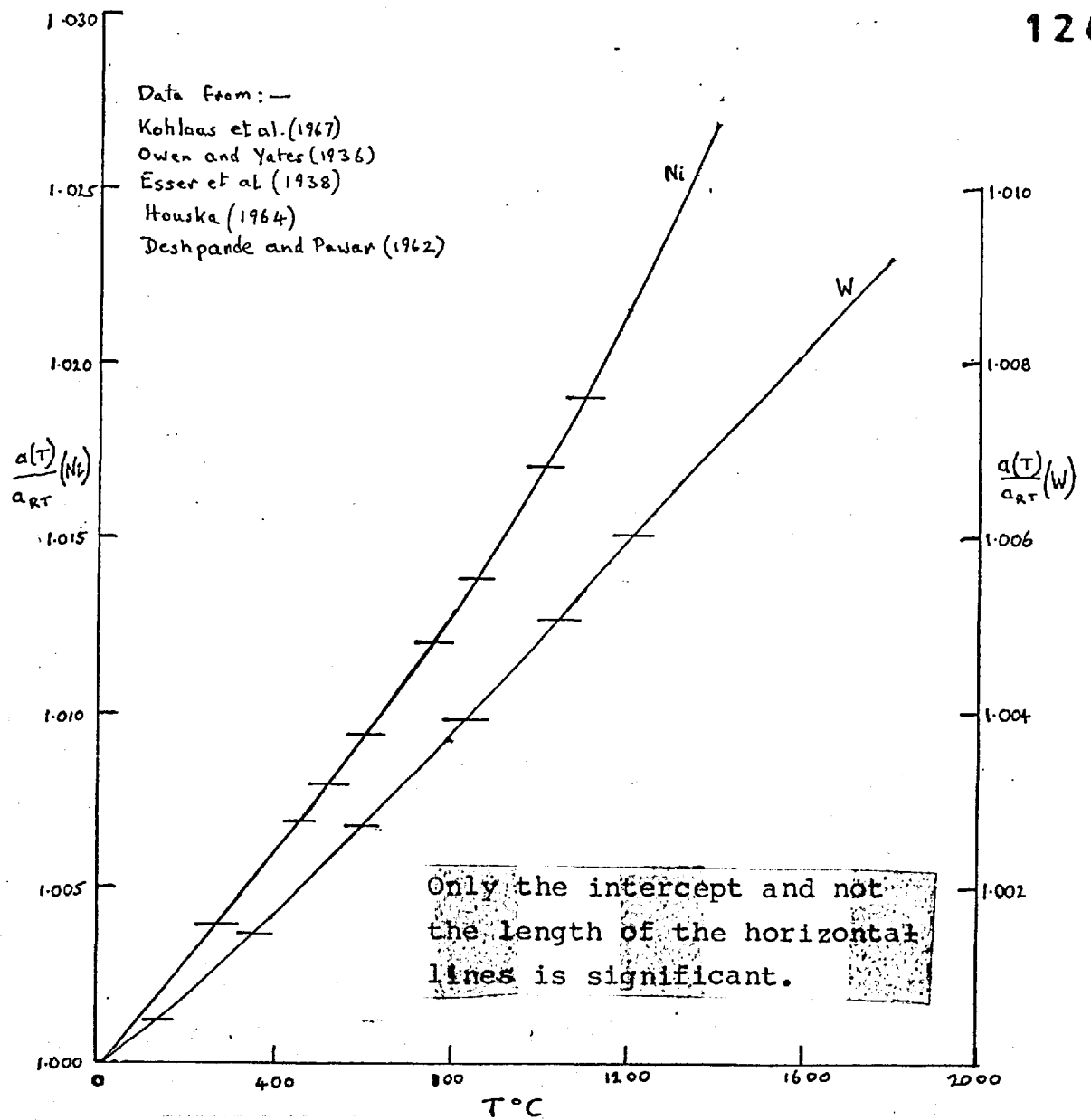


Figure 3.5a. Thermal expansion curves of tungsten and nickel with calibration points marked by horizontal lines.

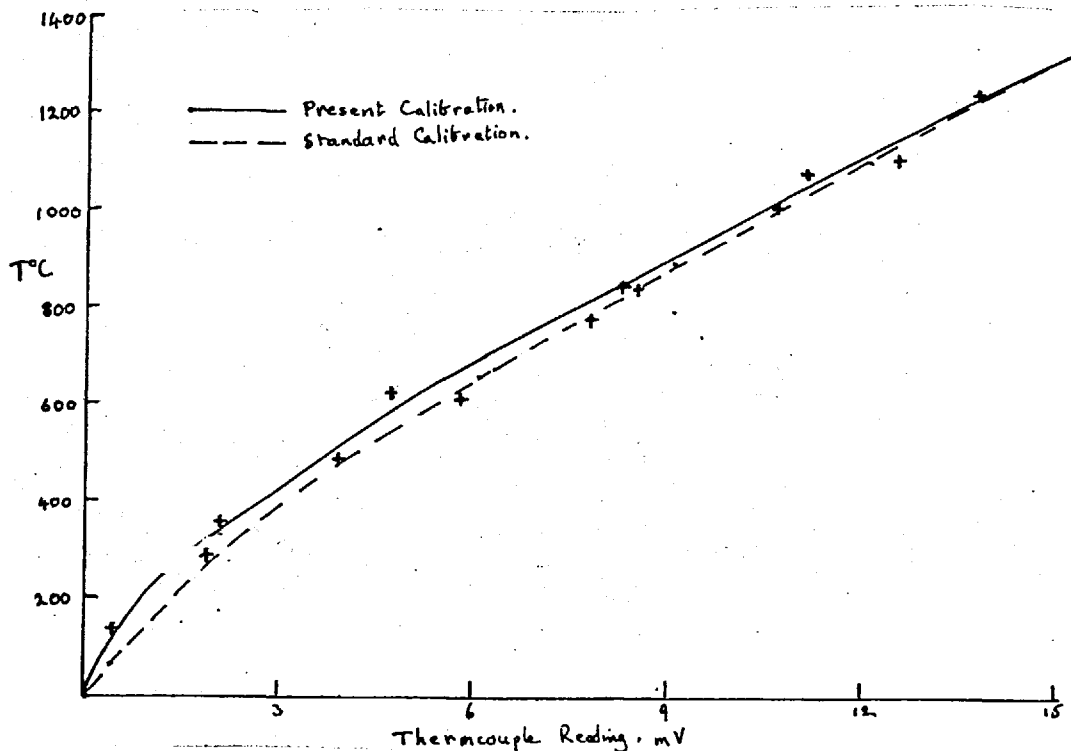


Figure 3.5b. Calibration curve of thermocouple in terms of specimen temperature

The accurate value of the thermocouple voltage was measured with a Croydon Precision Instruments Type P4 potentiometer and during exposures was monitored on a Honeywell strip-chart recorder which was calibrated against the potentiometer. In order to keep as constant a temperature as possible, the input voltage to the furnace was first taken to a 'Variac' transformer to step it up slightly in case of a drop in the supply voltage, and the output of this was taken to a Claude Lyons constant voltage transformer giving a 240 ± 5 v. output for an input of 225 v. to 245 v. In spite of this there were still variations in temperature which may have been due to spikes in the supply voltage or to changes in the resistance of the furnace arising from the recrystallisation in the windings which was observed, on cooling, to have occurred.

Errors in the measured temperature thus arise from three factors:-

1. Errors in calibration.
2. Variations in temperature across the furnace gap and hence across the sample.
3. Variations in temperatures during the exposure.

The maximum error in combining these is about $\pm 25^\circ \text{C}$ but in most cases, particularly at higher temperatures, the error is estimated to be of the order of $\pm 10^\circ \text{C}$.

3.4f Thermal Expansion Calculations

For the reasons discussed previously in section 3.4c, it was not possible to measure the line positions in the back reflection region. The change in lattice parameter with temperature was therefore calculated from the change in position of the low angle lines; 222, 320, 321 and 400, following Hume-Rothery and Lonsdale (1945).

This method assumes that the composition of the specimen and its position in the X-ray Camera remain unchanged for all exposures. In most cases this was the situation and where there were deviations of position, averaging over the four lines indicated the error involved. A change in composition will be reflected in a change in the room temperature lattice parameter on recooling and can thus be allowed for, if necessary.

The change in lattice parameter a_o for any one line is given by:

$$\frac{\Delta a}{a_o} = \frac{a_T - a_o}{a_o} = \frac{(\sqrt{N} \cdot \lambda / 2) \times \left(\frac{1}{\sin \theta_T} - \frac{1}{\sin \theta_o} \right)}{(\sqrt{N} \cdot \lambda / 2) \times \frac{1}{\sin \theta_o}} \quad (3.4a)$$

where a_o and a_T are the lattice parameters and θ_o and θ_T the Bragg angles at room temperature T_o and temperature T respectively and $N = h^2 + k^2 + l^2$ and λ is the wavelength. This expression can be reduced to:

$$\frac{\Delta a}{a_o} = \left(\frac{\sin \theta_o}{\sin \theta_T} - 1 \right) \quad (3.5)$$

and the coefficient of thermal expansion α is given by

$$\alpha = \frac{\Delta a}{a_o} \cdot \frac{1}{T - T_o} \quad (3.6)$$

As a_o is known from the Debye-Scherrer measurement, an estimate of a_T , is given by:

$$a_T = \left(1 + \frac{\Delta a}{a_o} \right) a_o \quad (3.7)$$

The standard deviations in α and in $\Delta a/a_o$ were calculated for the four lines. This number is not strictly large enough for statistical analysis to be really meaningful but the variation between the four lines gives an estimate of the accuracy of the calculated values. Neither in this calculation, carried out by the computer programme LAT EXP (Appendix 4d), nor in the direct calculation of lattice

parameters at high temperatures Programme HTLP, is a correction applied for errors in the knife edge measurement but errors in this are reflected in the variation between the lines. Errors in the knife edge calibration are within the limits of the experimental error, i.e. $\pm 0.0001\text{\AA}$ (see section 3.4d).

3.4g Measurement of Intensities

The X-ray intensities were transferred from the film to a chart trace using a Siemens Recording Photometer Attachment Type Z, the output of which was fed to a Honeywell Elektronik 194 Chart recorder. This chart recorder incorporated an integrator and the resultant output appeared as is illustrated in figure 3.6. The trace along the bottom of the chart represents the integrated output, which is frequency modulated.

In almost all cases, because Mo radiation was used, the peaks of interest overlapped and three possible methods of analysing the results were considered. The first was to use the method of Du Mond and Kirkpatrick (1931) for separating two overlapping peaks. If the reflections are assumed to possess the same profile, then the profile of the combined curve, $F(x)$, will consist of the sum of the two constituent profiles. If one of these profiles is $f(x)$, then the other will be $kf(x - \delta)$, where k is the ratio of the heights and δ their linear separation. Therefore:

$$F(x) = f(x) + kf(x - \delta) \quad (3.8)$$

Any profile may then be split into its component parts as is shown in figure 3.7a. This method was not considered satisfactory as it was not easy to determine accurately the width of the peaks and, therefore the points equivalent to A and B in figure 3.7a. A more sophisticated method was then adopted in which the thermal diffuse scattering curve was fitted to the measured background curve away from the

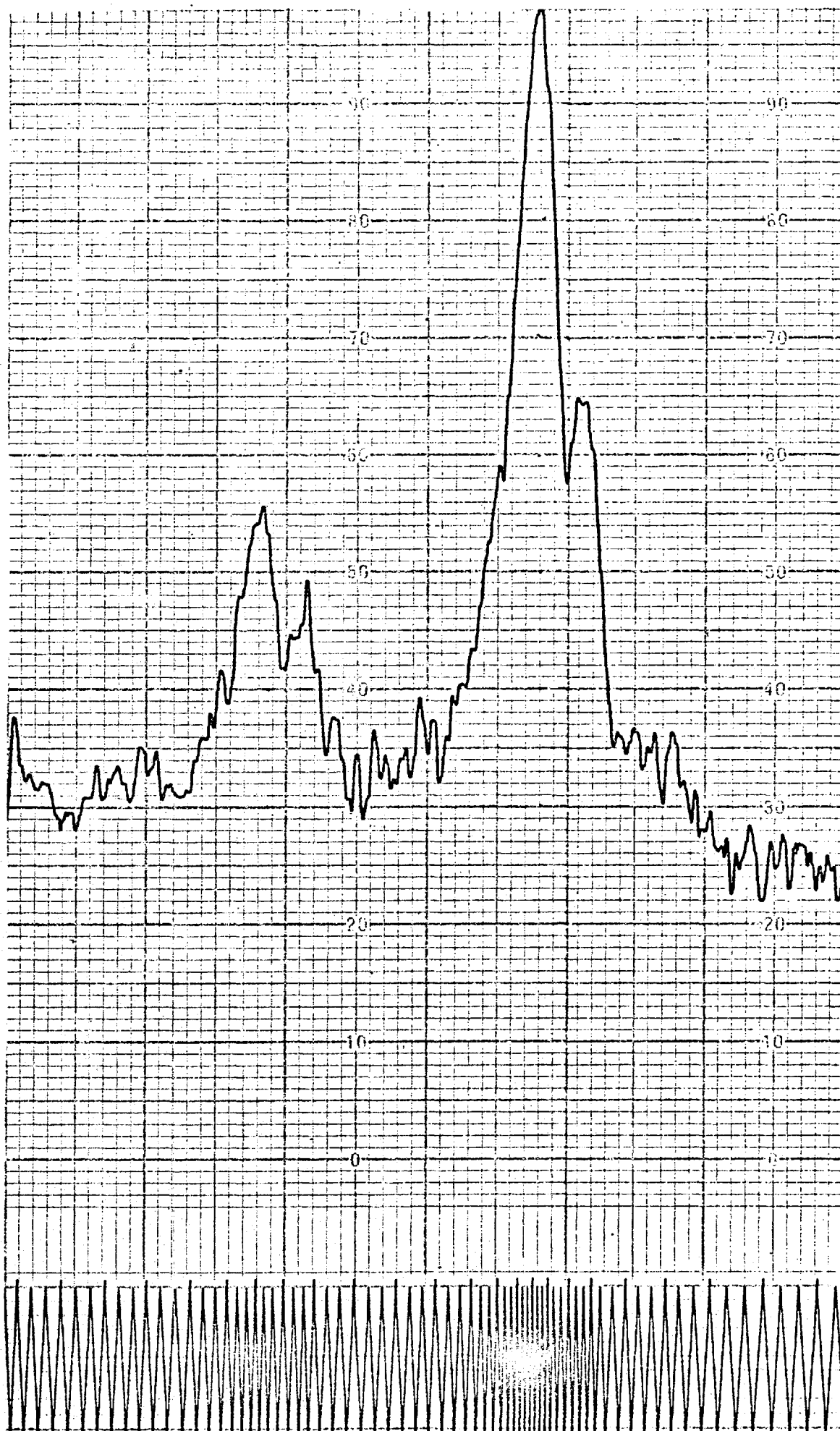


Figure 3.6.A typical chart record of the output from the photometer.

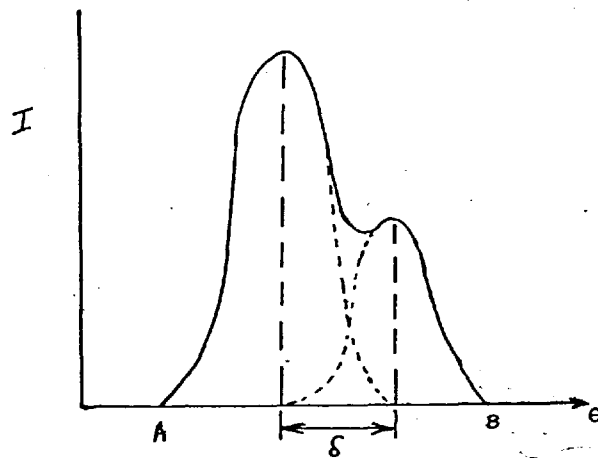


Figure 3.7a. The Du Mond and Kirkpatrick method of resolving two overlapping lines in an X-ray powder pattern.

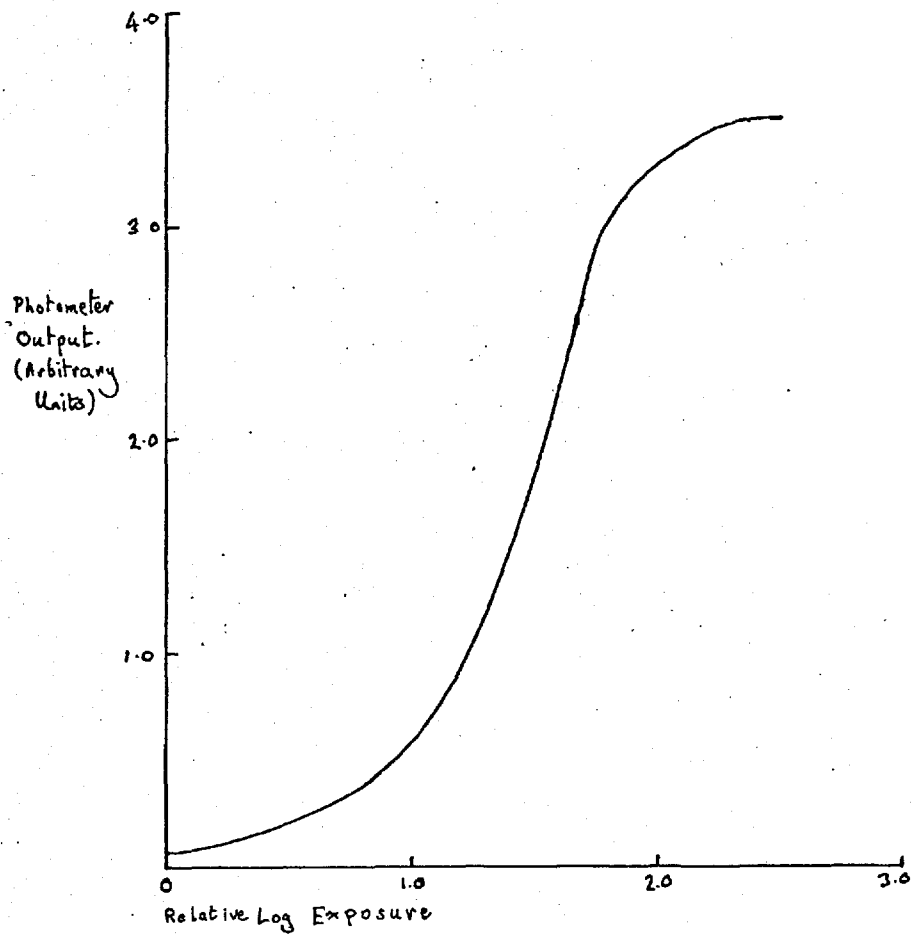


Figure 3.7b. The photometer output as a function of X-ray intensity. (Measured using a calibrated density wedge.)

Bragg peaks and the calculated intensity of the thermal diffuse peaks subtracted from the measured intensity to give the Bragg intensity. This method is described in Appendix 3, but was found to be unsuitable in the present case because the low peak to background ratio meant that the relative size of the random variations in the background intensity masked the variations in thermal diffuse intensity.

The third method, and that finally adopted, was to use the peak height above a background. The assumption made in this method is the same as that made in the Du Mond-Kirkpatrick method, that the widths of the bases of the peaks are the same and that because the profiles are the same the ratio of the areas under the peaks, and hence the ratio of the X-ray intensities is proportional to the ratio of the peak heights. The advantage of this method is that the use of it does not require the separation of the individual profiles. While the output of the photometer is not linear over the complete range of X-ray intensities (figure 3.7b), in the few cases where the measured intensity is outside the linear range, the effect on all the peaks except the smallest is similar. In the case of the low intensity peaks the accuracy is also low and any correction would be an order of magnitude smaller. No correction was therefore made for this in the calculation of intensity ratios (a correction was made, however, in the more accurate curve fitting procedure - Appendix 3). Lorentz-polarisation corrections were made to the intensity ratios, but not absorption or temperature corrections. In the case of the absorption correction, because the specimens were sealed under vacuum, it was not possible to determine accurately the effective density of the powders. A correction was made to the data assuming an effective density but this reduced the internal consistency of the results deduced by the method of chapter five. It was, therefore, concluded that a more reliable result would be obtained by not making a correction. The temperature correction was omitted because its effect is negligible ($\approx 1\%$) over the narrow angular range involved. Furthermore, the accuracy of any such correction would be very low in view of the uncertainty in the published values of the Debye temperatures of the β -W materials.

3.5 X-Ray Measurements at Low Temperature

3.5a Introduction

The occurrence of a cubic to tetragonal phase transformation and, in the case of transforming samples, the transformation temperature were investigated using a prototype cryostat loaned by the Oxford Instrument Company. Since this was the first such cryostat to be used for X-ray diffraction, its cryogenic and crystallographic performance were evaluated before studying the present β - W samples.

3.5b Principles of the Continuous Flow Cryostat

Most cryostats used for X-ray diffraction measurements at liquid helium temperatures have been of the "pool" type where liquid helium is stored in an insulated vessel surrounded by radiation shields. This type of cryostat was developed in order to keep specimens at low temperature for extended periods. As the helium evaporates, it is possible to transfer more helium into the cryostat, so that samples may be kept cold indefinitely. A schematic diagram of the "pool" type of cryostat is shown in figure 3.8a. The cryostat used in the present experiment, however, does not collect liquid helium but is cooled by a stream of liquid helium passing through the specimen holder. The flow of helium and hence the rough temperature of the specimen, is maintained by a rotary vacuum pump. This principle was first developed by Klipping (1961, 1964) in Germany and is described in detail by Klipping et al. (1965). It was later applied by Davey (1970), at the Engineering Laboratories, at Oxford University, to the calibration of temperature measuring devices. The Oxford Instrument Co. have used the principle for Mossbauer spectroscopy and the present version of the cryostat was adapted for X-ray powder diffractometry. A schematic drawing of the instrument is shown in figure 3.8b. No liquid nitrogen is required, the

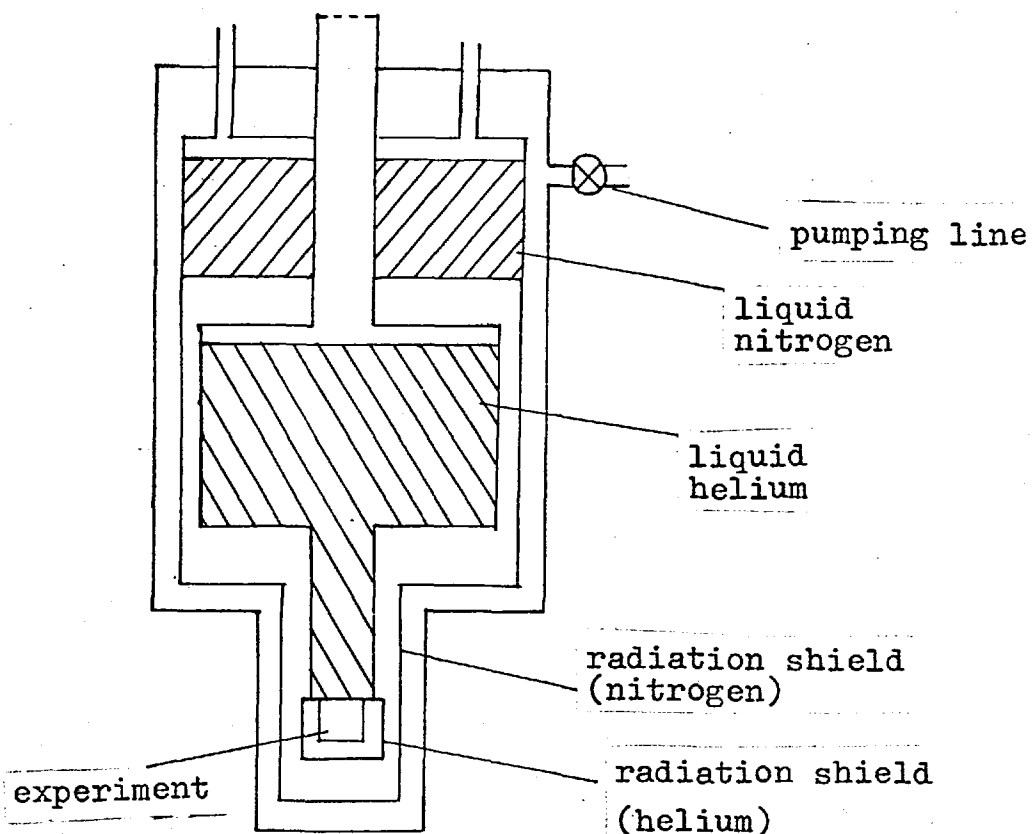


Figure 3.8a. Schematic drawing of a pool type cryostat.

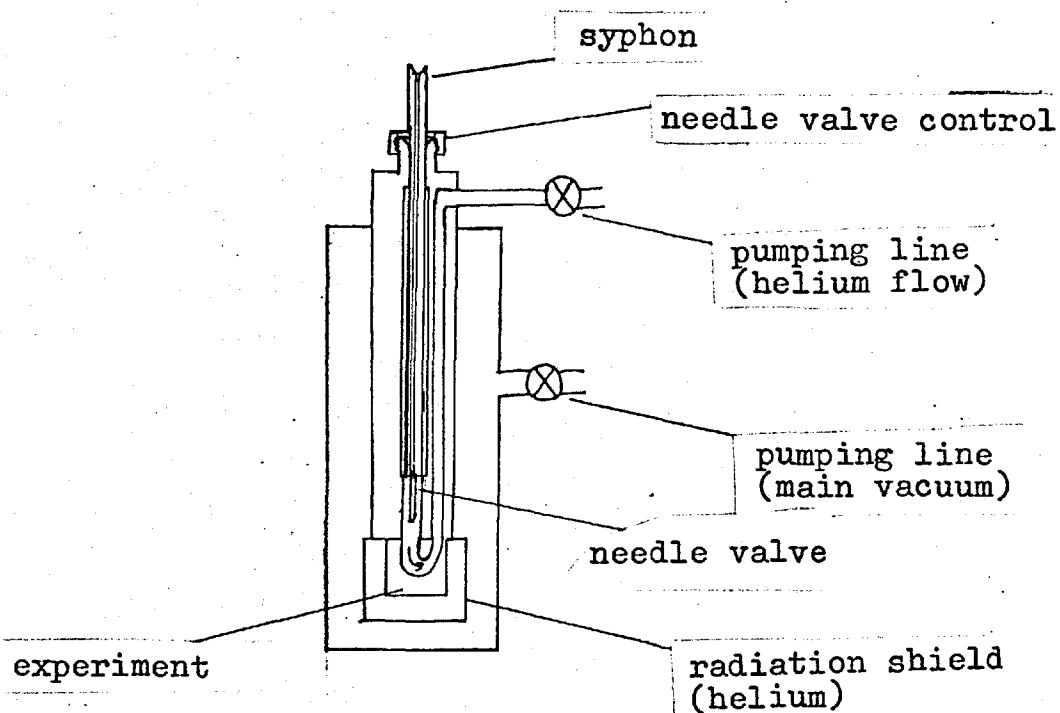


Figure 3.8b. Schematic drawing of a continuous flow cryostat.

only radiation shield being cooled by the helium (liquid or cool gas) after it has passed through the sample holder.

It can be seen from a comparison of figures 3.8a and 3.8b that the continuous flow type cryostat is much simpler than the "pool" type. Furthermore, for experiments of the present type, where the existence or lack of a transformation is being investigated and the principal measurement is that of temperature, the use of the continuous flow type cryostat leads to a considerable saving in time and in cost of liquid helium. The design also provides a greater degree of control over a wider temperature range than does the "pool" type.

3.5c The Design of the Continuous Flow Cryostat

A drawing of the cryostat used in the present work is shown in figure 3.9. The main body (A) is a vacuum tight stainless steel can with means of alignment on the diffractometer (section 3.5e) and a "mylar" window (B) through which the X-rays pass. The central section slides into the outer can through a double O-ring vacuum seal (C). The main vacuum space is evacuated using a rotary pump (Metrovac 6DRI) to a pressure between 10 and 40 μ Hg. The flow of helium through the specimen holder is controlled by the needle valve (E) at the end of the flexible transfer syphon (D). A second needle valve (F) is provided in the pumping line for further control of the flow and, hence, the temperature of the sample. For rapid cool-down this valve can be by-passed by operating the $\frac{1}{4}$ " Speedivalve (G). By controlling the flow rate a low temperature can be maintained for an indefinite period to $\pm 1^\circ$ K. For fine control of temperature a heater is provided in the specimen block. By using the heater and needle valves in conjunction a particular temperature can be selected and then maintained to an accuracy of $\pm 1^\circ$ K. This facility was not used extensively

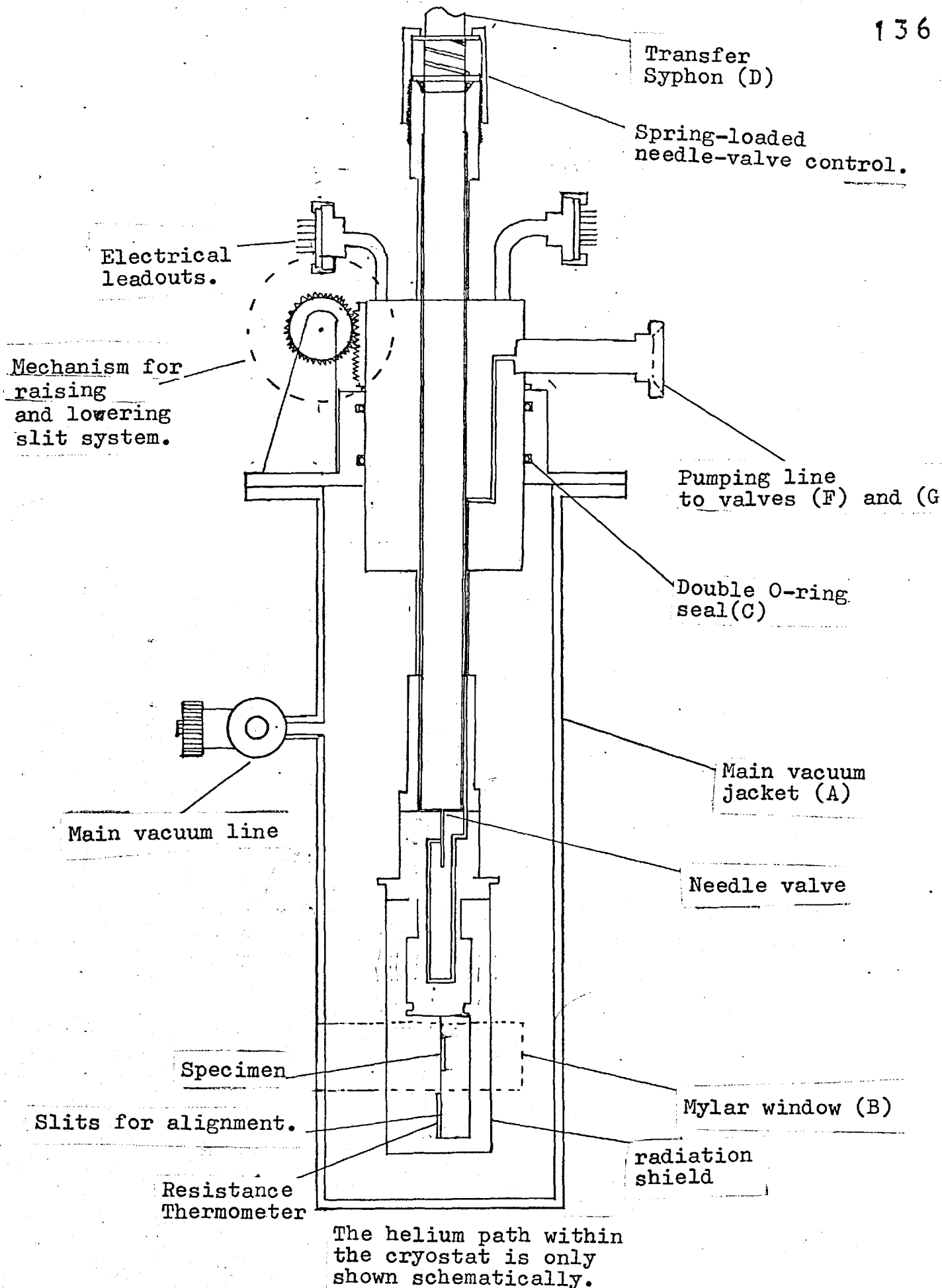


Figure 3.9. The continuous flow X-ray cryostat.

for the present work, since the measurements did not require long times at fixed temperatures. An overall picture of the cryostat, mounted on a Siemens Type F diffractometer, is shown in Figure 3.10.

The cryostat was also used with liquid nitrogen. Under these conditions the main vacuum of the instrument had to be pumped to 10^{-6} mm. Hg, because of the reduced cryopumping action of liquid nitrogen. The cooling time to liquid nitrogen temperatures was much longer than to liquid helium temperatures, principally because of the narrow bore of the transfer syphon used. The results of the measurements of cryogenic performance at both liquid helium and liquid nitrogen temperature are given in Table 3.2 and the detailed use described in Appendix 2.

3.5d Temperature Measurement

The temperature of the specimen block in the cryostat was measured using a resistance thermometer CLTS - 2 (Weir Electronics Ltd), (D in Figure 3.13a), which is linear from liquid helium temperature to room temperature. It was calibrated at room temperature (20°C), liquid nitrogen temperature (77°K) and liquid helium temperature (4.2°K). The liquid helium point was determined as the lowest temperature reached by pumping with all the valves open so that the reading of resistance was constant for half an hour. Under these conditions liquid helium will collect in the specimen block. As the specimen mount was made of high conductivity copper, it was reasonable to assume that the block was in thermal equilibrium at 4.2°K and that within the accuracy of the measurement, the resistance of the thermometer corresponded to liquid helium temperature. The assumption appears justified by the linearity of the calibration curve obtained (Figure 3.11). The resistance of the thermometer was measured, using a two lead system, with a Wayne Kerr Universal Bridge Type B 221. For very precise measurement

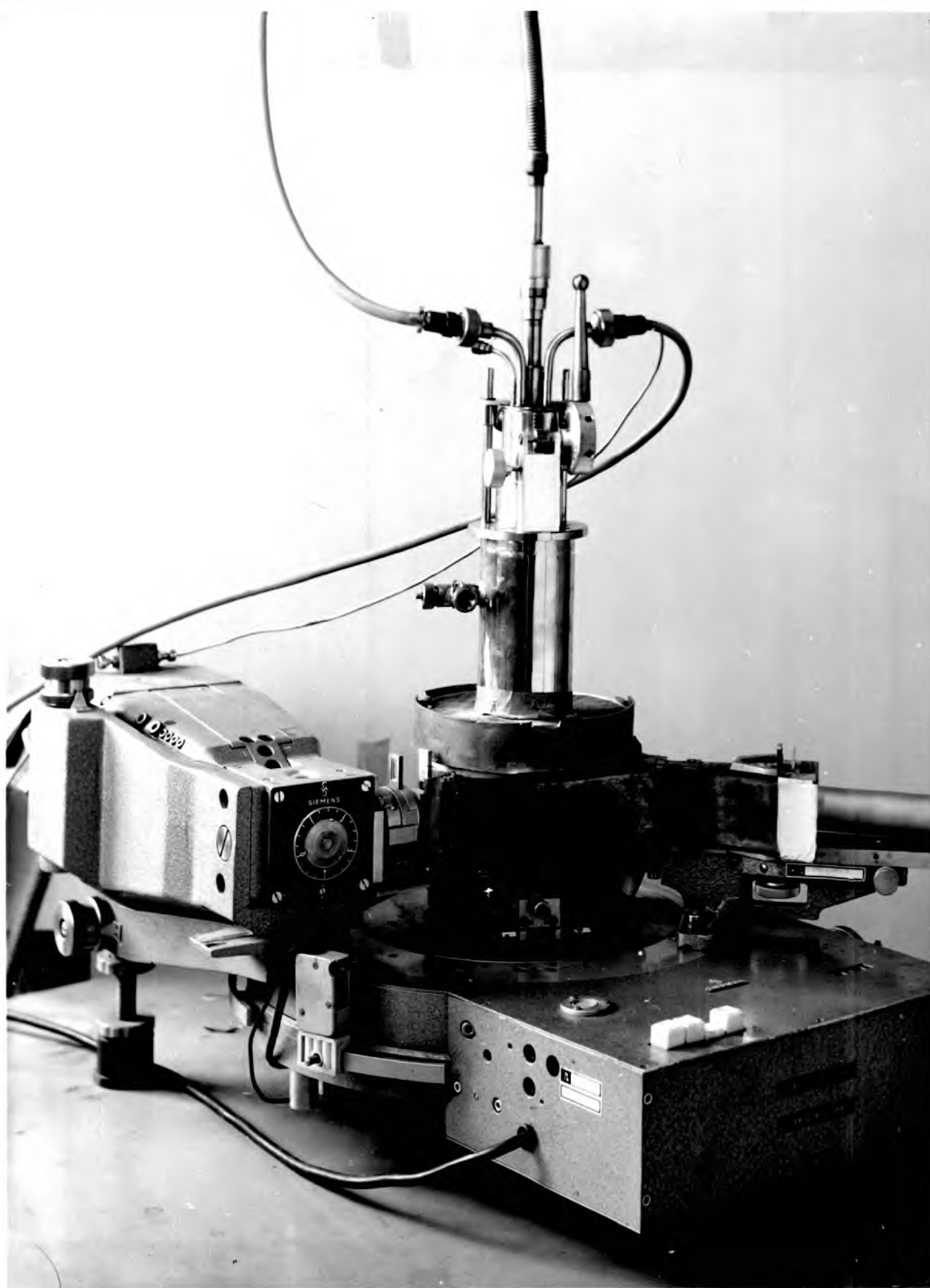


Figure 3.10. The continuous flow cryostat mounted on the Siemens Type F diffractometer.

Table 3.2

Cryostat Performance

Parameter	Helium Operation	Nitrogen Operation
Vacuum Required	40 μ	1x10 ⁴ μ
Time to Cool	(to 25°K) 10 min. (to 4.2°K) 20 min.	(to 77°K) 30 min.
Consumption	To cool 1 litre. At 4.2°K 1 litre/hr.	Negligible (not measurable)
Temperature Control	$\pm 1^\circ\text{K}$	$\pm 1^\circ\text{K}$
Temperature Range	4.2 - 77°K In both cases the temperature can be taken higher but the control becomes less accurate.	77 - 140°K

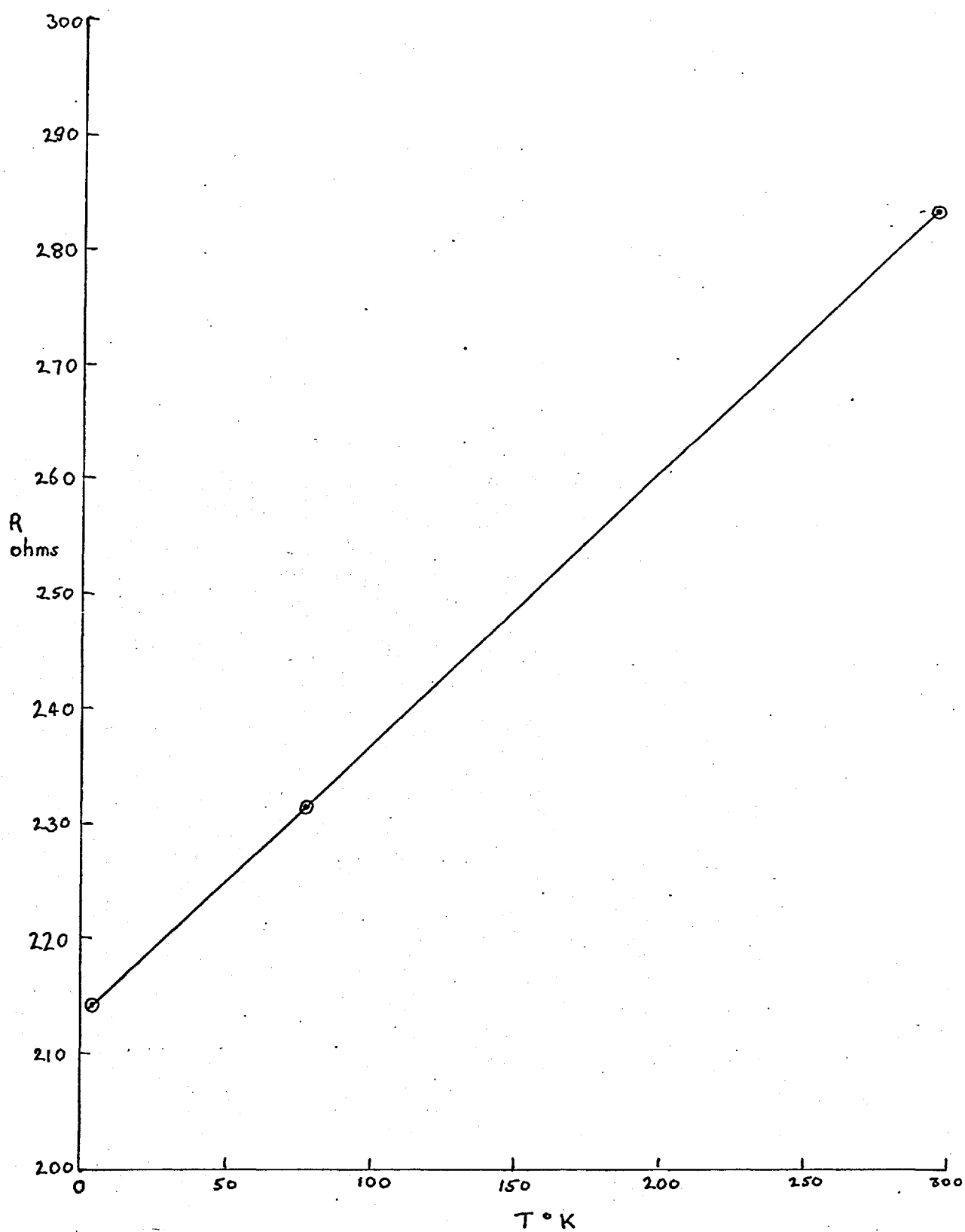


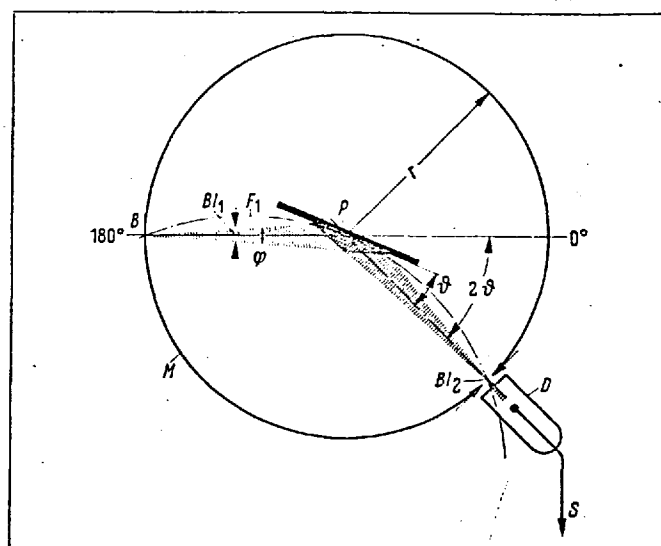
Figure 3.11. The calibration curve of the CLTS-2 resistance thermometer.

of temperature it would have been possible to use a four lead network, but this was considered unnecessary in the present case.

3.5e Crystallography at Low Temperatures

The cryostat was mounted on a Siemens Type F diffractometer (Figure 3.10), the focussing geometry of which is shown in Figure 3.12a. The diffractometer was aligned in the normal way (Vassamillet & King, 1967) by superimposing the 111 peaks of gold on either side of the mainbeam. The crystal was then attached to the diffractometer via a dovetail slide and a rotation plate as shown in Figure 3.12b. The cryostat could then be adjusted by the means of the screws A so that the plane of the specimen lay tangential to the focussing circle, and by the means of screws B so that the Bragg angle θ equalled zero when the specimen angle 2θ equalled zero.

This was achieved by use of a collimator slit system described by King and Preece (1968), which can be seen in the drawing showing the whole tail of the cryostat given in Figure 3.13a and the photograph of the inside of the cryostat and the transfer syphon in Figure 3.13b. The specimen is first aligned approximately by dividing the beam, so that half the incident intensity is received at the counter tube and then maximising the signal by rotating the cryostat so as to bring the specimen plane parallel to the centre line of the incident beam. The cryostat is then raised so that the slit system is in the beam. (In the present cryostat only the centre section was raised, but this was unsatisfactory because of the strain required to overcome the force arising from the vacuum, and in later models the whole cryostat is to be raised). The screws AA and BB are then adjusted to maximise the signal. The profile of the 111 reflection of



- | | | | |
|-----------|-------------------------|----------|--|
| B | Focus of the x-ray tube | α | Aperture angle |
| Bl_1 | Aperture slit | M | Measuring circle of the diffractometer |
| Bl_2 | Detector slit | r | Radius of the measuring circle |
| D | Detector | F_1 | Bragg-Brentano focusing circle |
| P | Specimen | S | Towards the counting rack |
| θ | Glancing angle | | |
| 2θ | Diffraction angle | | |

Figure 3.12. the focussing geometry of the Siemens Type F powder diffractometer.

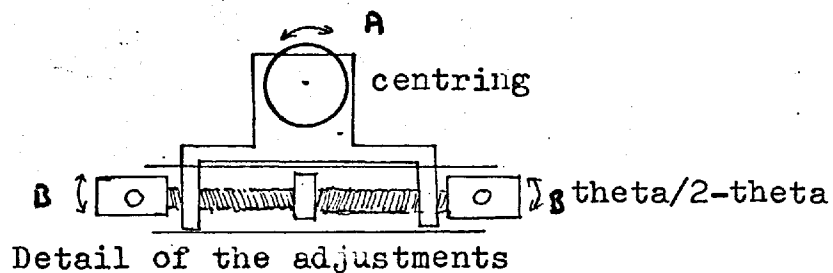
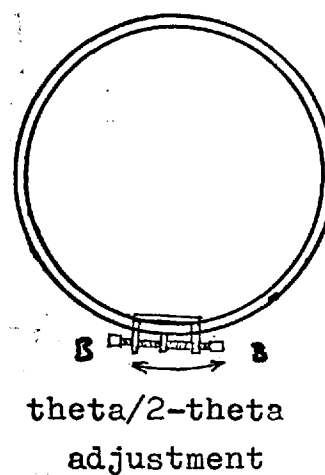
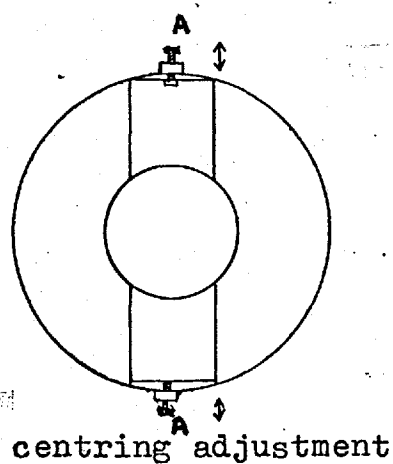


Figure 3.12b. The centring and theta/2-theta adjustments on the cryostat/diffractometer coupling.

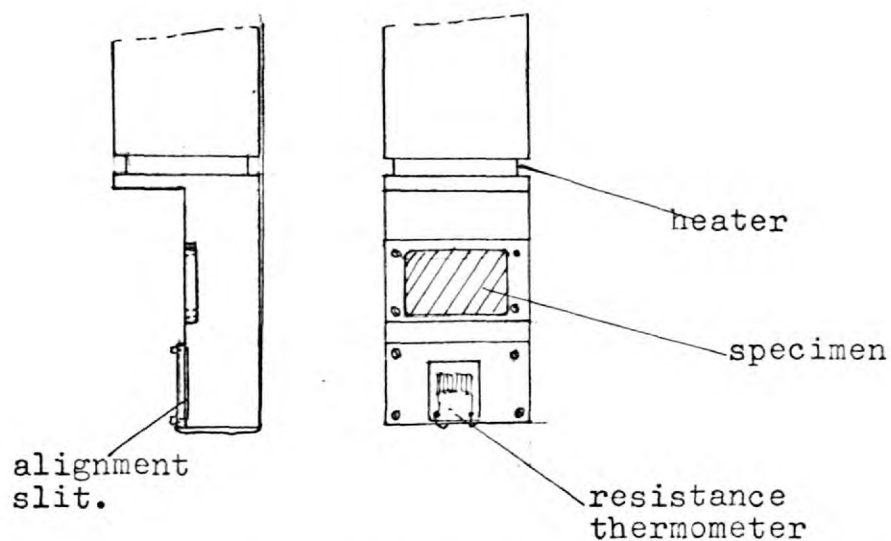


Figure 3.13a. The tail of the X-ray cryostat.

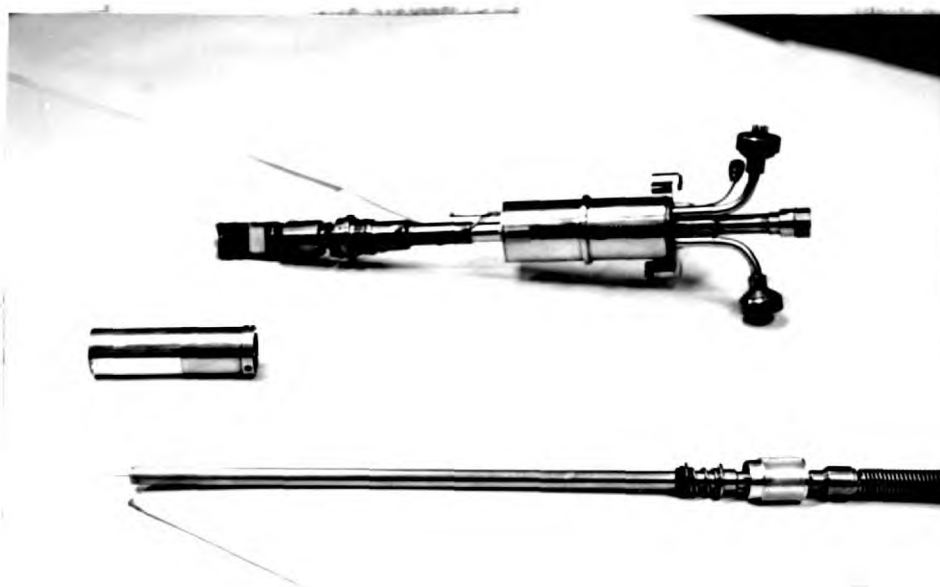


Figure 3.13b. The central section of the cryostat, the radiation shield and the needle-valve end of the syphon,

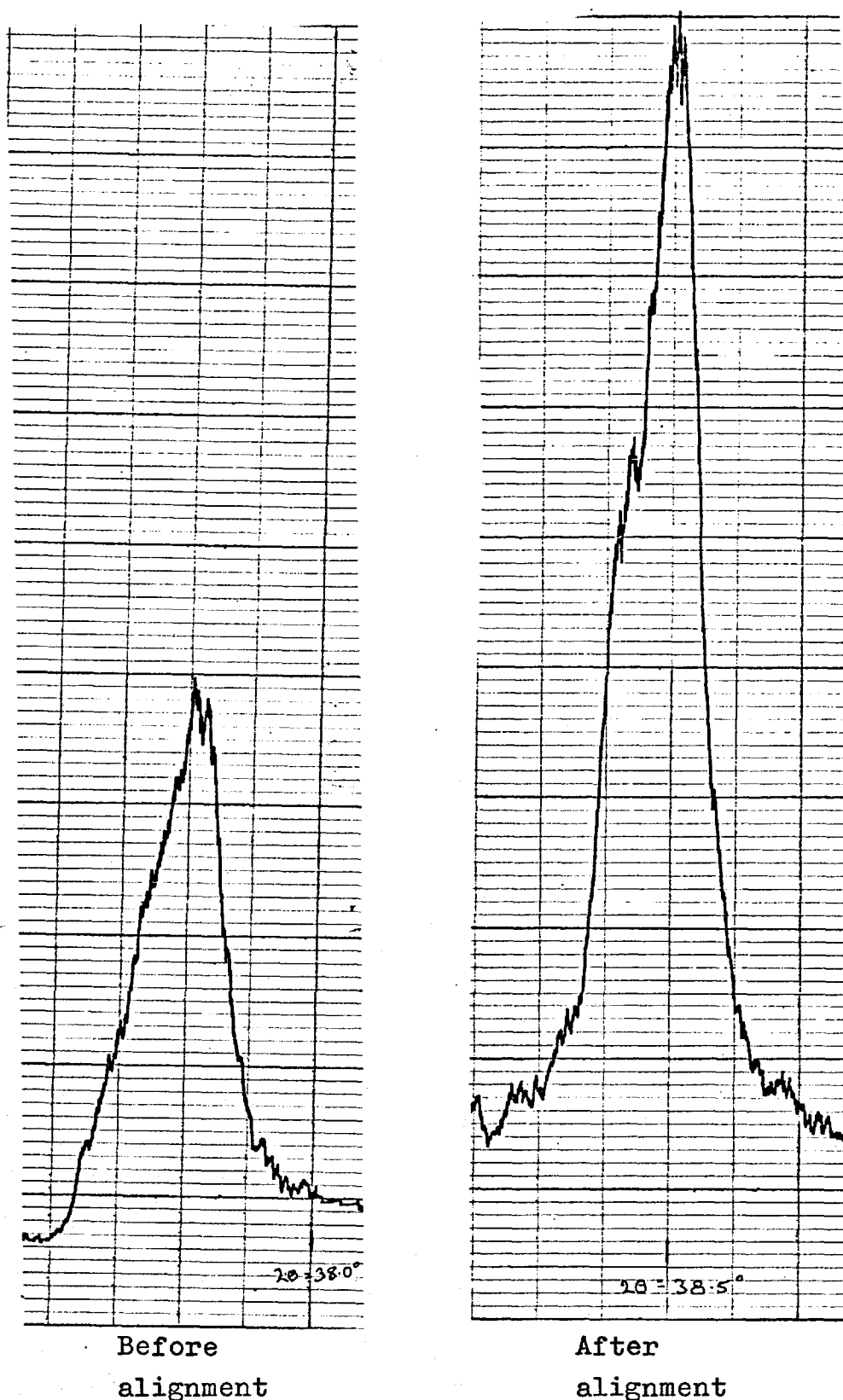


Figure 3.14. The 111 line of silver before and after alignment using the slit system.
 Conditions: scale- 1×10^4 , 1° divergent slit, 0.1° receiving slit, $1/8^\circ$ per min scanning speed, 2% error, chart speed 1 cm/min.

silver before and after alignment is shown in figure 3.14. The accuracy of this method depends on the width of the slits, in this case 0.0025 cm. and their distance apart l , here 2.5 cm. The collimation of the slit is then $= 2d/l = 0.024^\circ$ which compares favourably with 0.034° , the angle subtended by the X-ray source at the sample, which is the limiting accuracy of the $2\theta/\theta$ setting of the diffractometer. Further, with slits of width 0.0025 cm. this distance of 0.0025 cm. is the maximum distance possible between the specimen and the goniometer axis. This alignment technique can be used at any temperature, but in the present series of experiments, it was not possible to check the alignment at low temperatures, except by dividing the beam, because of the difficulty encountered in raising the slit system, and hence the specimen mount, against atmospheric pressure. In practice, it was observed that on cooling the cryostat the specimen would move away from the position tangential to the focussing circle but did not twist. The diffraction profiles thus moved to lower angles but did not alter their shape. It was therefore possible to use the equipment to detect the presence of line broadening due to the phase transformations, but not to measure the thermal expansion of the specimens. The radiation used for the low temperature measurements was copper $K\alpha$.

3.6 Measurement of Superconducting Critical Temperatures

3.6a Introduction

The critical temperatures of the alloys were measured using the change in A.C. susceptibility observed on entering the superconducting state. It was originally intended that the measurements should be made on the 0.5 mm. diameter powder specimens used for the high temperature X-ray measurement and a probe was built for this purpose. However, the volume of the sample proved to be too small to generate a change in signal, on

going through the superconducting transition, which was detectable above the noise level. Filtering and amplification by factors of up to a thousand times did not make the change sufficiently clear for measurements to be made of the temperature. The critical temperatures of the β -W materials were therefore measured on bulk specimens.

3.6b The Experimental Arrangement

The measurements of the transition temperatures T_c , of the bulk samples, which varied from approximately $1 \times 4 \times 4$ mm. to $6 \times 4 \times 4$ mm. in size, were made by adapting a magnetisation probe constructed by Larbalestier (1970). A drawing of this is shown in Figure 3.15 and photographs given in figure 3.16. The probe consists of a balanced pair of coils and for magnetisation measurements in either a superconducting or copper solenoid the magnetisation curve is obtained by plotting the integrated difference signal, which corresponds to the magnetisation M , against the applied field H . For measurements of T_c , the cryostat tail was removed from the copper wound 6 K-gauss magnet and placed in a small copper solenoid, of approximately 6 cm. internal diameter and 23 cm. length. This was connected to a Muirhead K-205A oscillator to give a low A.C. field at a frequency approximately equal to 1800 cps, (but not exactly 1800 cps, so as to avoid harmonics of the supply frequency). The in-balance signal from the detector coils will change significantly when a sample located in one of them enters the superconducting state due to the consequent expulsion of the magnetic flux. To detect this effect, the output signal from the coils was taken to a Dymar A.F. Wave Analyser Type 771 A tuned to the input frequency. (In practice, the coils were used slightly out of balance so that the wave analyser could be accurately tuned). This acted as an A.C. voltmeter and the change in signal was observed on its meter and also on an oscilloscope which showed a trace of the

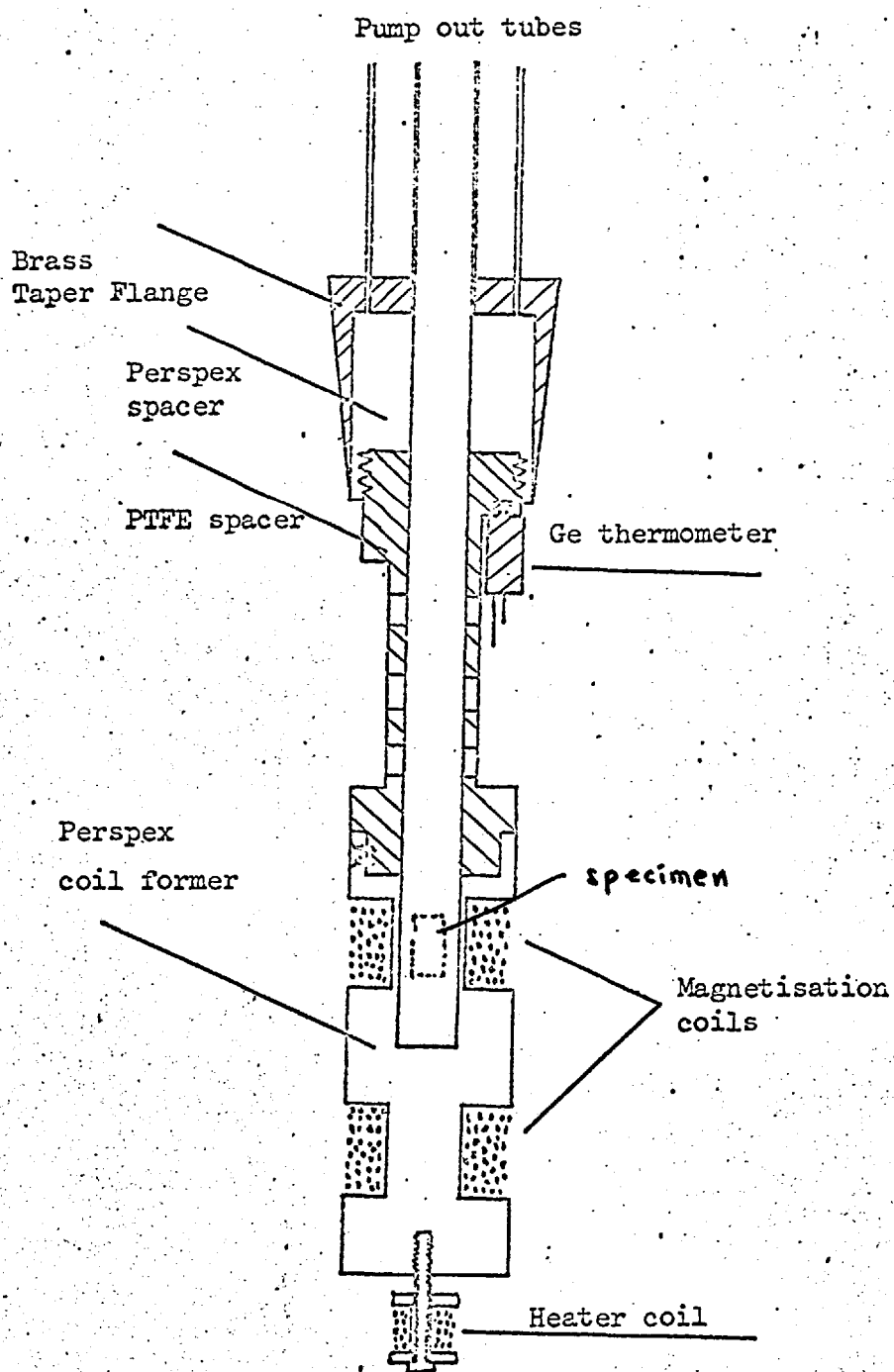


Figure 3.15. probe used to measure critical temperatures.

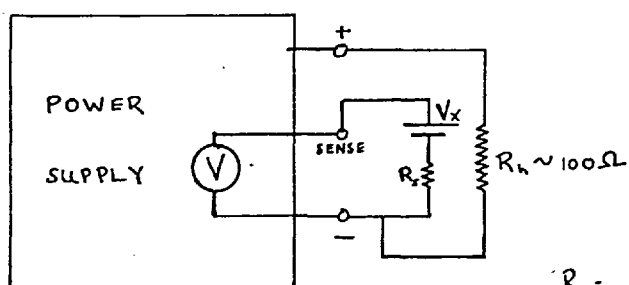


Figure 3.16. The probe used to measure critical temperatures.

selected frequency.

The temperature of the sample was controlled by a heater connected to a Minireg Type 401-1 stabilised power supply and making use of its built-in sensing system. The circuit is shown in Figure 3.17a. The rate of heating could thus be set as low as $\approx 1^{\circ}\text{K}/\text{min}$ and the temperature could be held constant within the limits of measurement as long as required, subject to the limitation at higher temperatures ($\approx 20^{\circ}\text{K}$), set by the evaporation of the liquid helium. The temperature was measured using an Au. 0.03 at.% Fe / Chromel Thermocouple which was situated in the specimen holder (Figure 3.17b). This was calibrated using liquid helium temperature and the T_c 's of known materials (Table 3.3). The calibration curve fitted by a least squares method (see section 3.6c) is shown in Figure 3.18. The temperature was recorded on a Honeywell Elektronik 194 Chart recorder and the transformation was marked on the chart manually when a change in signal was detected on the meter of the wave analyser.

The specimen holder (Figure 3.17b), which can be seen in the photograph in Figure 3.16b, was a split copper cylinder on the end of a long thin-walled stainless steel tube and the sample was surrounded by silicon grease to keep it in place and to give good thermal conductivity. The sample could be changed without returning the entire probe to room temperature. To prevent icing up during this operation, the cold gas from the main helium dewar was taken back into the double-walled can of the probe providing a slight over-pressure and thus preventing the inflow of air when the sample holder was removed. A photograph of the complete experimental arrangement is shown in Figure 3.19.



R_s = sense carbon resistor
 V_x = 9V (dry cell.)

Figure 3.17a. Heating and temperature control circuit for critical temperature measurement.

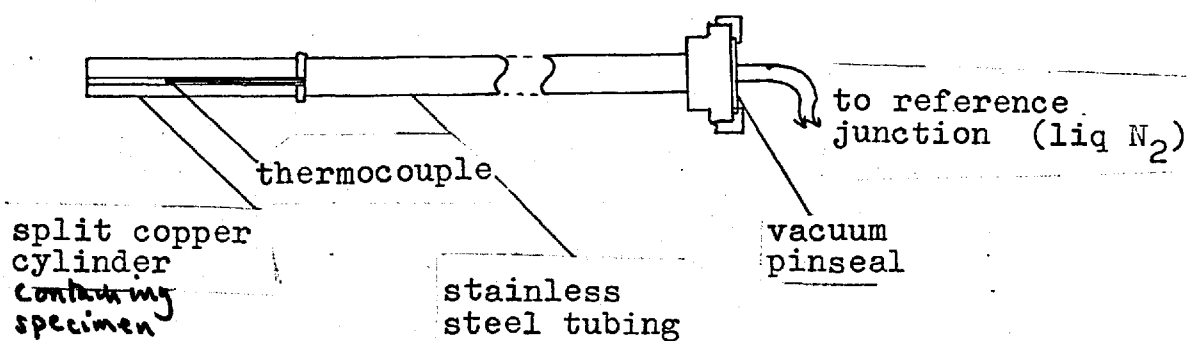


Figure 3.17b. The specimen holder for critical temperature measurement.

Table 3.3

Calibration Points of
The Thermocouple.

Liquid He.	4.22°K	0.807 ₀ mV
T _c of Pb.	7.20°K	0.757 ₆ mV
T _c of Nb.	9.30°K	0.729 ₀ mV
T _c of V-Si.	17.0°K	0.624 ₇ mV
T _c of V-Si.	16.9°K	0.624 ₇ mV

The values of T_c for the two V-Si specimens were taken from Pollock(1966) and Finlayson(1968).

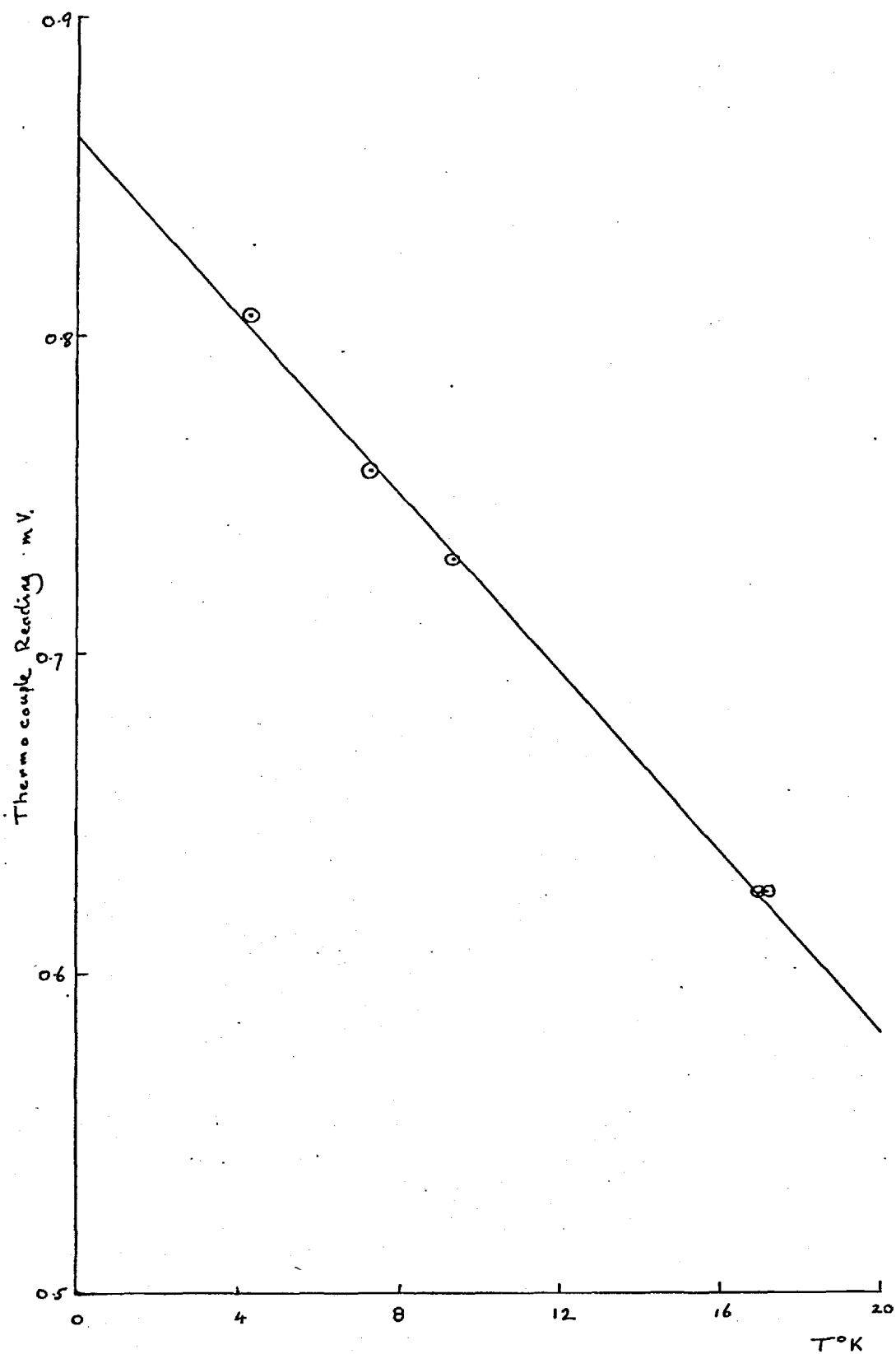


Figure 3.18. Calibration curve of Au.0.03 at% Fe/chromel thermocouple used in critical temperature measurement.

3.6c Calculation of Critical Temperatures
 from Measured Data

The critical temperature of each sample was measured several times both on cooling and heating. The actual critical temperature was then calculated using the computer programme AI5TC (see Appendix 2e). This programme first calculated a calibration curve for the thermocouple by fitting a straight line to the calibration points. Then for each sample a mean value of the thermo-electric e.m.f. was calculated. For samples for which the transition had finite breadth the beginning and end of the transition were treated as separate points as it was not possible to distinguish random error in measurement from the breadth of the transition. The temperature of the transition was then measured from the thermocouple calibration curve and the standard deviation of this calculated, including both the experimental error, the breadth of the transition and the error in the thermocouple calibration.

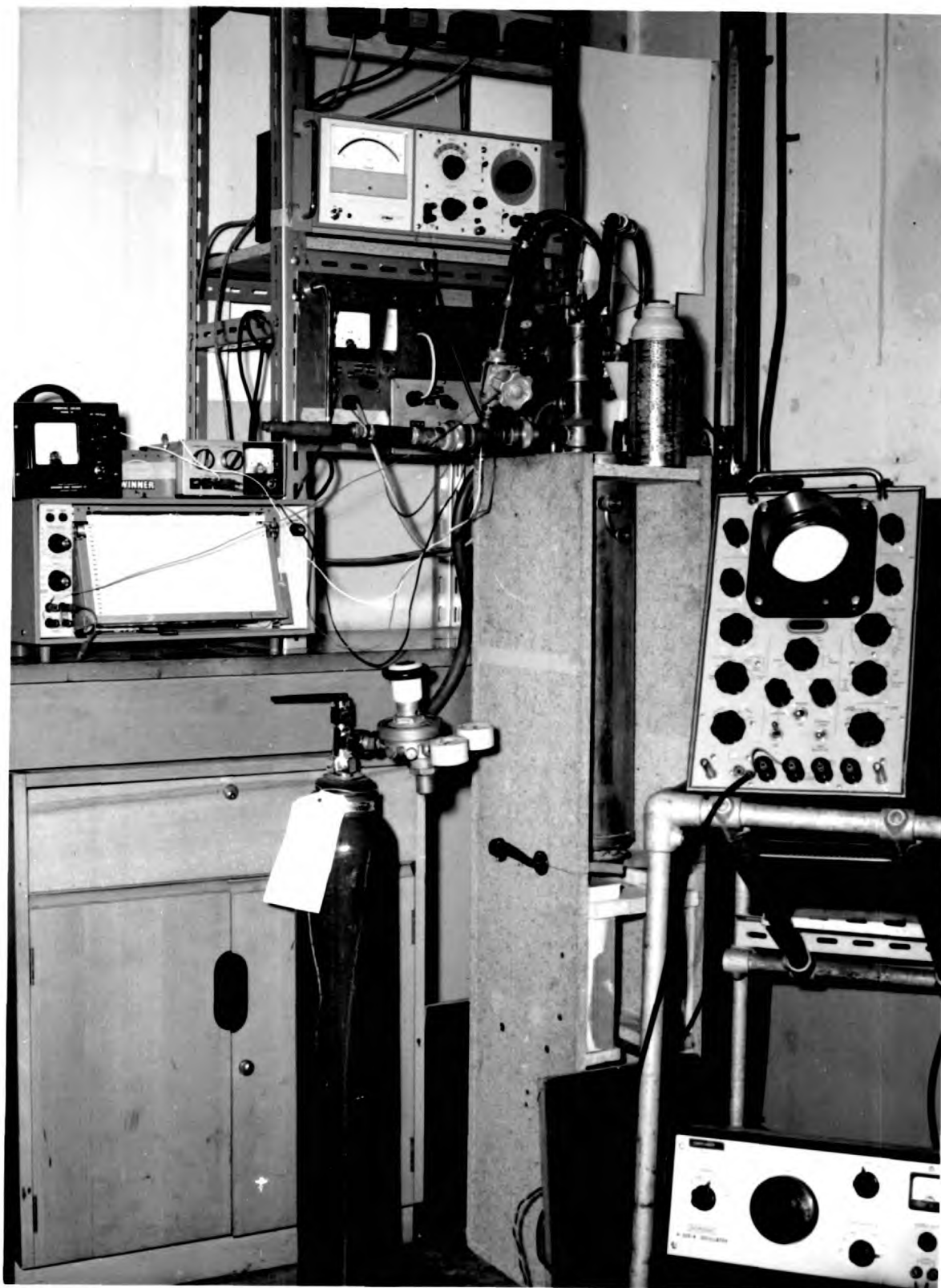


Figure 3.19. The experimental arrangement used for measuring critical temperatures.

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Chapter Four

Experimental Results

"Observe his various bumps,
His head as I uncover it:
His morals lie in lumps
All round about and over it".

- W. S. Gilbert

4.1 Room Temperature Lattice Parameter Measurements

The sources of alloys used in this investigation, their method of preparation and their heat treatments are summarised in Table 4.1. The room temperature lattice parameter of every alloy was measured by the method described in section 3.1, unless otherwise specified in Table 4.1, and these lattice parameter values which were used to characterise the chemical composition of the alloys are included in Table 4.1 together with the composition deduced from published data. Figures 4.1a, 4.1b, 4.1c and 4.1d show the composition-lattice parameter relationship taken from figures 2.7, 2.9, 2.11 and 2.14, together with the measured lattice parameters as horizontal lines. Where nominal compositions are known these are also shown on the figures and it is clear that nominal compositions can be very misleading in describing the composition of the β -W phase, due to weight loss in melting and the formation of second phases. On certain of the X-ray films, lines arising from other phases were visible and the metallography was performed to investigate these more fully.

The composition deduced for the Nb-Sn(1) specimen, prepared by diffusion, may not be correct since it lies outside the range of composition expected from the phase diagram (figure 2.6). The non-equilibrium state of this alloy was confirmed by heating a sample for 72 hours at 1000°C , which caused the room temperature lattice parameter to be reduced to $5.2912\text{ \AA}$ (Nb-Sn₂), placing its composition well within the accepted limits for the β -W phase. The lattice expansion in the original specimen may be caused by the absorption of hydrogen from the hydrochloric acid used in removing the excess free tin in the diffusion couple, or by the presence of excess tin in the β -W phase itself due to the high pressure at which the diffusion process takes place.

To check the possibility of hydrogen absorption, some of the powder (after heat treatment) was treated in a concentrated solution of hydrochloric acid at temperatures

Table 4.1.

Alloys used in the present investigation.

Sample	Source	Preparation	Heat Treatment	R.T. Lattice Parameter Å	Deduced Comp. at% Si
V-Si, 1	Monash	Arc cast	1 wk/1200°C	4.7241	25
2	I.C.	R.F. Induct.	None	4.7242	25
3	I.C.	Arc cast	1 wk/1450°C	4.7246	25
4	I.C.	R.F. Induct.	100hr/1000°C	4.7245	25
5	Fulmer	Diffusion ?	None (?)	4.7246	25
6	I.C.	Arc cast	None	4.7246	25
7	I.C.	R.F. Induct.	100hr/1000°C	4.7247	25
8	Metals Research	Floating Zone (Single Xtal)	None	4.7248 ϕ	25
9	I.C.	Arc cast	1 wk/1350°C	4.7295	22
10	I.C.	Arc cast	1 wk/1000°C	4.7327	20
11	Monash	Arc cast	1 wk/1350°C	4.7333	20
12	I.C.	Arc cast	1 wk/1350°C	4.7352	19
ϕ lattice parameter measured			by Dr. J.T.A. Pollock.		
					at% Ga
V-Ga, 1	Fulmer	?	None (?)	4.8172	26
2	Harwell	Arc cast	1 wk/300°C +2 mths/600°C	4.8166	25
3	Harwell	Arc cast	1 wk/1200°C	4.8183	26
4	Harwell	Arc cast	1 wk/1100°C	4.8192	27
5	Harwell	Arc cast	1 wk/300°C +1 wk/1250°C	4.8200	28
6	Harwell	Arc cast	None	4.8203	28
7	Harwell	Arc cast	1 day/1400°C +1 wk/1000°C	4.8191	27
8	Harwell	Arc cast	1 wk/1075°C	4.8183	26
9	Harwell	Arc cast	1 wk/1000°C	4.8187	26
					at% Al
Nb-Al, 1	I.C.	Arc cast	1 hr/800°C	5.1862	22
2	I.C.	Arc cast	1 wk/1000°C	5.1871	21
3	I.C.	Arc cast	1 wk/1000°C	5.1893	20
4	I.C.	Arc cast	1 hr/800°C	5.1914	18
5	I.C.	Arc cast	1 wk/1000°C	5.1942	16

Table continued overleaf

Table 4.1. continued.

					at% S
Nb-Sn1	Harwell	Diffusion	None	5.2950	29
2	Harwell	Diffusion	72 hr/1000°C	5.2912	26
3	Berkely	Sintering	2 hr/900°C	5.2827 σ	20
4	Berkely	Sintering	2 hr/900°C	5.2961 σ	29
5	Berkely	Sintering	2 hr/900°C	5.2858 σ	23
6	Berkely	Sintering	2 hr/900°C	5.2865 σ	23
7	Berkely	Sintering	2 hr/900°C	5.2874 σ	24
8	Berkely	Sintering	2 hr/900°C	5.2911 σ	26
9	Berkely	Sintering	2 hr/900°C	5.2910 σ	26
10	Berkely	Sintering	2 hr/900°C	5.2883 σ	25
11	Berkely	Sintering	2 hr/900°C	5.2868 σ	24
12	Berkely	Sintering	2 hr/900°C	5.2909 σ	26

σ Lattice parameters measured by Dr.H.W.King at Berkely.

Table 4.2.

Treatment of Nb-Sn with Hydrochloric Acid

Temperature °C	Time min.	Lattice Parameter After Treatment Å
-	0	5.2912
23	150	5.2906
60	90	5.2906
85	80	unmeasurable
90	90	unmeasurable

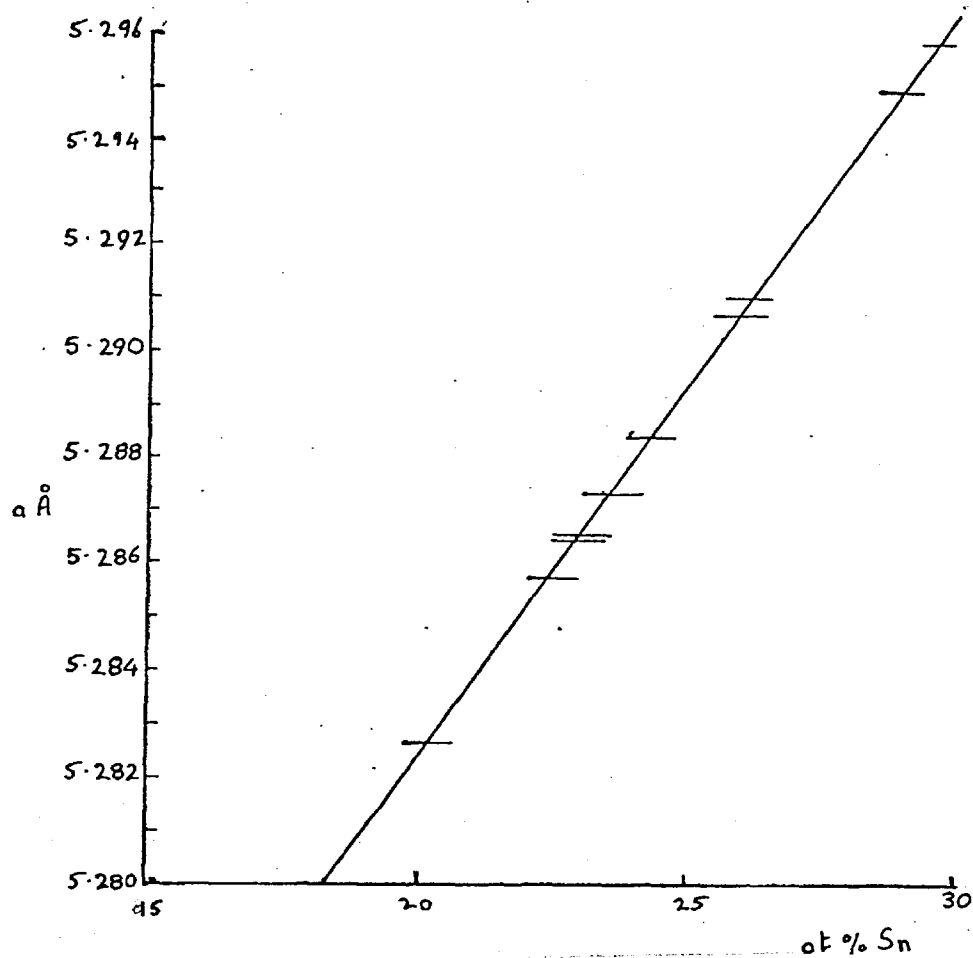


Figure 4.1a. The composition dependence of the lattice parameter of Nb-Sn.

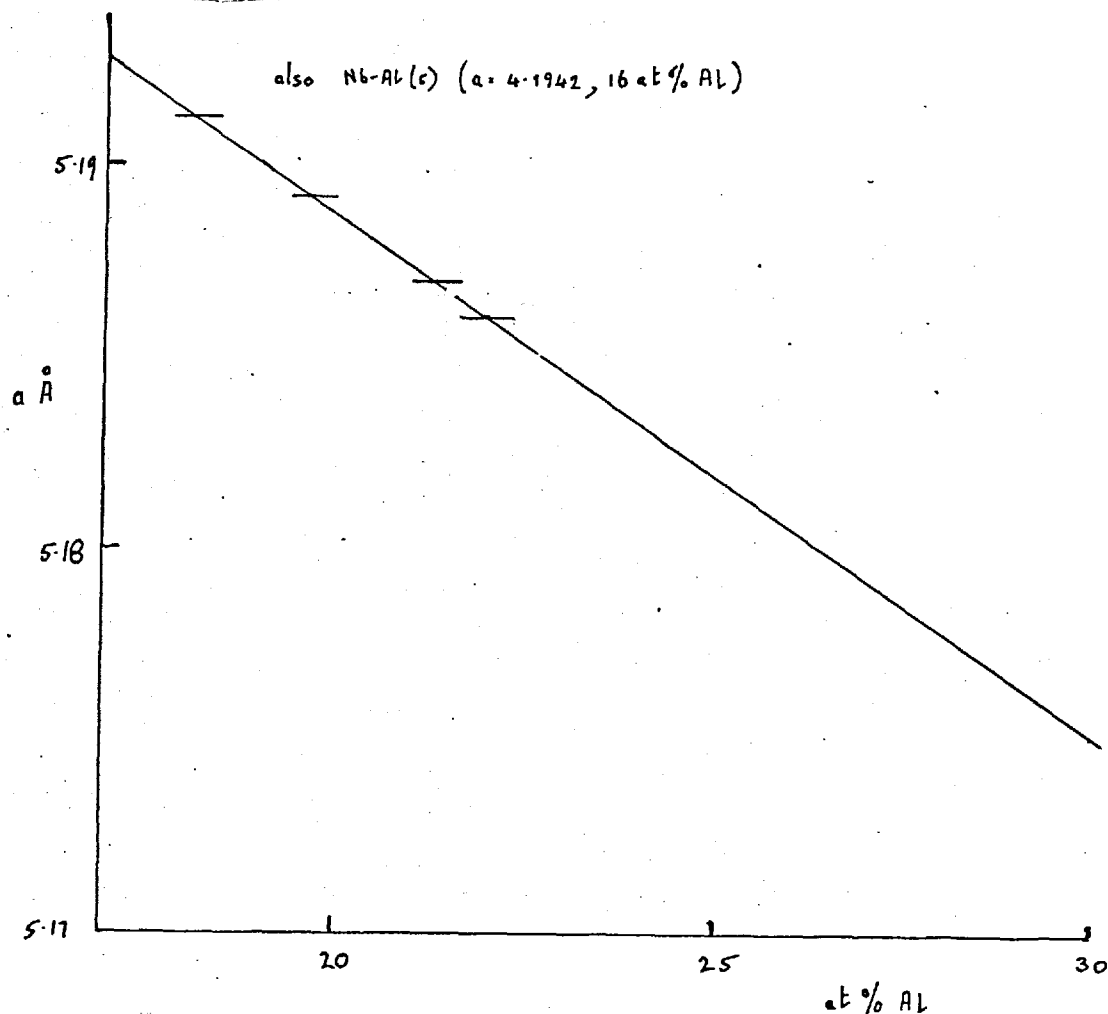


Figure 4.1b. The compositional dependence of the lattice parameter of Nb-Al.

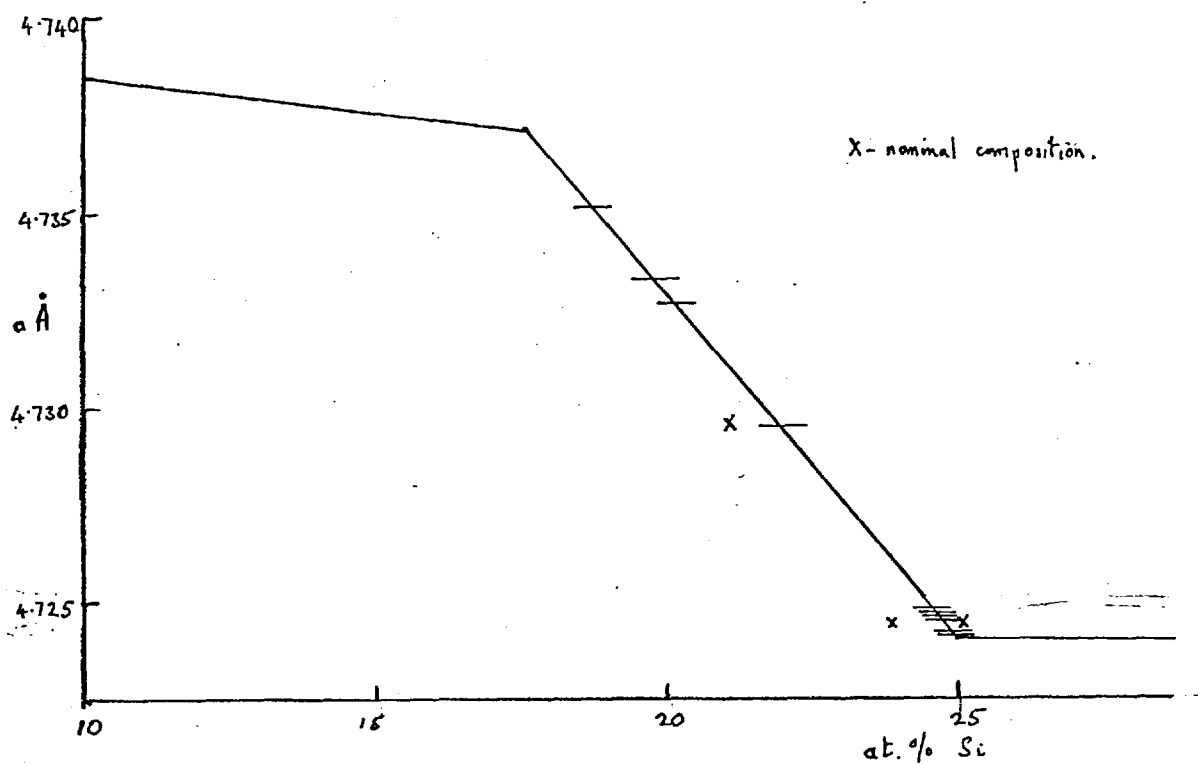


Figure 4.1c. The compositional dependence of the lattice parameter of V-Si.

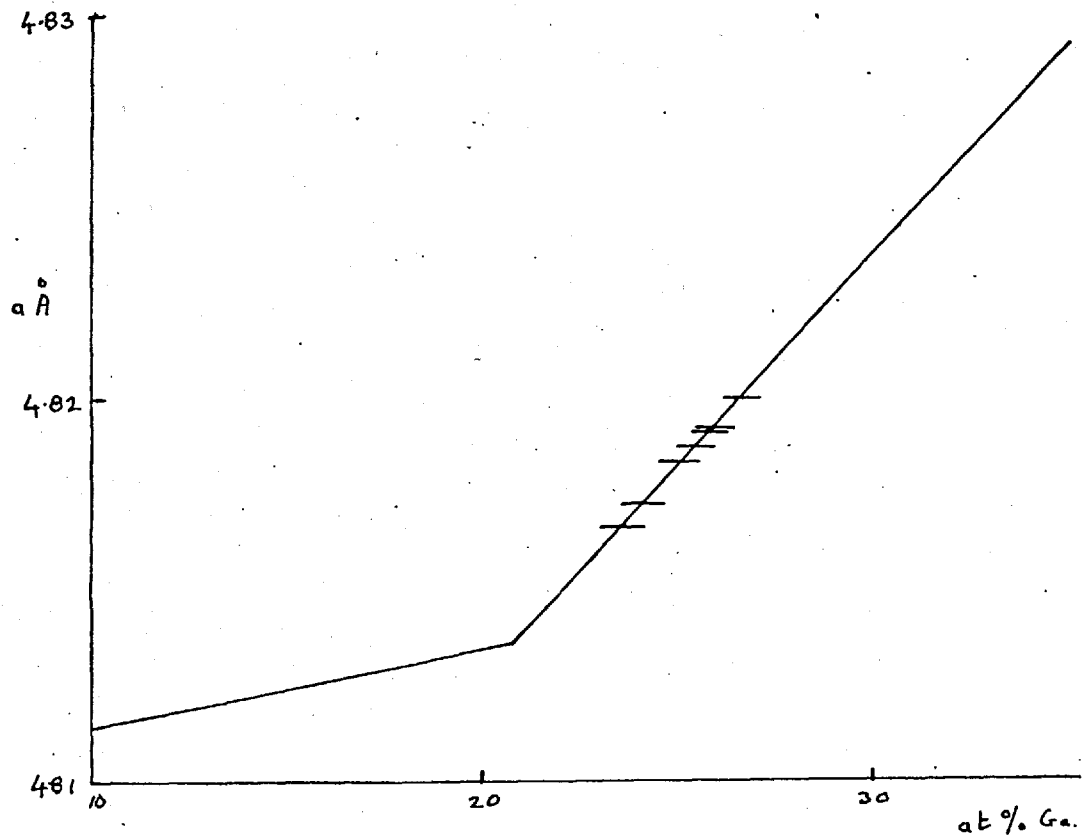


Figure 4.1d. The compositional dependence of the lattice parameter of V-Ga.

and for times given in Table 4.2. After treatment at 85°C and 90°C so much line broadening was observed on the Debye-Scherrer films that it was impossible to measure the high angle line positions. This implies that hydrogen has been absorbed and the lattice strained. Moreover, a comparison of the low angle lines on the films H1 and H4 indicated that the lattice had expanded considerably, indeed to a higher lattice parameter than that measured for the original material. It is interesting to note, however, that after the acid treatment at 60°C , which approximated to the conditions originally used to dissolve away the free tin (Old 1969), only a small increase in lattice parameter and very little strain were observed, as compared to the large increase in lattice parameter with little strain in the original material.

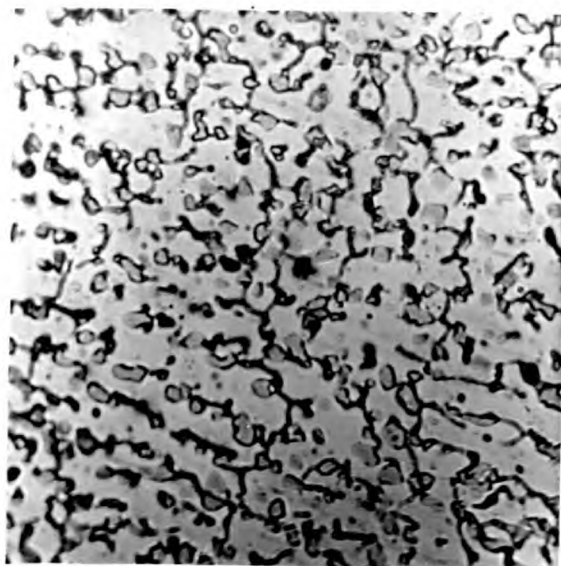
4.2 Photomicrography

All the samples, except those from Berkely, were examined metallographically and a representative selection of micrographs are shown in figures 4.2a and 4.2b. No micrographs are shown of Nb-Sn as the Harwell samples were either powder or single crystals. A single crystal was examined and found to contain no second phase.

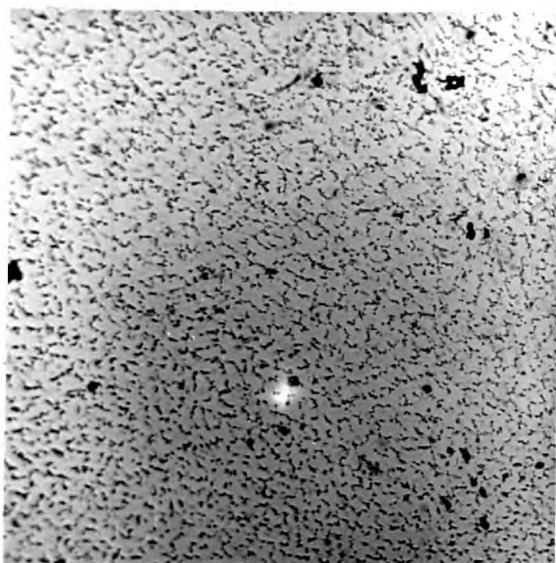
The V-Si microstructures reflect the methods of preparation and heat treatment. The arc-cast samples e.g. V-Si (10) show a dendritic structure even after treatment at 1000°C , while all those annealed at 1350°C e.g. V-Si (3), V-Si (1) and V-Si (11) show uniaxed grain structures which are similar in spite of the differences in deduced composition between the three samples. In V-Si(11), the V-rich end of the β -W phase, the second phase observed is the α -V solid solution, while in V-Si (1) at the Si-rich end of the β -W phase the second phase is V_5Si_3 (Finlayson 1968). From their deduced compositions it is probable that in V-Si (10), the second phase observed is the α -V solid solution and V-Si (2) and V-Si (3), the phase V_5Si_3 , which has a tetragonal Ni_3P type of structure (Bruning 1967).



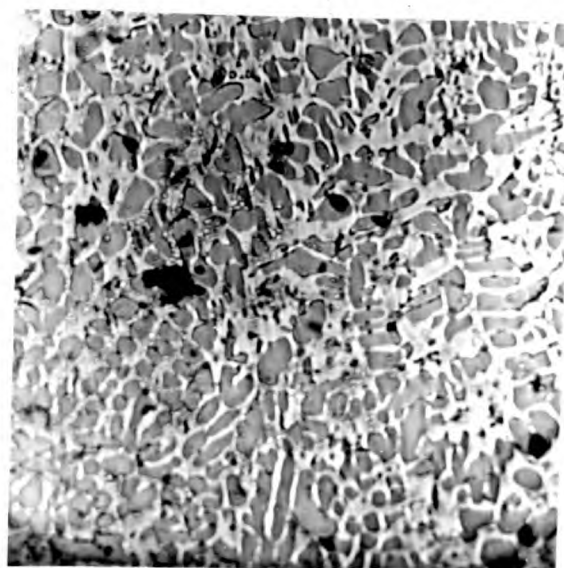
V-Si(1)



V-Si(2)



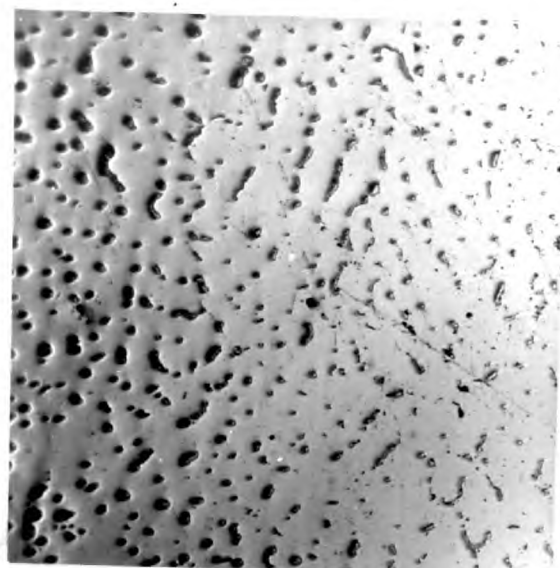
V-Si(3)



V-Si(5)

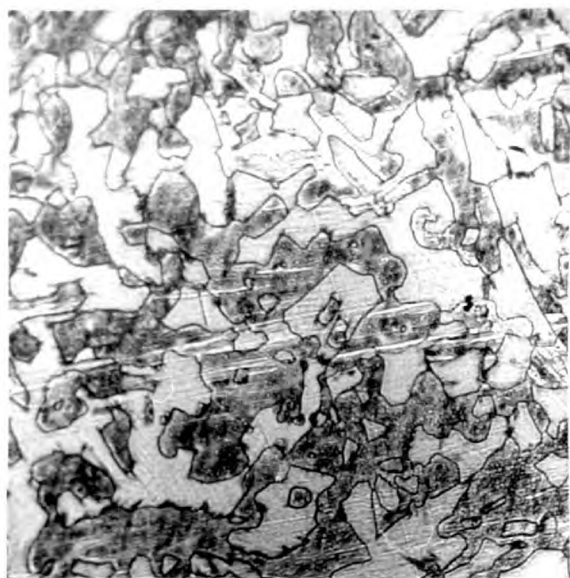


V-Si(10)

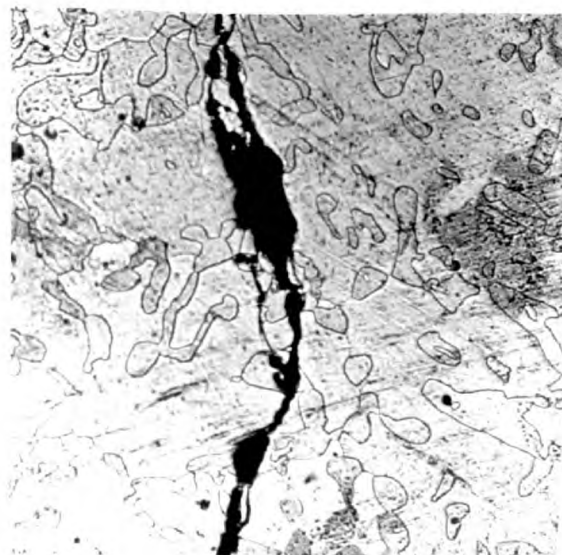


V-Si(11)

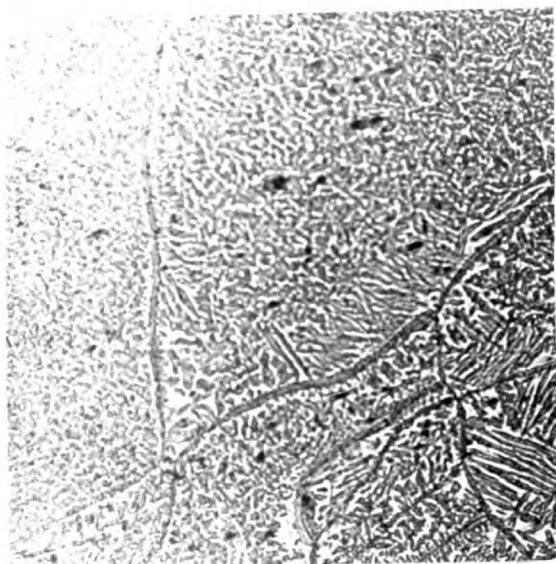
Figure 4.2a. Micrographs (magnification x 64)



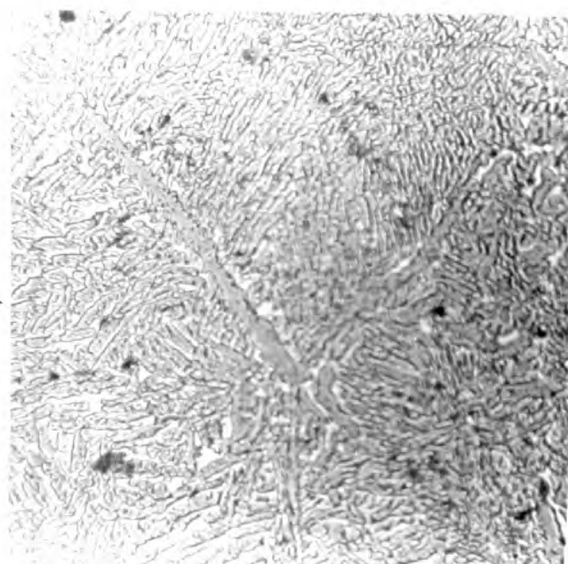
V-Ga(2)
(x 64)



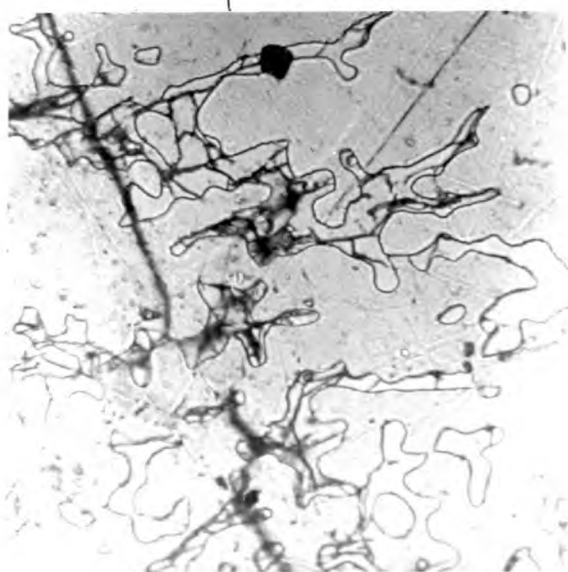
V-Ga(5)
(x 64)



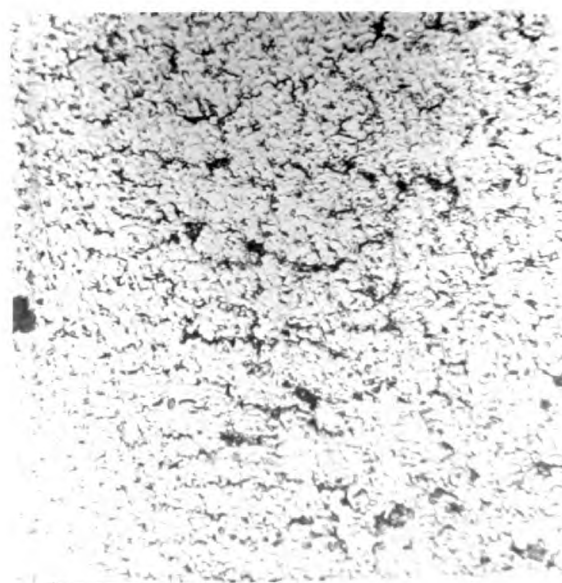
V-Ga(7)
(x 64)



V-Ga(9)



Nb-Al(1)



Nb-Al(3)

Figure 4.2b. Micrographs (magnification x 184)
except where specified

The induction melted samples e.g. V-Si (2) show a microstructure similar to that of the arc-cast samples annealed at 1350°C , in spite of not being annealed at high temperature, and V-Si (5) (nominally 30 at % Si) has a microstructure similar to this in which the second phase is probably V_5Si_3 .

The V-Ga alloys were all arc-cast except V-Ga (1), the method of preparation of which is unknown but may also have been arc-cast. This sample was difficult to polish in that it tended to fragment, possibly due to impurities at the grain boundaries. A dendritic structure was observed in V-Ga (7) and V-Ga (9), in spite of the difference in heat treatments. V-Ga (7) was held for a day at 1400°C before being treated for a week at 1000°C while V-Ga (9) received only the 1000°C treatment. In V-Ga (2) and V-Ga (5), the dendrites were also present but appeared in cross-section, which probably accounts for the crack observed on V-Ga (5). These two samples were originally parts of the same casting and the second heat treatments have caused the composition and microstructural differences observed. V-Ga (2) annealed at the low temperature for a long time shows larger areas of the second phase and has a lower lattice parameter than V-Ga (5) which was annealed at 1250°C for one week. At this temperature the stable phase may be the "Cs-C1" type found by Savitskii et al. (1966). If this is so the change in lattice parameter and, presumably, composition may be explained. All the other heat treatments do not take the alloys within the stable area of the "Cs-C1" phase (1400°C is above the high temperature limit of the phase), though some of the second phase observed may arise from the freezing in of this phase in the original water quench to which the samples were subjected after being cast.

Of the Nb-Al samples, in Nb-Al (1) the second phase appears in large connected areas, probably the cross-sections of dendrites. This is the only sample which is in the β -W phase range at the peritectic temperature and will have formed directly from the liquid, while in Nb-Al (3) the finer dispersion of the second phase indicates that the

β -W phase formed at a lower temperature for the α -Nb solid solution. For Nb-Al (4) and (5), however, both in the micrographs (not shown) and in the X-ray photographs, no second phase is visible. As they have an apparent lower Al content than Nb-Al (3), and will have thus formed at lower temperatures, the reasons for this are not immediately obvious.

4.3 X-Ray Measurements at High Temperatures

Thermal expansion and X-ray intensities were measured on a series of V-Si alloys across the composition range of the β -W phase and on two alloys from each of the systems V-Ga, Nb-Al and Nb-Sn. In the V-Ga and Nb-Al systems the two samples were chosen in different parts of the β -W composition range and in the Nb-Sn system the measurements were made principally to investigate the drop in lattice parameter after heat treatment in the diffusion prepared samples.

4.3a Thermal Expansion Measurements

The change in lattice parameter for each alloy at each temperature was computed using the method described in section 3.4f and computer programme LATEXP. The lines measured were 222, 320, 321 and 400. The results are given in Table 4.3 and plotted in figures 4.3 to 4.12, on which the lines joining the experimental points indicate only the order in which the temperatures were reached, and the error bars indicate the difference between the results from the films on the two sides of the camera. There is one defect in the method of calculation of the lattice expansion, in that changes are measured relative to the initial room temperature film. If there is an error in the measurement of this film, then it will be reflected in all the subsequent lattice expansion results. An example of this may be for the sample Nb-Sn (2) where an anomalous drop in lattice parameter is observed on returning to room temperature. As the intensity ratio

Thermal Expansion Data.

Nb-Sn 1

T °C	20	483	631	801	890	972	880
a Å	5.2950	5.3173	5.3222	5.3553	5.3435	5.3533	5.3601
	587						
	5.3498						

Nb-Sn 2

T °C	20	500	730	932	1069	680	20
a Å	5.2912	5.2945	5.2972	5.3222	5.3236	5.3141	5.2723

V-Si 2

T °C	20	550	620	810	925	1031	1245
a Å	4.7242	4.7227	4.7618	4.7659	4.7693	4.7907	4.7884
	816	20					
	4.7609	4.7279					

V-Si 3

T °C	20	554	801	1052	811	520	20
a Å	4.7245	4.7471	4.7570	4.7761	4.7998	4.7442	4.7502

V-Si 4

T °C	20	441	660	822	932		
a Å	4.7245	4.7472	4.7539	4.7643	4.7614		

V-Si 9

T °C	20	395	715	919	1078	739	
a Å	4.7295	4.7614	4.7667	4.7804	4.7757	4.7641	

V-Si 10

T °C	20	510	701	894	1024	1112	806
a Å	4.7327	4.7540	4.7492	4.7702	4.7888	4.7690	4.8059

V-Si 11

T °C	20	593	817	1036	1260		
a Å	4.7333	4.7601	4.7665	4.7787	4.7994		

V-Si 12

T °C	20	481	632	794	946	1059	
a Å	4.7352	4.7362	4.7670	4.7714	4.7761	4.7989	

Table continued overleaf.

Table 4.3. continued.

V-Ga 1

T ^{°C}	20	594	786	976	1107	980
a Å	4.8172	4.8425	4.8529	4.8767	4.8182	4.7996

V-Ga 6

T ^{°C}	20	482	640	798	941	832	638
a Å	4.8203	4.8410	4.8365	4.8505	4.8544	4.8511	4.8441

Nb-Al 2

T ^{°C}	20	367	740	922	1072
a Å	5.1871	5.1928	5.2100	5.2145	5.2388

Nb-Al 5

T ^{°C}	20	538	726	891	1023	627	20
a Å	5.1942	5.2068	5.2124	5.2182	5.2217	5.2395	5.2325

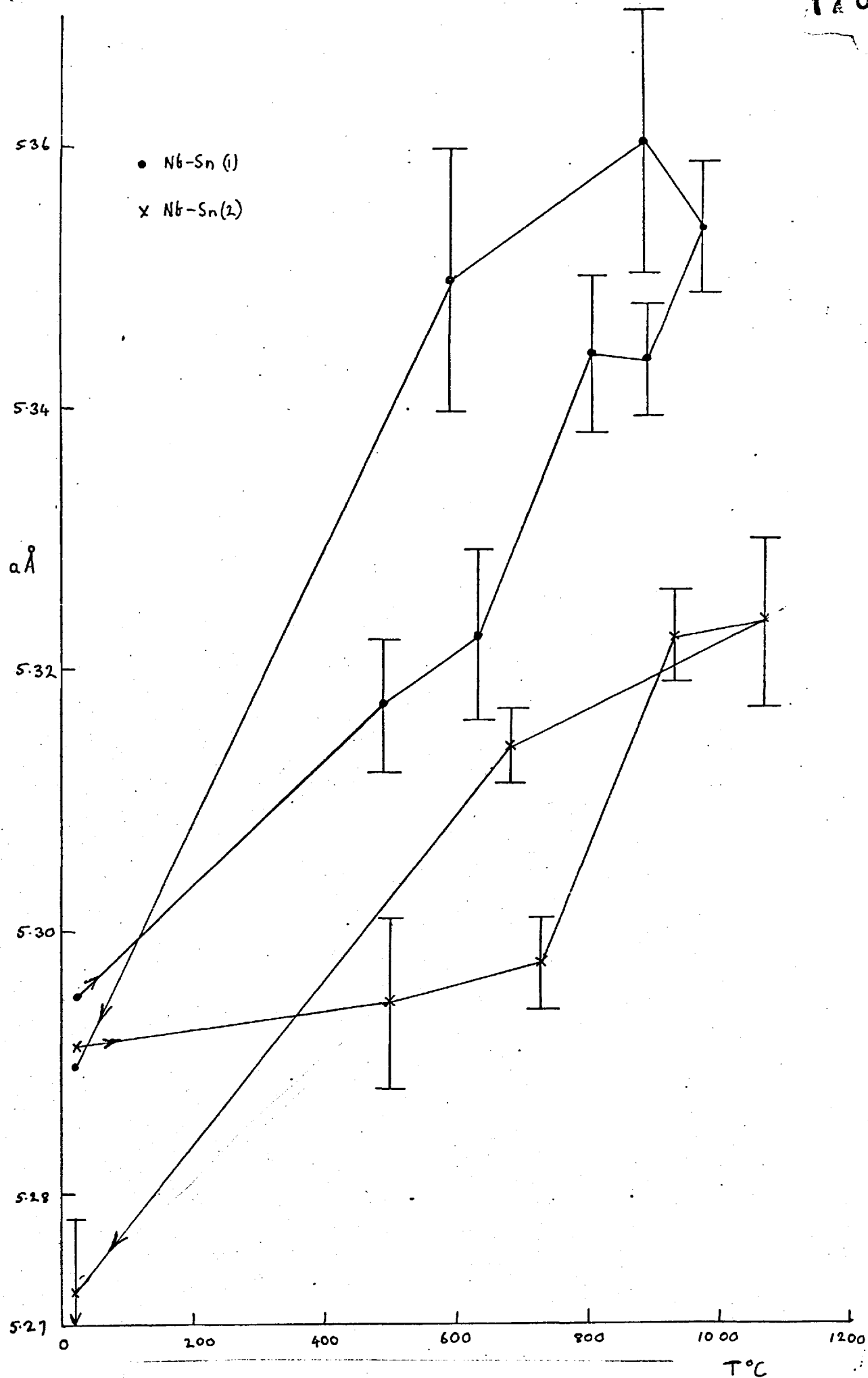


Figure 4.3. Thermal expansion of Nb-Sn(1)
Nb-Sn(2)

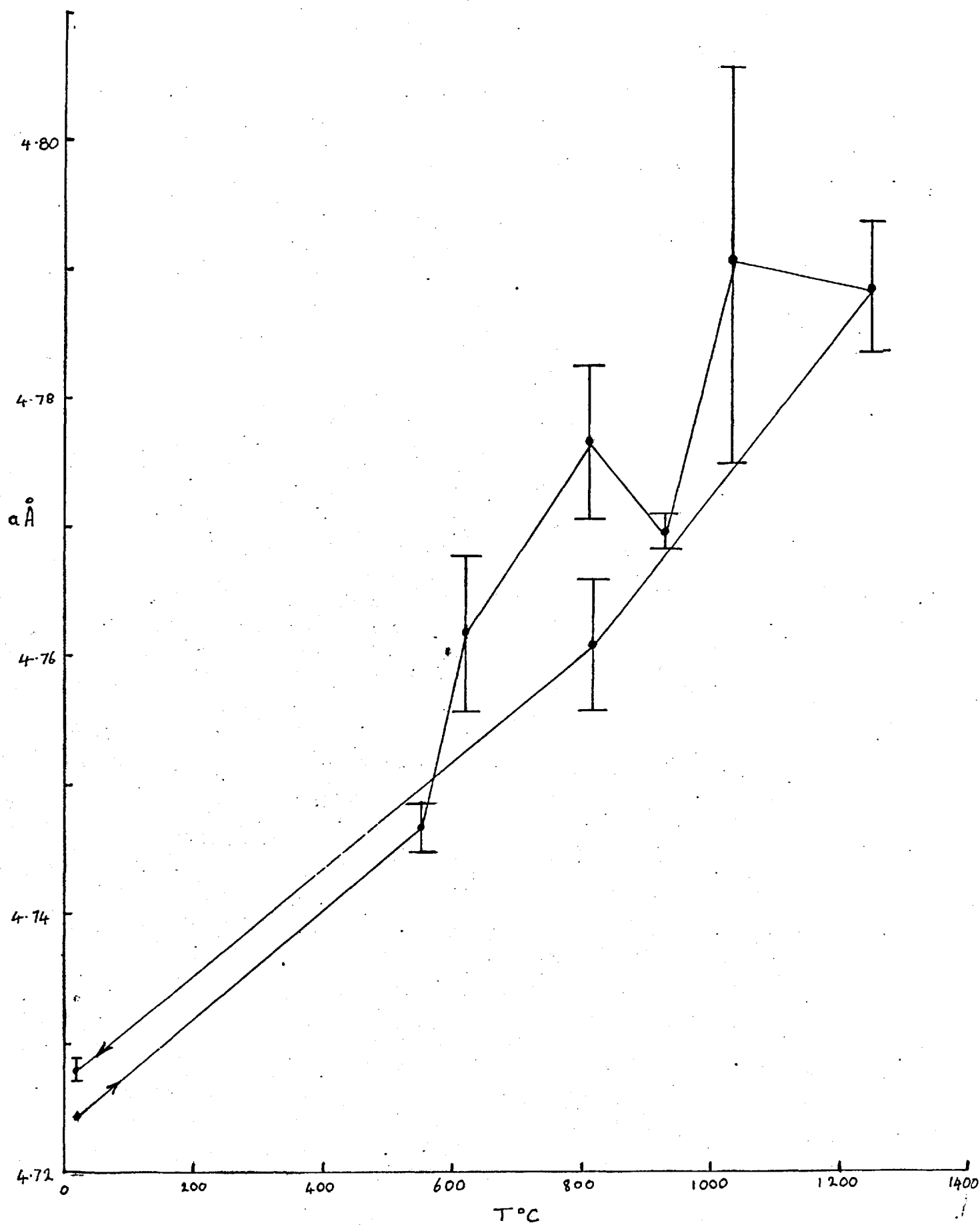


Figure 4.4. Thermal expansion of V-Si(2).

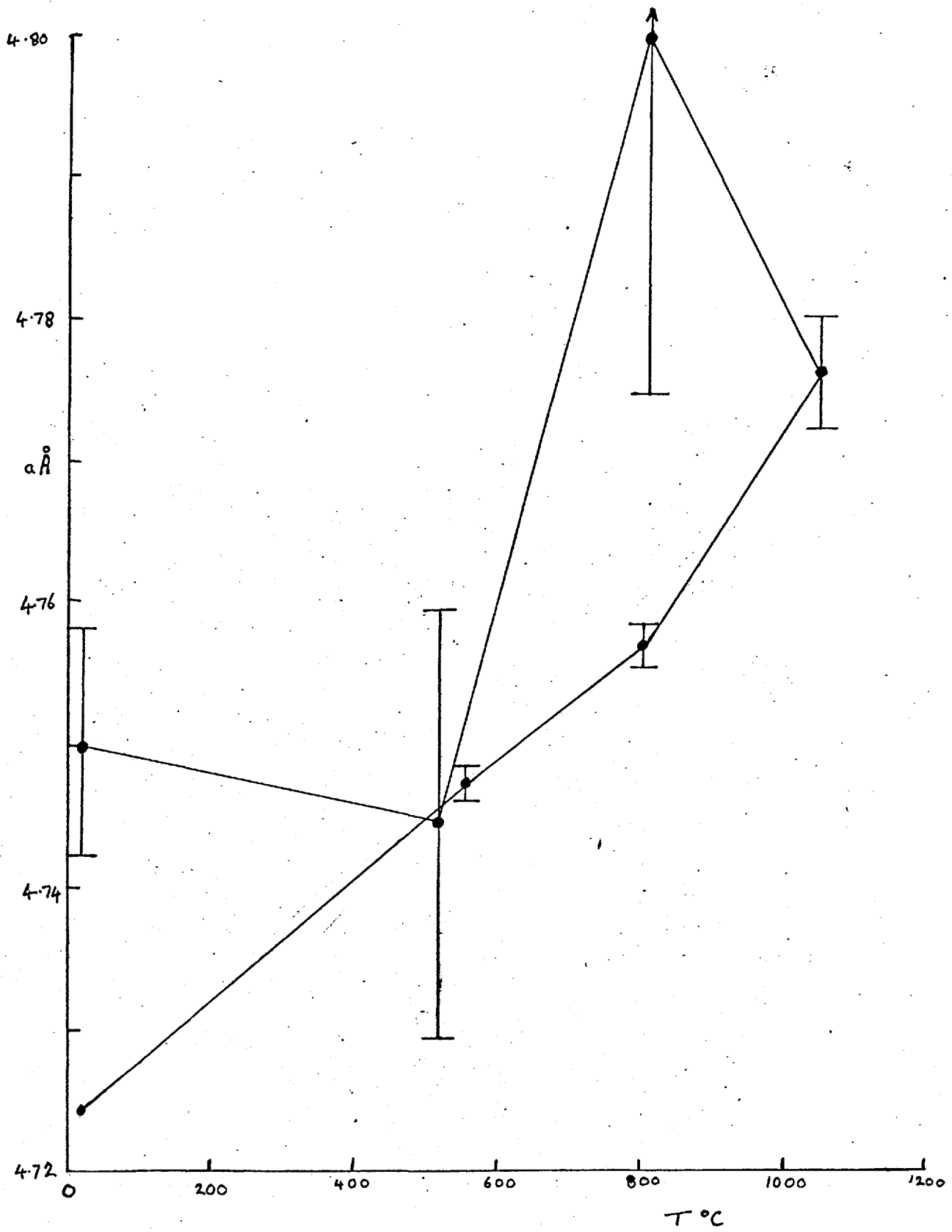


Figure 4.5. Thermal expansion of V-Si(3).

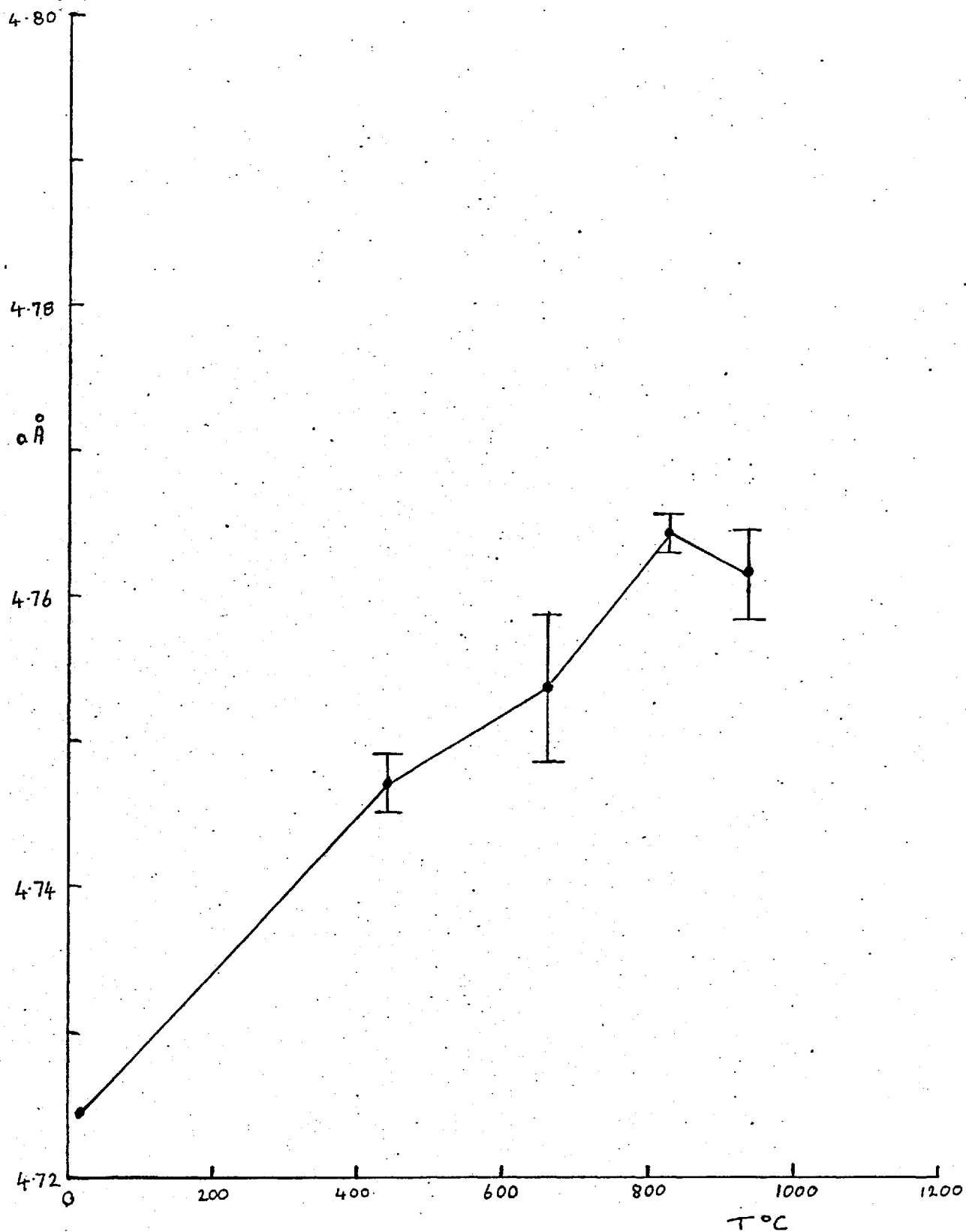


Figure 4.6. Thermal expansion of V-Si(4).

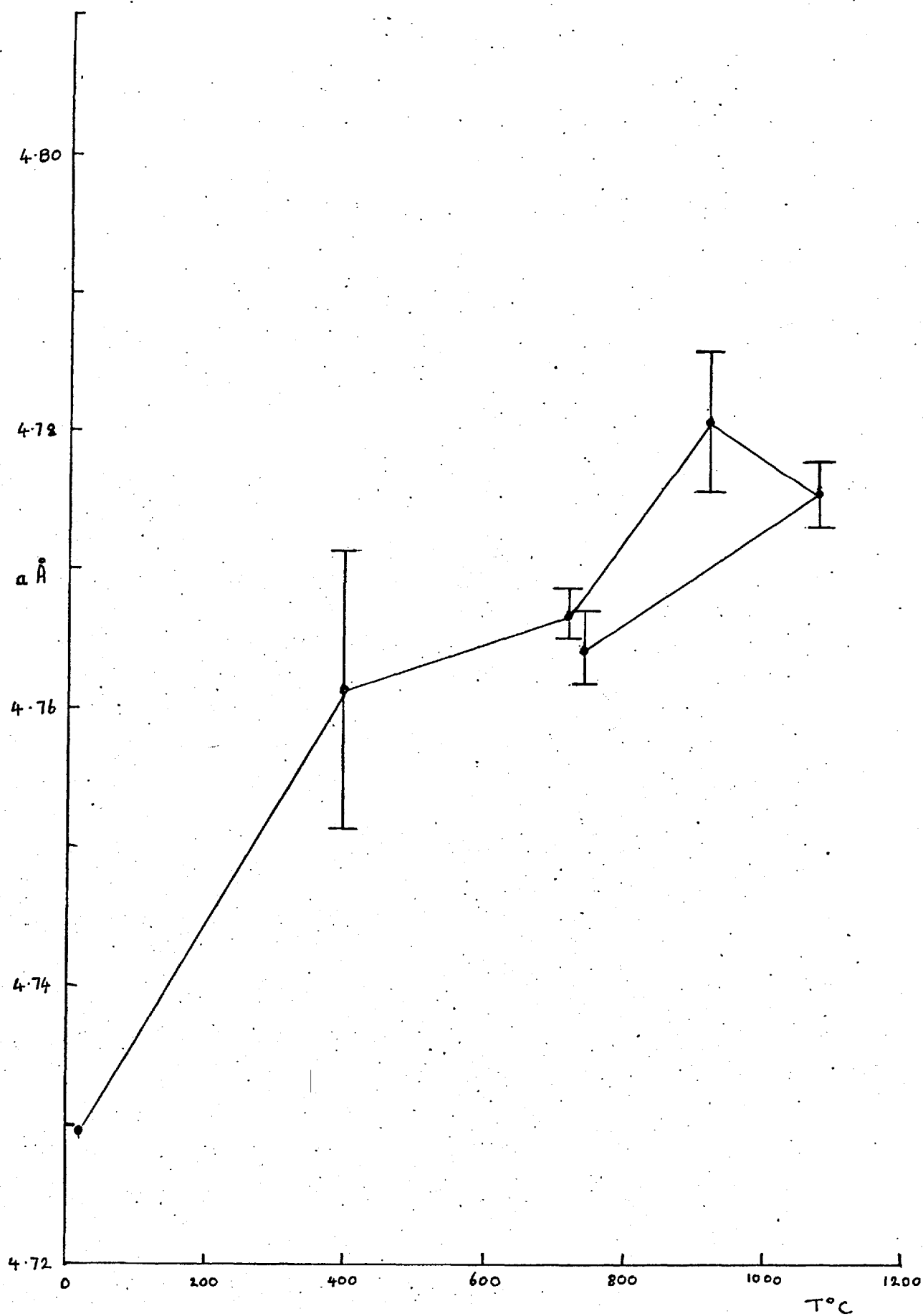


Figure 4.7. Thermal expansion of V-Si(9).

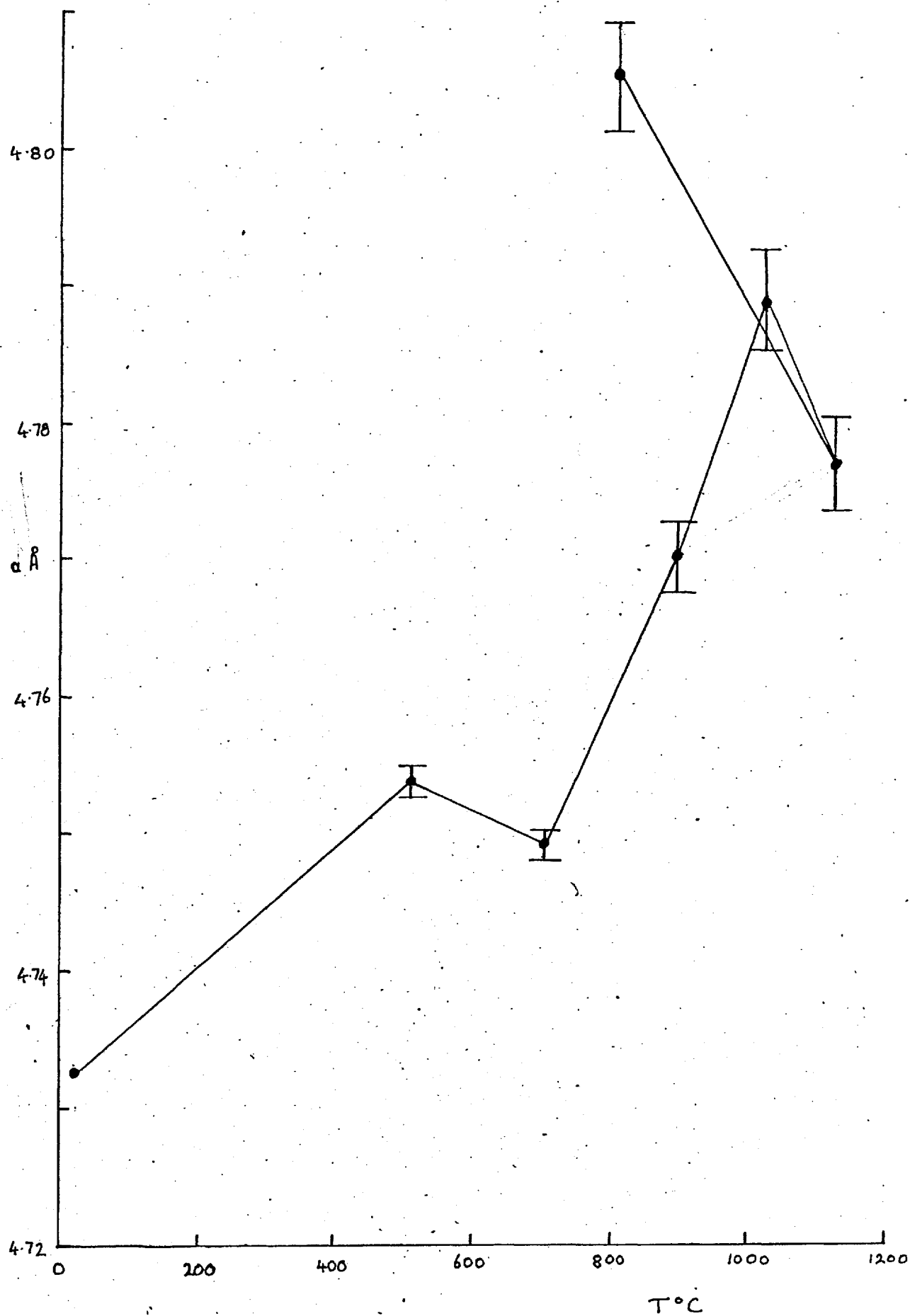


Figure 4.8. Thermal expansion of V-Si(10).

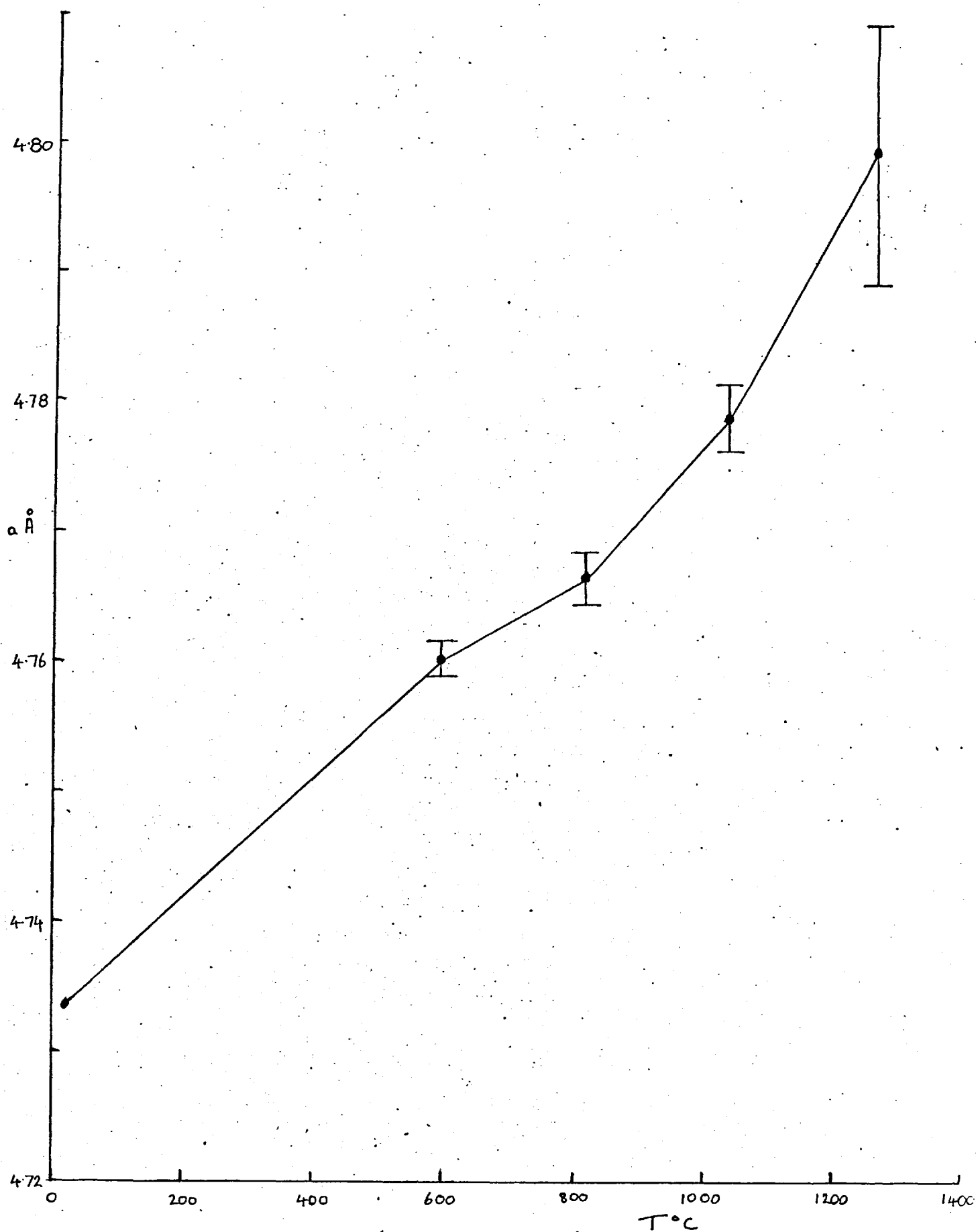


Figure 4.9. Thermal expansion of V-Si(11).

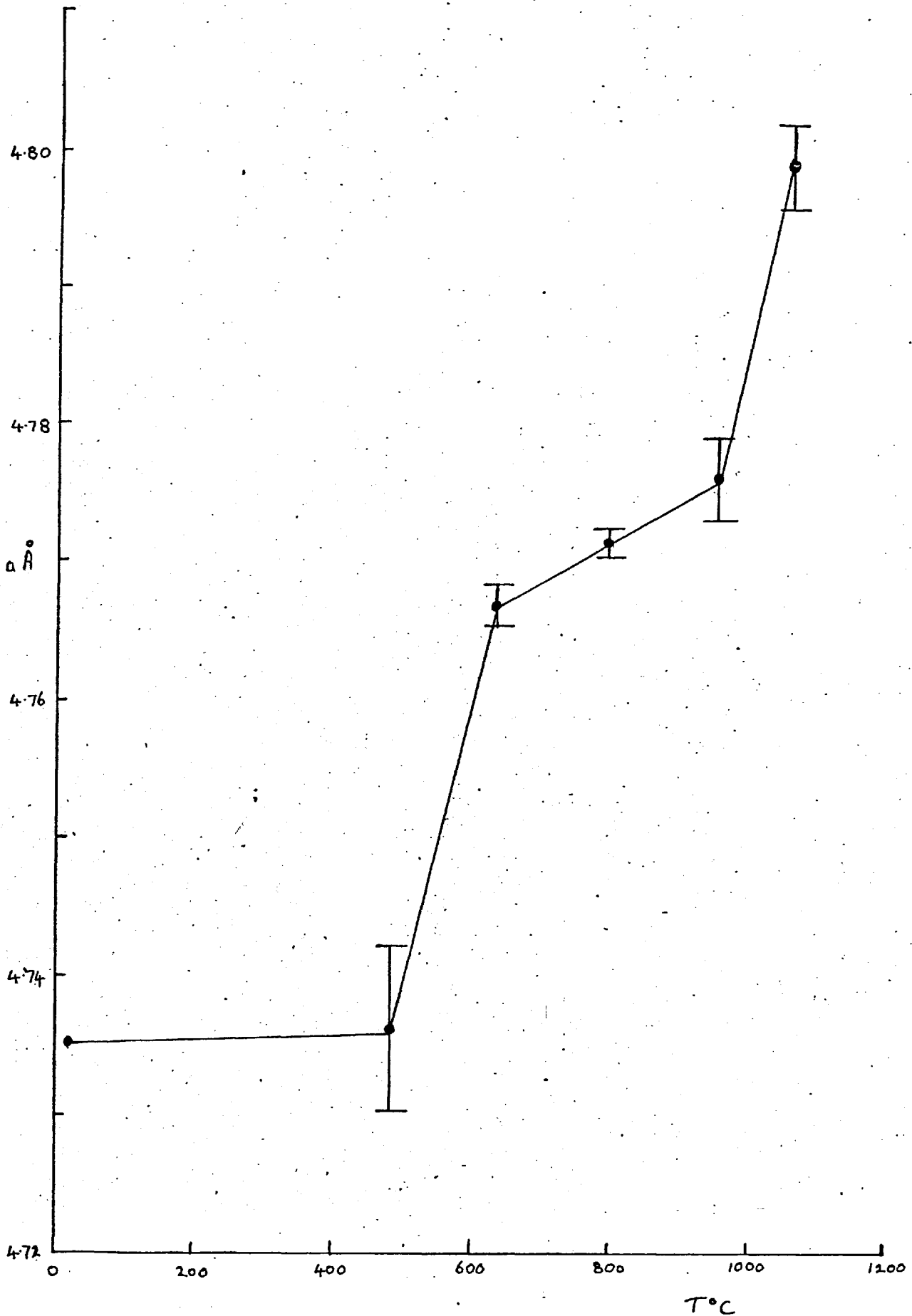


Figure 4.10. Thermal expansion of V-Si(12) .

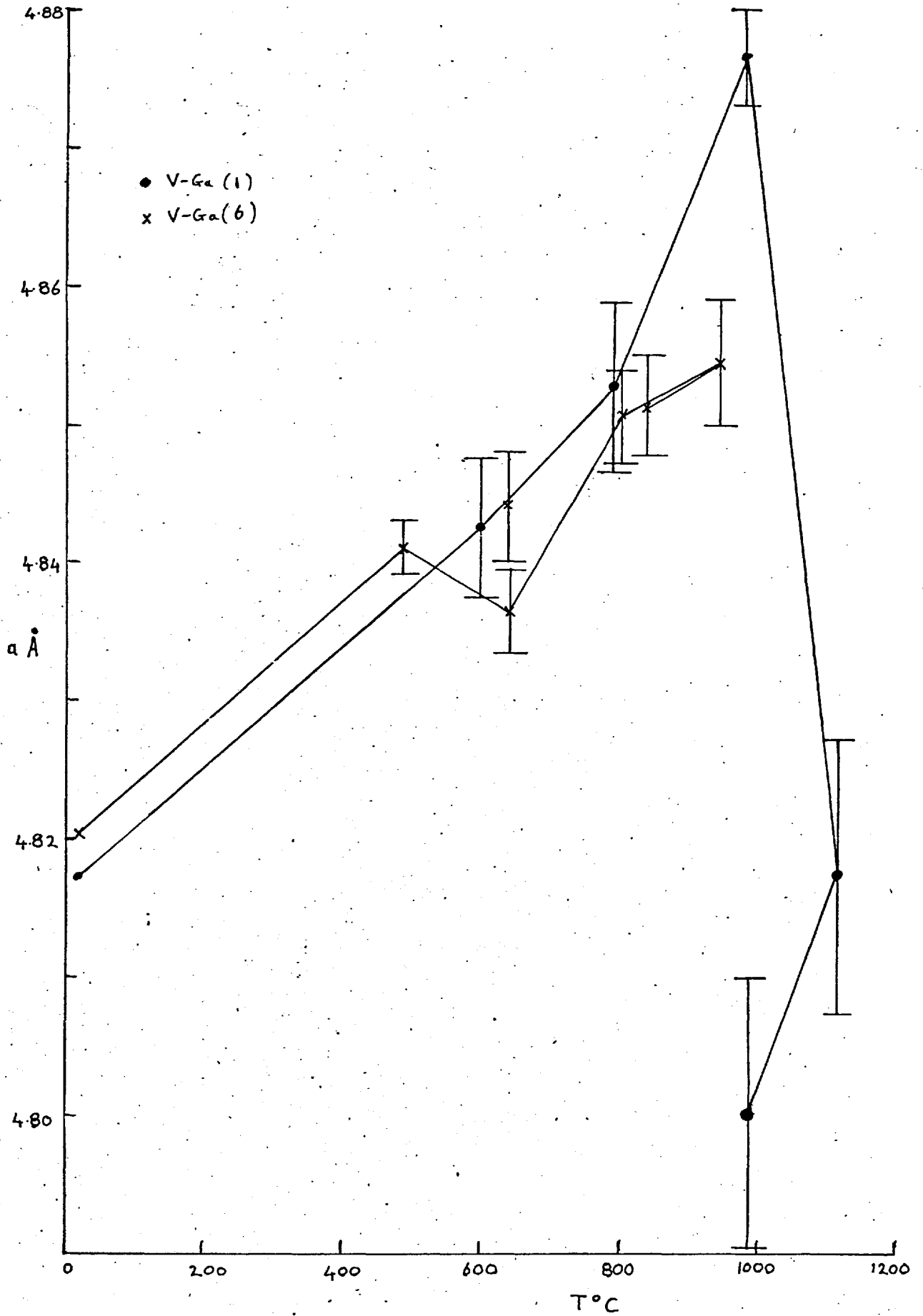


Figure 4.11. Thermal expansion of V-Ga(1) and V-Ga(6).

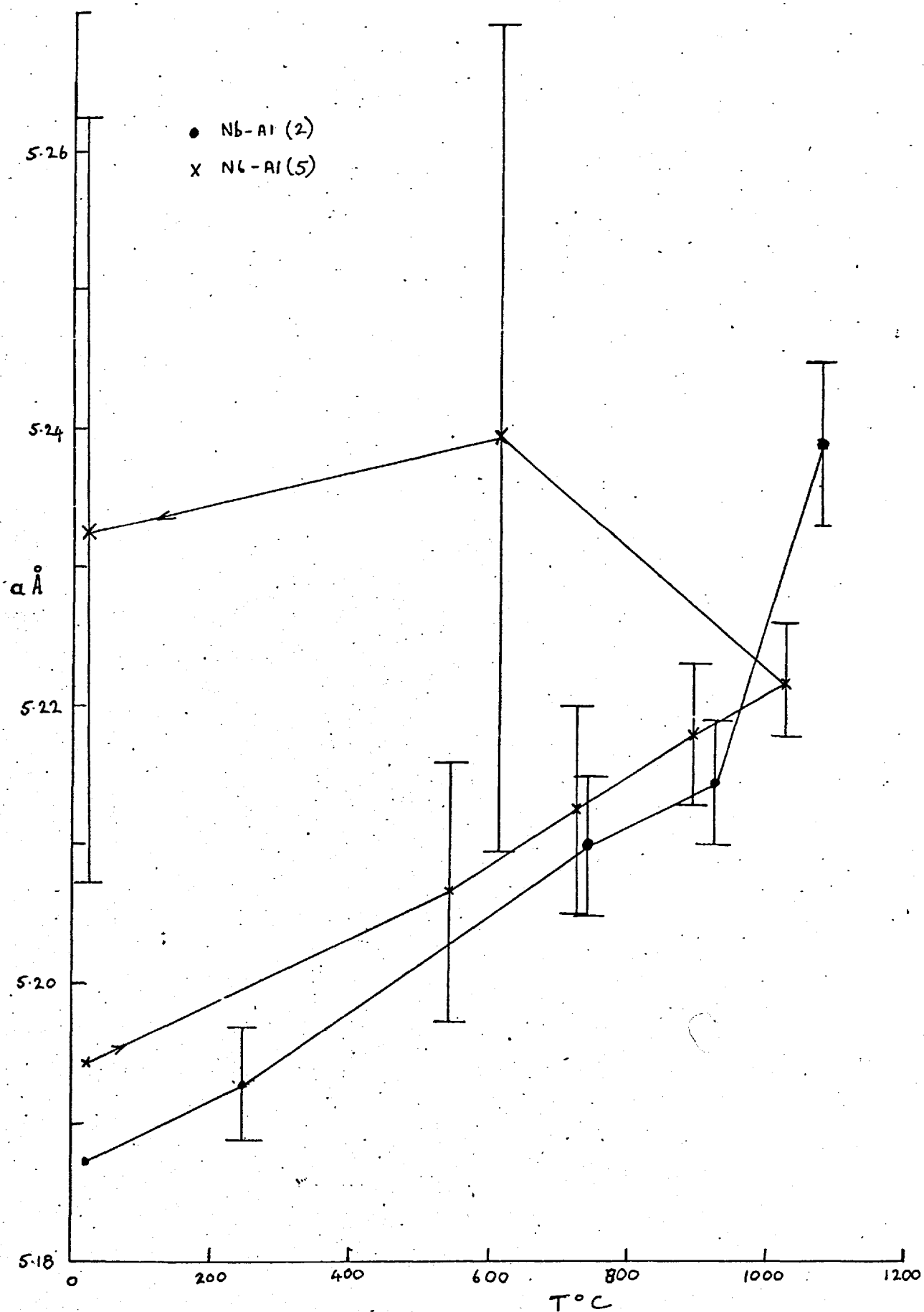


Figure 4.12. Thermal expansion of Nb-Al(2) and Nb-Al(5).

seems to be the same before and after heating, an error in the first measurement appears to be the reason for this anomalous result. The error bar on these results, however, indicate that the two films give similar results, making an error less likely.

The changes in slope of the thermal expansion curves may arise from errors in measurement as described above but an alternative cause is a change in composition of the β -W phase. Such a change will also be reflected in the intensity measurements as will be discussed in the next section. Extreme examples of this are in V-Ga (1) and Nb-Al (2), particularly the latter where a complete phase transformation takes place. Of the V-Si samples those with high room temperature lattice parameters appear to exhibit this effect more than those with low lattice parameters, probably as the Si content of the β -W phase increases.

4.3b X-Ray Intensity Measurements

The X-ray intensities were measured from the same films as the thermal expansion data and the lines measured were also the same, namely the 222, 320, 321 and 400 reflections. The data taken from the densitometer charts are presented in Table 4.4. The values listed are peaks above a trapezoidal background. As the positioning of this background line was not exact the error (± 2) is proportionally greatest in the lowest intensities. The values are plotted in figures 4.13 to 4.24, not as measured but as ratios I_{hkl}/I_{400} . This normalises the intensities. The 400 intensity was chosen as the divisor as this is a fundamental line for a stoichiometric alloy. For a non-stoichiometric alloy or one containing vacancies this is not strictly true but the intensity of this line is always comparable with that of the other lines for all the systems studied. So as not to make the plots too complex no error bars are shown but an average difference between the two films is shown. The lines joining the spots indicate the order in which the temperatures were

Table 4.4.

X-Ray Intensity Data

Sample No.	Temp. °C	Intensity							
		Right Film				Left Film			
		222	320	321	400	222	320	321	400
V-Si 2	20	46.4	72.8	75.7	42.0	44.6	69.6	71.5	42.2
	550	39.6	62.8	66.0	33.1	35.5	64.6	67.3	33.4
	620	32.6	60.7	56.0	30.5	37.5	76.5	76.0	39.0
	810	40.1	68.7	68.2	38.1	38.1	63.6	62.5	32.0
	925	44.3	72.8	68.3	36.0	41.9	68.7	62.3	32.0
	1031	42.2	69.6	66.1	31.2	47.0	71.8	71.4	34.5
	1245	49.7	70.3	57.1	33.8	48.5	69.8	54.7	27.2
	816	49.3	63.8	49.4	31.0	44.0	62.0	49.5	26.5
	20	47.7	65.5	52.6	32.0	44.1	58.1	46.3	29.0
V-Si 3	20	39.9	71.6	81.3	38.1	39.5	69.5	77.5	39.2
	554	45.9	72.9	76.1	39.9	45.4	74.9	78.6	38.0
	801	42.6	67.7	70.7	36.6	41.6	65.6	70.5	33.1
	1052	20.7	36.8	40.3	19.5	49.0	77.7	74.6	36.6
	811	32.2	56.0	51.2	23.0	35.5	60.0	55.5	26.0
	520	28.5	50.6	53.6	29.0	32.0	45.4	43.0	27.0
V-Si 4	20	37.2	60.0	62.2	33.0	40.8	65.2	67.9	36.2
	441	34.4	58.6	59.9	27.3	38.8	65.8	66.9	37.7
	660	33.5	60.1	65.0	30.7	35.0	55.2	60.6	28.4
	872	37.7	58.9	63.6	34.0	35.6	60.0	59.6	28.6
	932	37.8	62.9	65.7	36.0	43.7	67.7	69.6	37.6
V-Si 9	20	22.5	41.6	48.2	38.6	25.5	45.1	53.1	41.8
	ε 395	23.6	42.8	47.8	34.7	20.7	39.8	45.4	35.7
	ε 715	20.6	36.0	43.6	34.0	22.9	40.1	46.3	35.8
	ε 919	19.8	37.9	40.7	26.6	20.4	38.0	40.3	28.0
	ε 1078	20.0	35.2	27.8	26.0	21.8	31.3	22.5	21.8
	ε 739	25.2	40.0	33.4	28.0	20.7	36.3	31.7	22.0
V-Si10	20	23.0	45.7	54.1	37.7	24.8	47.2	57.3	40.3
	ε 510	18.1	33.0	39.6	29.0	26.1	42.0	51.2	40.2
	ε 701	21.0	35.5	40.9	33.3	25.5	40.9	47.0	37.0
	ε 894	20.7	35.4	40.5	31.5	22.5	36.8	40.9	30.5
	ε 1024	22.2	33.8	35.3	28.6	25.3	37.8	42.8	32.1
	ε 1112	34.4	45.1	47.6	37.7	33.2	46.9	45.6	34.2
	ε 806	31.6	45.2	41.9	30.6	36.2	52.0	47.9	32.0
V-Si11	20	33.0	57.6	69.6	36.1	31.9	61.6	70.6	37.7
	593	27.1	50.7	54.8	26.6	32.3	61.0	66.6	36.1
	817	39.9	57.7	65.2	29.6	31.4	54.8	58.9	29.0
	1036	28.7	50.2	54.0	28.9	28.6	50.6	54.2	29.2
	ε 1260	31.7	42.2	30.2	20.5	41.6	46.3	35.2	21.0
V-Si12	20	22.6	47.6	58.5	27.4	19.0	39.0	48.8	21.5
	481	21.5	45.0	51.1	26.2	24.0	46.5	61.2	33.5
	632	35.6	58.9	69.9	38.5	31.3	52.7	64.1	34.0
	794	33.8	52.5	60.1	36.5	36.7	56.2	62.5	36.9
	ε 946	41.3	65.2	68.2	38.4	40.0	63.0	67.5	38.0
	ε 1059	31.5	51.5	57.3	25.6	27.5	55.0	63.0	28.8

ε denotes the presence of lines due to second phase.

Table continued overleaf.

Table 4.4. continued.

Nb-Sn1	20	13.2	48.6	93.4	36.8	14.1	46.7	91.9	35.1
	483	10.0	34.6	69.2	26.3	11.6	40.3	78.5	29.1
	631	19.0	54.7	78.1	45.5	18.1	50.9	71.5	41.0
	801	25.5	52.7	92.8	47.3	23.3	61.0	90.7	45.5
	890	16.1	48.0	84.8	39.1	17.1	49.7	81.9	38.9
	972	16.0	52.8	78.9	33.7	16.8	48.9	78.6	32.1
	880	17.4	47.4	66.7	22.4	17.0	47.2	69.9	26.0
	587	20.3	52.8	82.7	34.2	21.6	51.9	78.2	29.1
Nb-Sn2	20	6.0	16.2	29.9	12.3	8.4	18.1	37.8	15.5
	500	14.0	25.6	38.8	18.1	14.1	21.8	36.9	16.9
	730	11.9	32.0	58.5	24.1	13.7	39.3	60.8	22.5
	932	9.0	22.2	34.0	12.4	6.7	19.4	31.5	14.7
	1069	22.3	43.0	68.4	28.6	23.6	42.6	66.0	23.5
	680	27.3	49.2	77.8	32.3	25.5	45.7	73.1	33.8
	20	24.7	50.0	74.7	36.8	26.8	56.5	90.3	40.2
V-Ga 1	20	6.5	26.3	71.1	23.1	6.0	23.9	58.3	16.3
	594	5.0	22.3	59.5	18.0	6.5	21.0	59.3	17.0
	786	5.0	23.5	57.6	20.9	5.0	22.1	62.6	21.3
	ε 976	20.7	21.5	50.1	19.0	17.6	23.8	44.9	14.0
	ε 1107	20.0	20.4	34.0	16.8	28.0	22.0	35.6	16.5
	ε 980	24.5	30.0	46.5	27.3	24.3	28.6	47.3	26.5
V-Ga 6	20	10.8	30.4	64.8	28.0	7.0	26.8	59.0	28.6
	482	8.0	23.5	58.5	27.7	11.6	27.6	56.3	26.5
	640	5.0	27.5	60.1	29.5	6.0	22.1	56.7	25.0
	798	12.8	32.6	70.7	29.8	9.0	35.4	67.3	31.9
	941	7.0	29.5	65.8	29.5	5.0	16.5	34.6	13.8
	832	0	14.9	39.0	16.6	0	16.4	37.4	16.5
	638	0	10.1	22.8	13.2	7.0	25.8	49.3	22.2
Nb-Al2	20	46.9	59.8	56.2	35.6	41.0	54.3	49.7	35.0
	367	28.1	35.3	32.5	23.1	28.5	37.2	36.1	23.0
	740	18.0	21.3	21.5	14.8	75.9	92.3	87.7	59.8
	922	70.7	85.9	80.0	45.6	61.9	74.6	76.0	50.3
	1072	29.4	40.2	39.6	23.8	26.6	41.0	36.7	21.3
Nb-Al5	20	38.1	42.4	41.8	32.7	48.6	59.1	58.6	37.2
	538	57.9	69.8	70.0	45.4	41.7	50.8	51.1	32.9
	726	54.5	60.4	59.4	45.9	53.7	65.6	68.3	39.7
	ε 891	33.8	60.4	65.9	49.8	38.3	51.6	55.9	34.8
	ε 1023	24.5	29.1	35.2	34.1	22.2	27.5	35.5	30.4
	ε 627	No longer β-W structure							
	ε 20	No longer β-W structure							

ε denotes the presence of lines due to second phase.

In this figure and in figures
4.14 to 4.24 the intensity
ratios are

$$\times I_{222}/I_{400}$$

$$\bullet I_{320}/I_{400}$$

$$\blacklozenge I_{321}/I_{400}$$

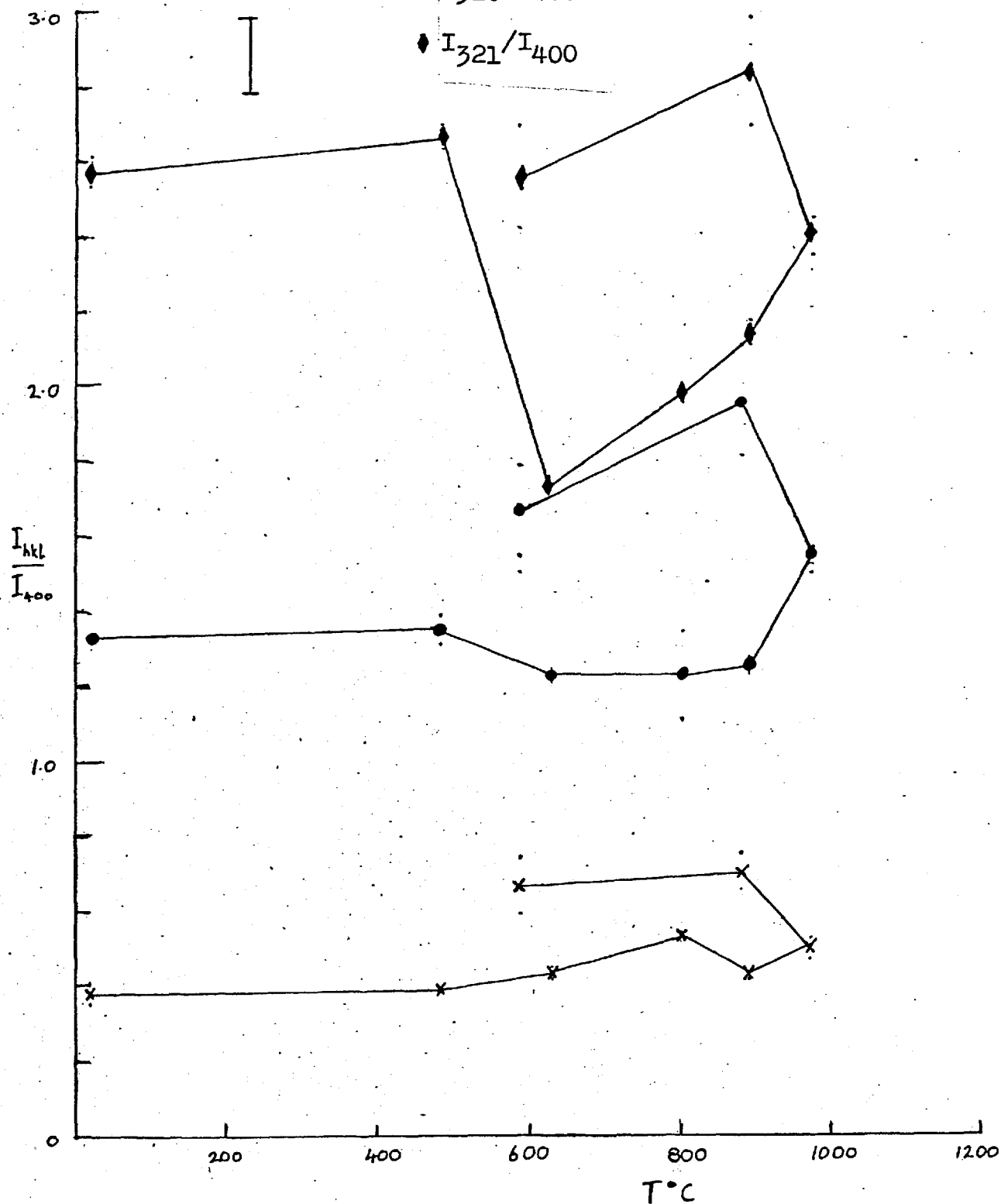


Figure 4.13. Intensity ratios of Nb-Sn(1) as a function of temperature.

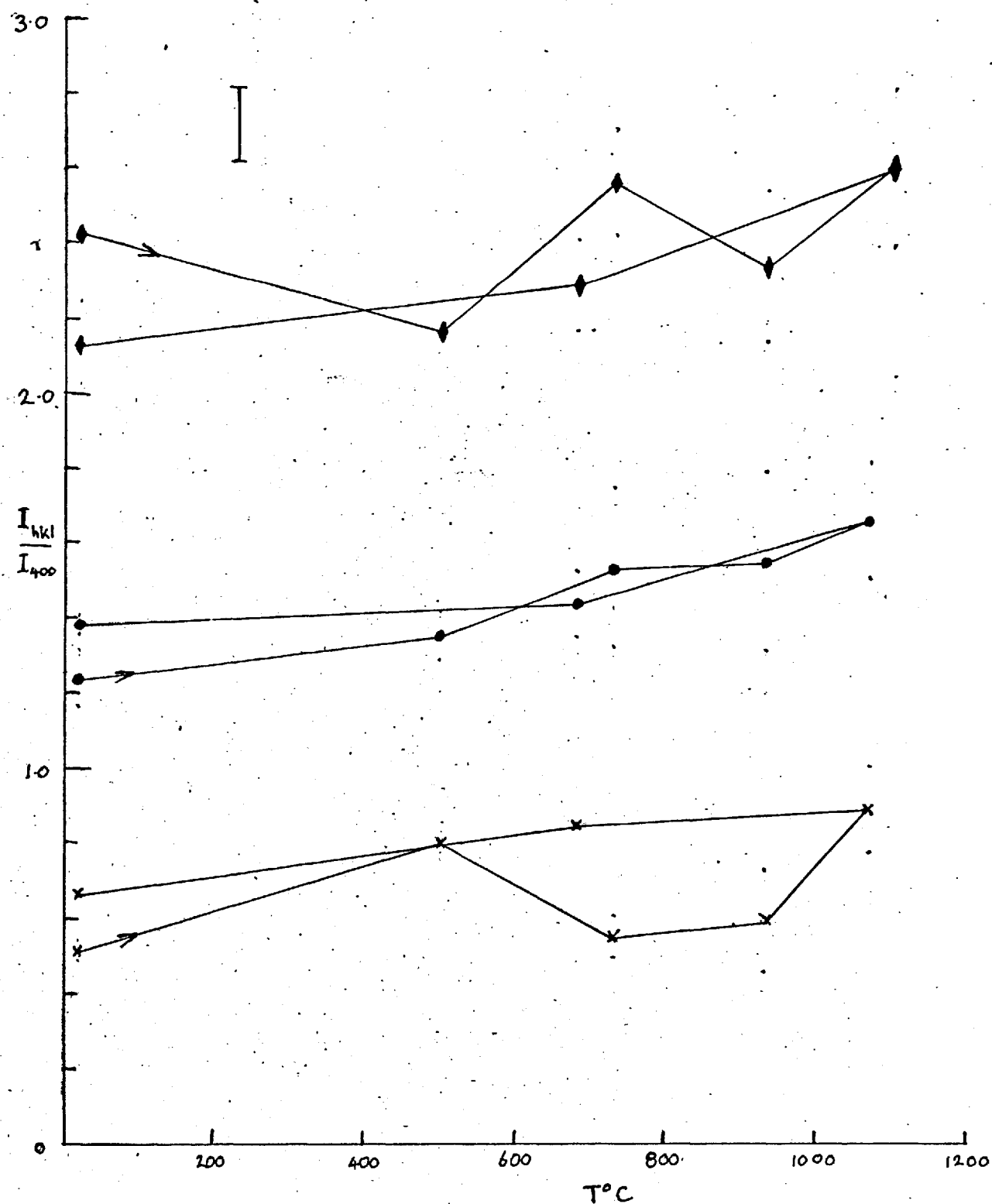


Figure 4.14. Intensity ratios of Nb-Sn(2) as a function of temperature.

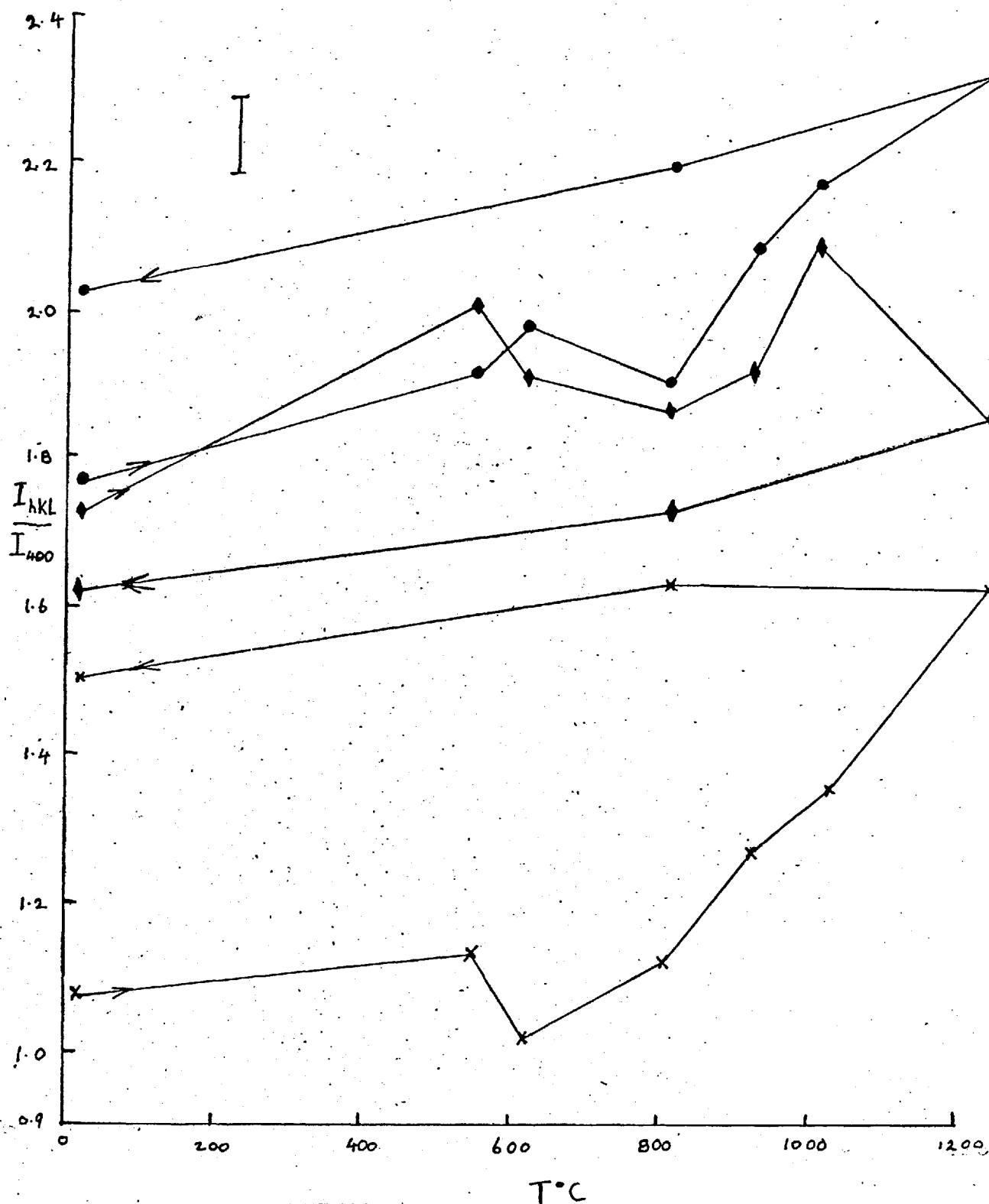


Figure 4.15. Intensity ratios of V-Si(2) as a function of temperature.

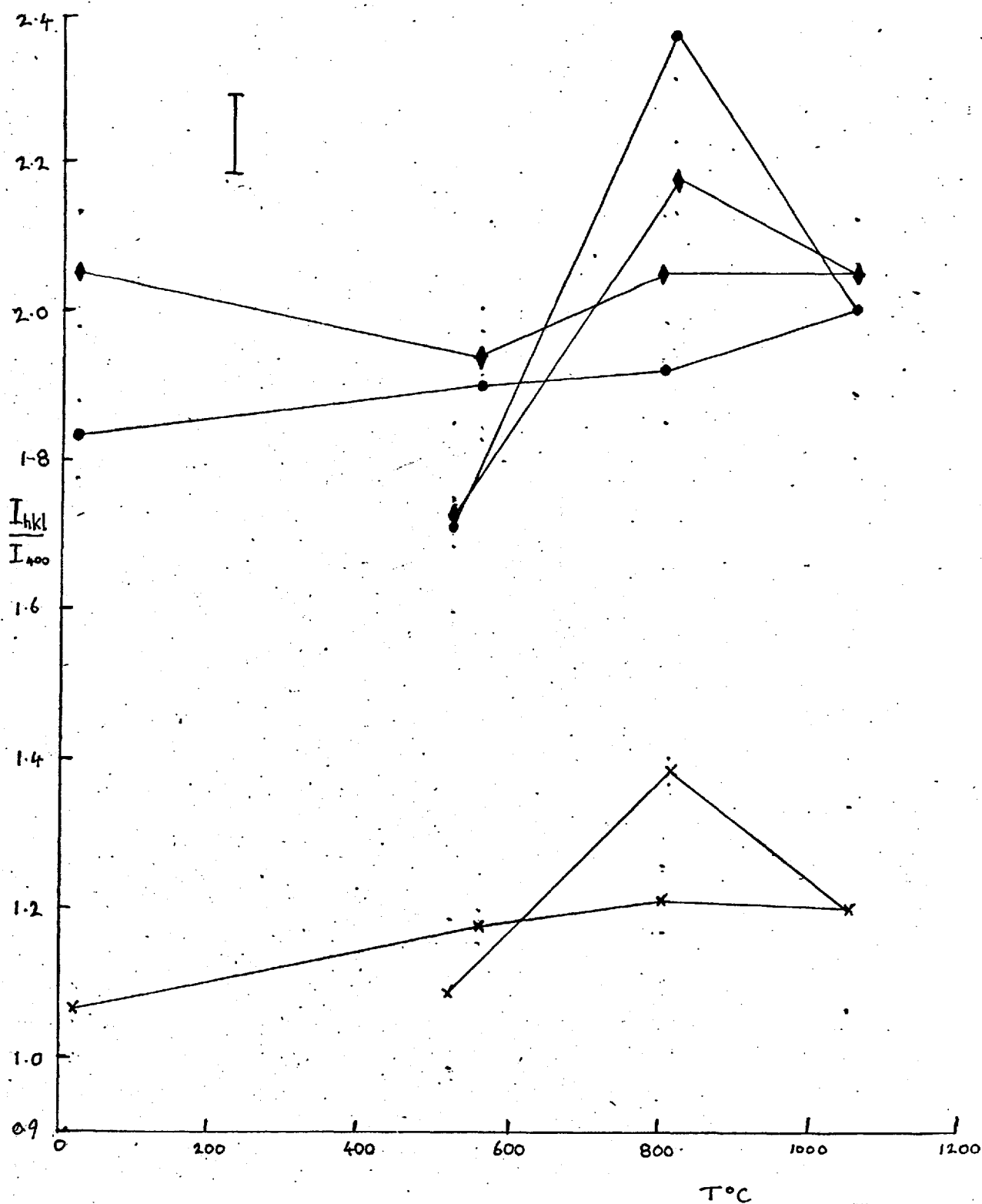


Figure 4.16. Intensity ratios of V-Si(3) as a function of temperature.

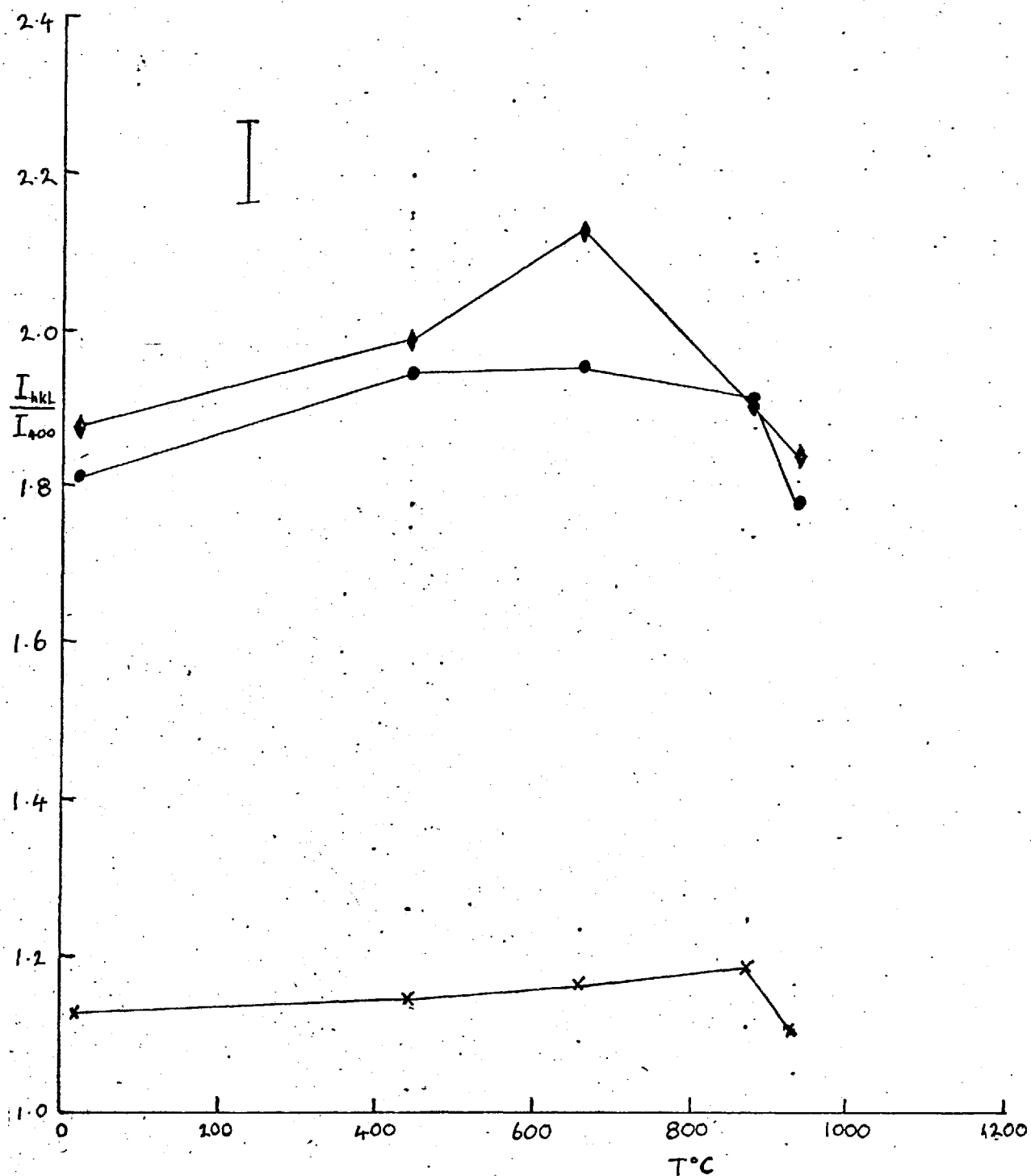


Figure 4.17. Intensity ratios of V-Si(4) as a function of temperature.

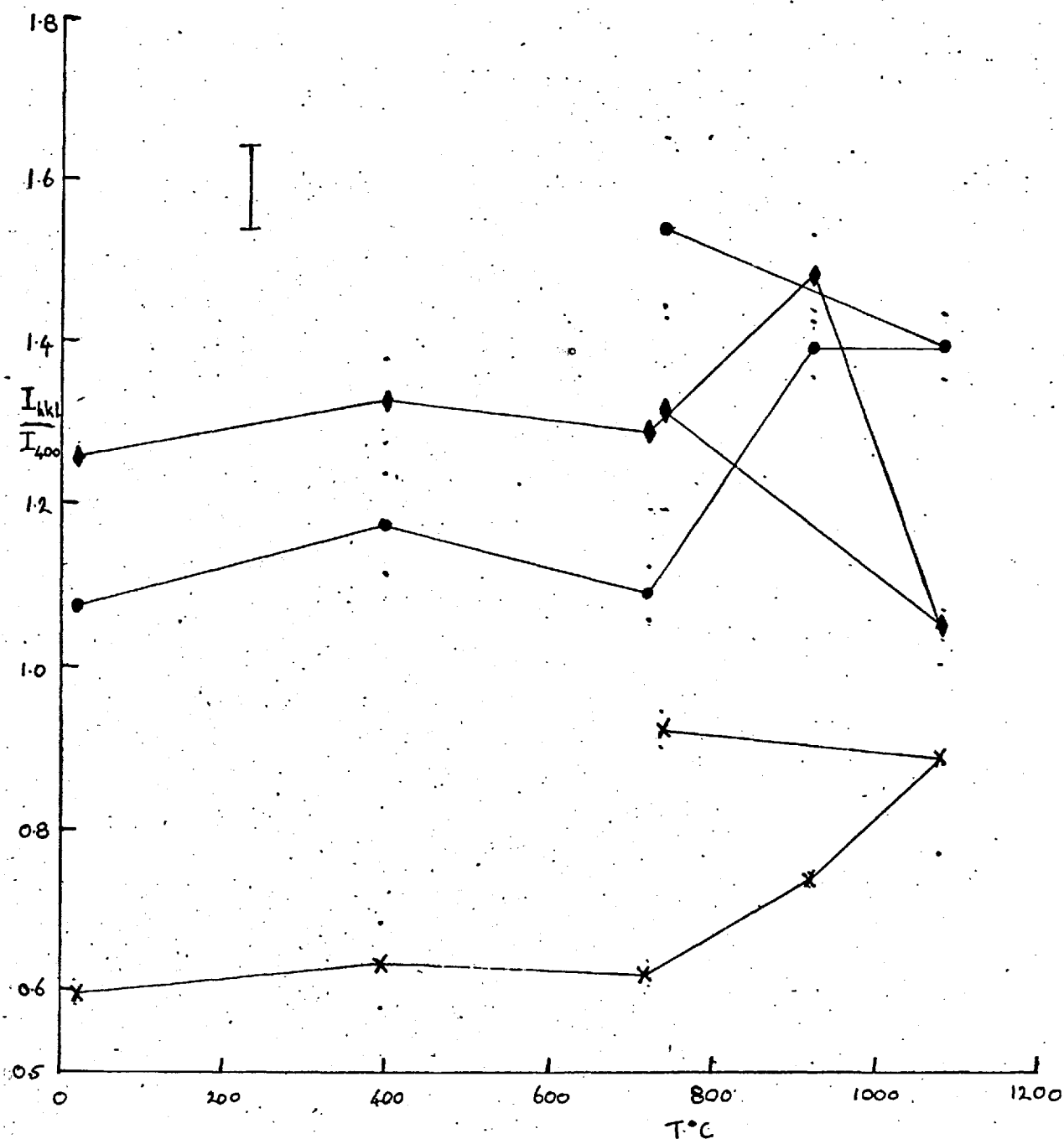


Figure 4.18. Intensity ratios of V-Si(9) as a function of temperature.

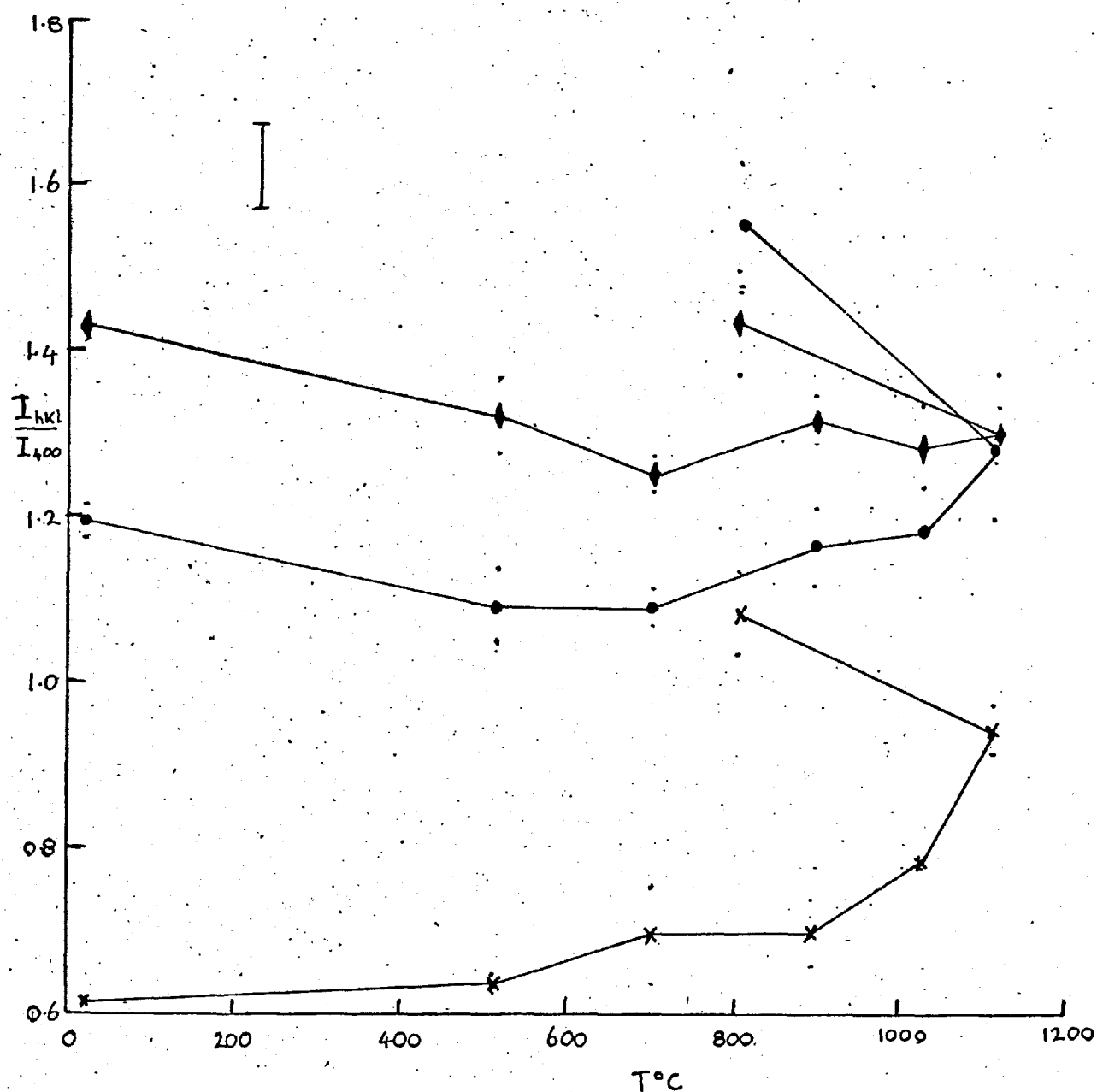


Figure 4.19. Intensity ratios of V-Si(10) as a function of temperature.

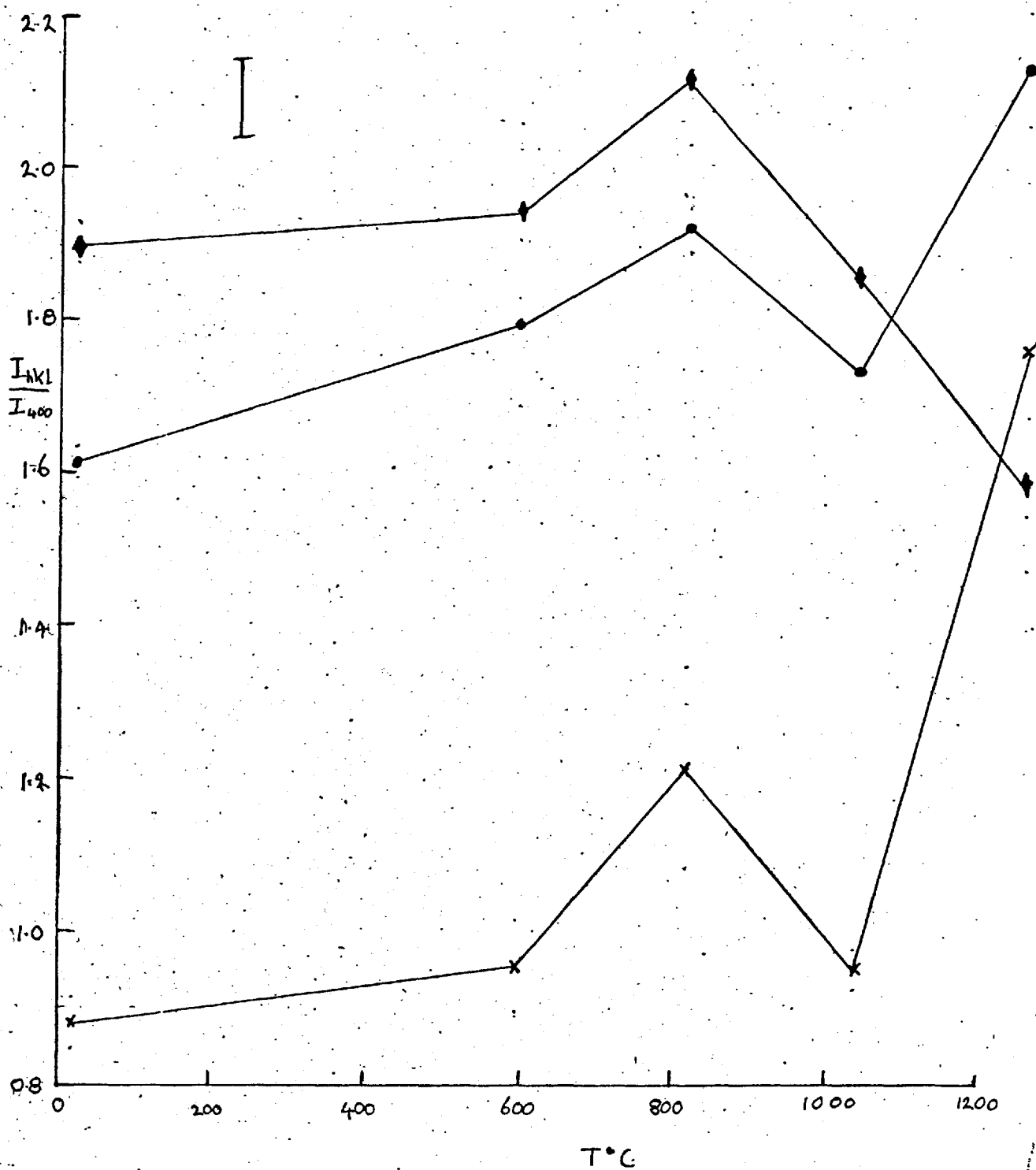


Figure 4.20. Intensity ratios of V-Si(11) as a function of temperature.

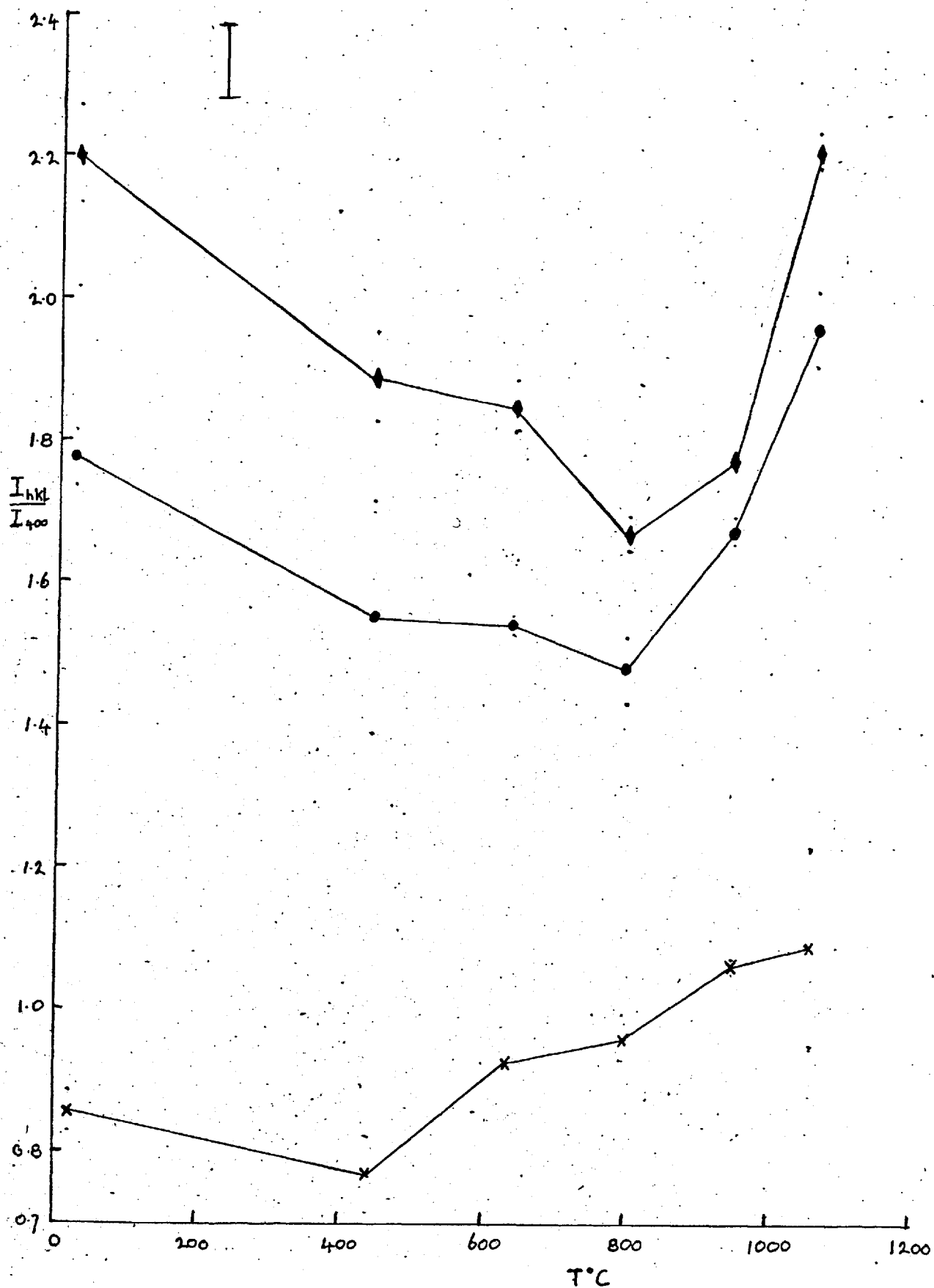


Figure 4.21. Intensity ratios of V-Si(12) as a function of temperature.

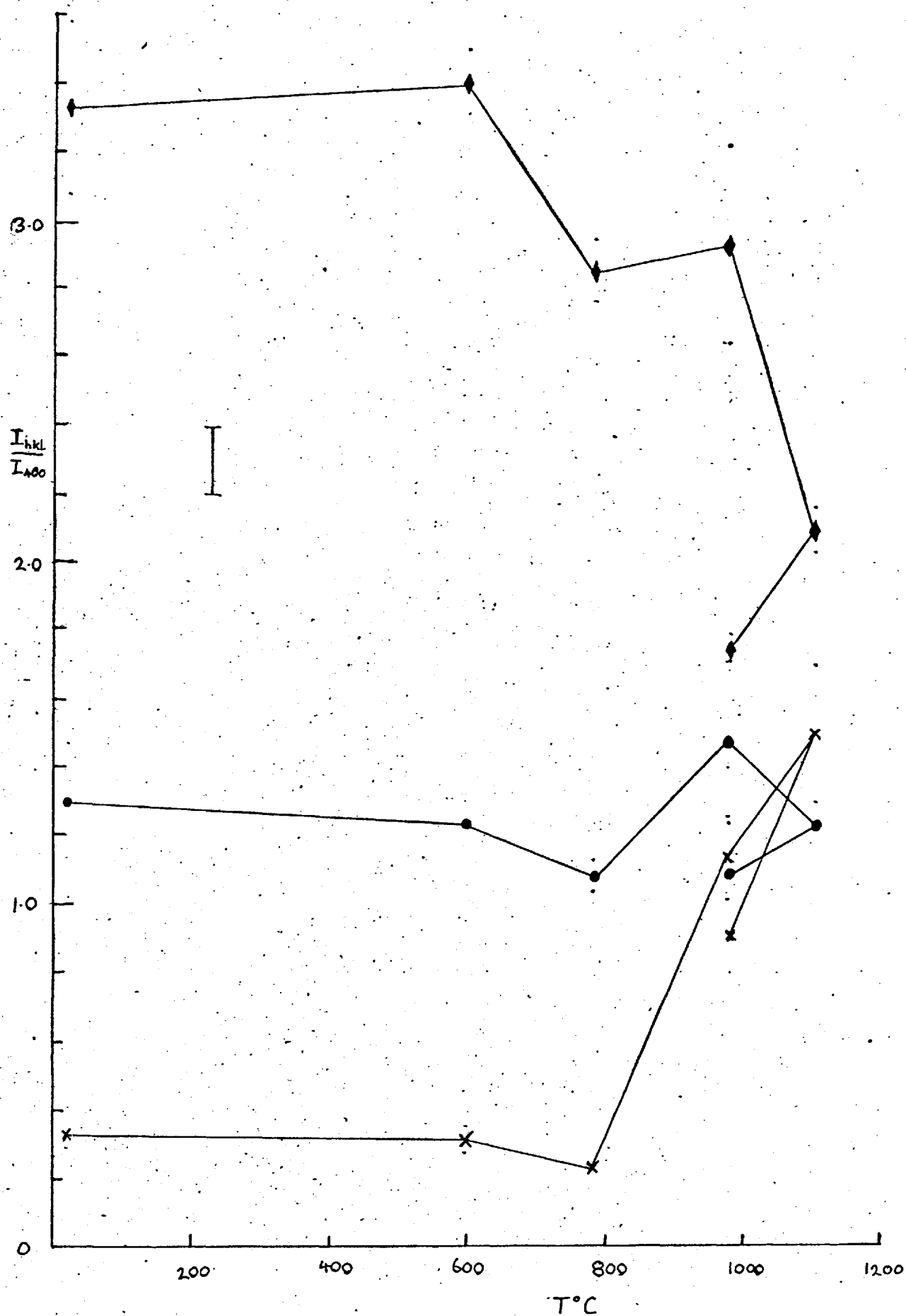


Figure 4.22. Intensity ratios of V-Ga(1) as a function of temperature.

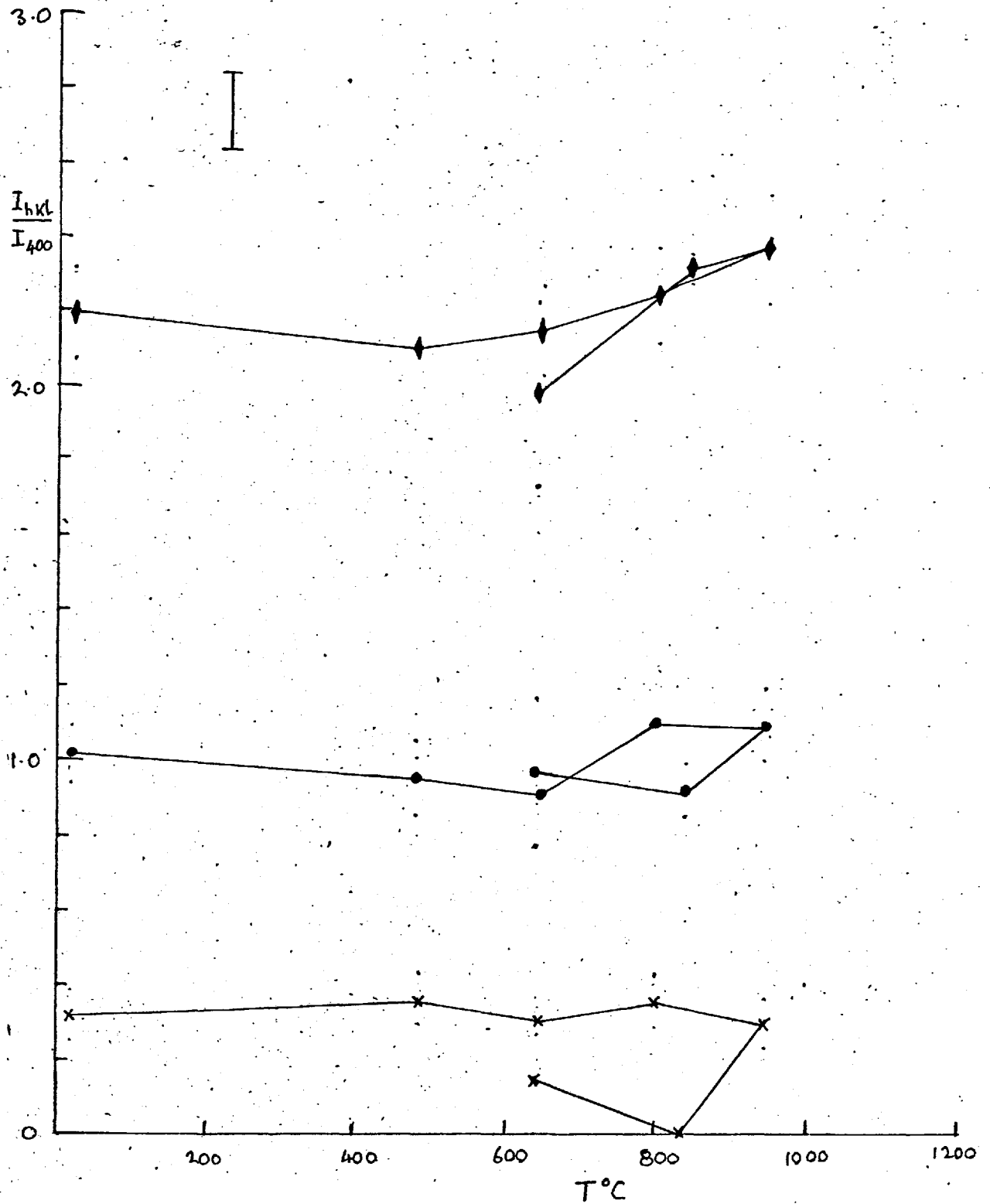


Figure 4.23. Intensity ratios of V-Ga(6) as a function of temperature.

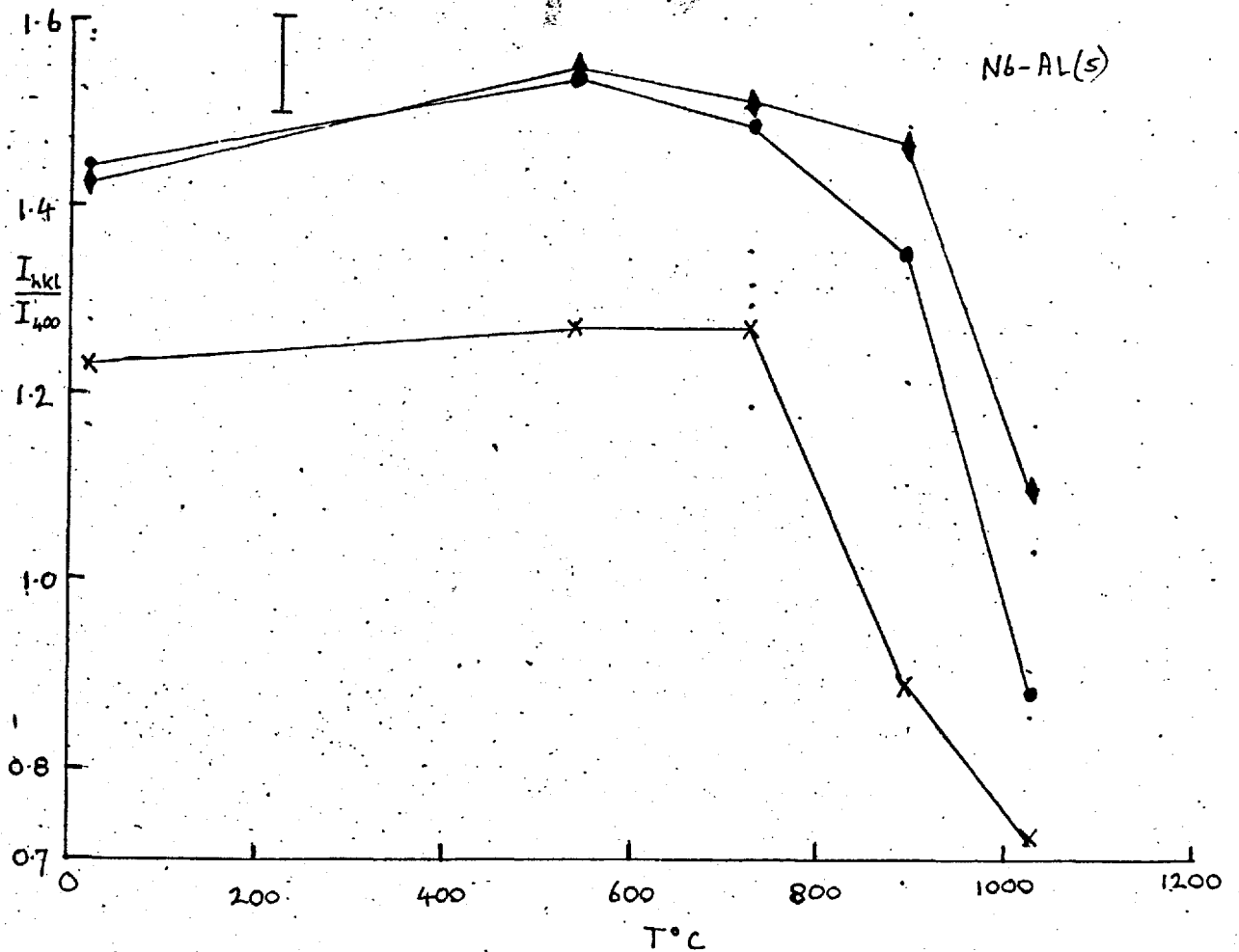
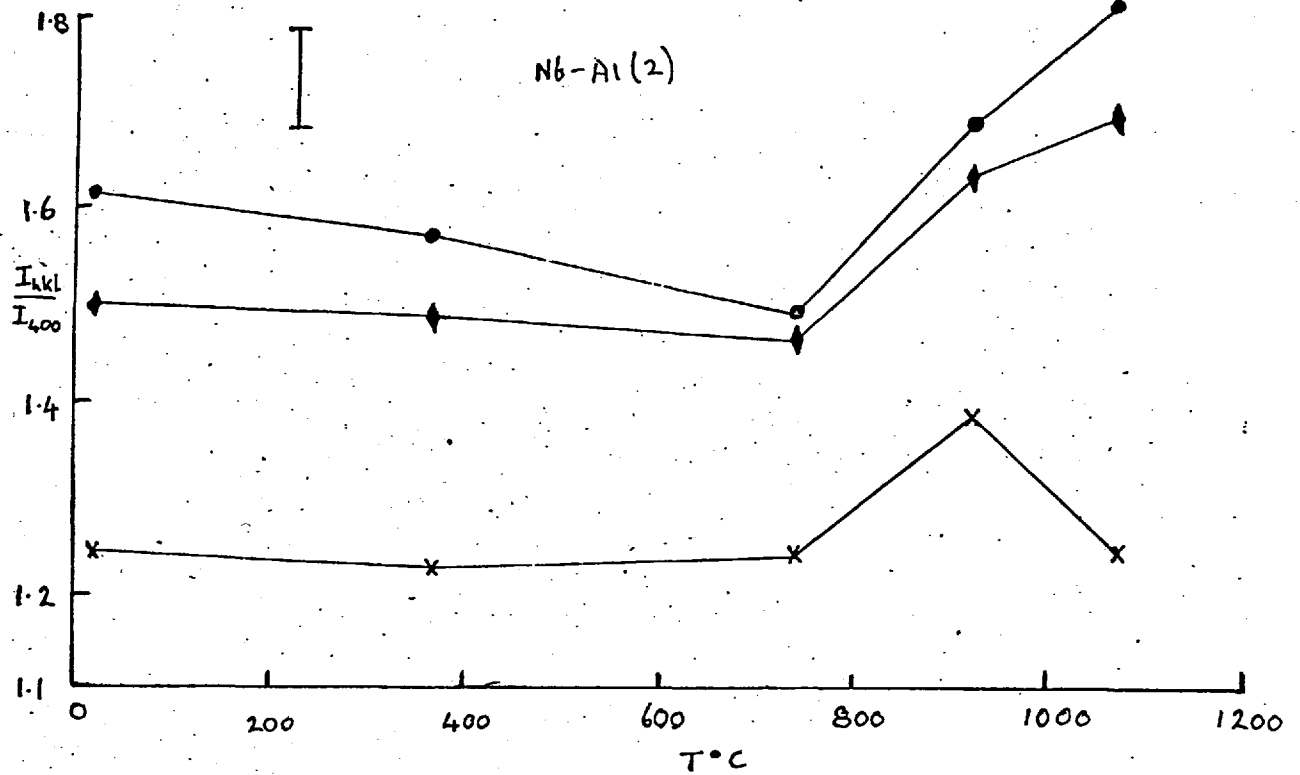


Figure 4.24. Intensity ratios of Nb-Al(2) and Nb-Al(5) as a function of temperature.

reached and have no other significance.

It is relatively easy to distinguish between true changes in order and random errors in intensity measurement. Firstly, if both films give a similar change in intensity ratio, then it is likely to be genuine and secondly, as will be discussed in Chapter 5, a change in order will cause a change of opposite sign in the I_{321}/I_{400} ratio to that in the other two ratios, so that errors in the I_{400} measurement will be detectable. Similarly changes in intensity ratios due to composition changes are distinguishable from changes due to ordering or disordering at a fixed composition. The former, as noted earlier, are, moreover, associated with changes in the thermal expansion curve. The changes in intensity of lines arising from second phase also assist the interpretation of the intensity data. The presence of such phases is indicated in Table 4.4. The interpretation of the high temperature data will be discussed more fully in the next chapter, but a further point to be noted is that many of the capillaries fractured on cooling and it was, then, not possible to measure the lattice parameters after the heating cycle.

4.4 X-Ray Measurements at Low Temperatures

The cubic to tetragonal structural transformation in the β -W materials was investigated by considering the splitting of the powder lines on cooling. The interplanar spacing in an orthorhombic lattice is given by the equation:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (4.1)$$

where a , b and c are the lattice constants. In a cubic crystal $a = b = c$ and the reflections $h k l$, $k l h$ and $l h k$ are superimposed in a powder pattern. However, if there is a transformation to a tetragonal form $a = b \neq c$ and the three lines will not now be superimposed. If,

however, the reflections $h h l$, $h l h$ and $l h h$ are considered, two of the three, $h l h$ and $l h h$ will be superimposed and the cubic peak will split into two elements, with an intensity ratio of two to one. In the present work this was the effect which was sought.

The samples which were cooled are given in Table 4.5 with martensite start and finish temperatures, M_s and M_f , if a transformation occurred. As no hysteresis was observed in the transforming samples within the error of measurement ($\pm 1^\circ \text{K}$), M_s and M_f can be identified with A_f and A_s , the "austenite" finish and start temperatures. The M_s temperature was determined as the temperature at which clear splitting into two peaks could be seen. It was at this temperature that the axial ratio was measured and this is also shown in Table 4.5. The axial ratio was determined, from the splitting of the line and is a measure of the spontaneous strain in the lattice. Its value was calculated from the equation

$$\frac{c}{a} = 1 + \frac{\Delta\theta}{\tan\theta} \quad (4.2)$$

where $\Delta\theta$ is the splitting and θ the Bragg angle of the cubic line, and its sign from the direction of the splitting.

For the Nb-Sn samples a plot of M_s & M_f against room temperature lattice parameter (and deduced composition) is shown in figure 4.25. The dashed lines in this graph are the A_s and A_f temperatures taken from King (1968). A plot of the axial ratio at the transformation against room temperature lattice parameter is given in figure 4.26 and a typical chart record of a line splitting in figure 4.27. A possible transformation was observed in V-Ga (2) and the chart record is shown in figure 4.28. This broadening may be the result of misalignment, but the possibility of a transformation in this sample will be discussed in the last chapter.

No transformation was observed in the Nb-Al system as expected from the literature. Further, no

Table 4.5.

Transformation Temperatures.

Sample No.	M_s °K	M_f °K	c/a	a_{RT} Å
Nb-Sn 3	None			5.2827
Nb-Sn 4	None			5.2961
Nb-Sn 9	54	46	0.9967	5.2910
Nb-Sn 5	None			5.2858
Nb-Sn 6	18	10	1.0049	5.2865
Nb-Sn 7	45	34	1.0049	5.2874
Nb-Sn 2	41	36	0.9963	5.2911
Nb-Sn 12	60	56	0.9963	5.2909
Nb-Sn 10	53	50	1.0041	5.2883
Nb-Sn 11	23	16	1.0041	5.2868
V-Ga 2	15	-	(?)1.0005	4.8166

The following samples were also cooled and no evidence of a transformation was found:-

V-Si (1-12) ,Nb-Al(1,2,4,5) and V-Ga(1,3,4,5,8,9)

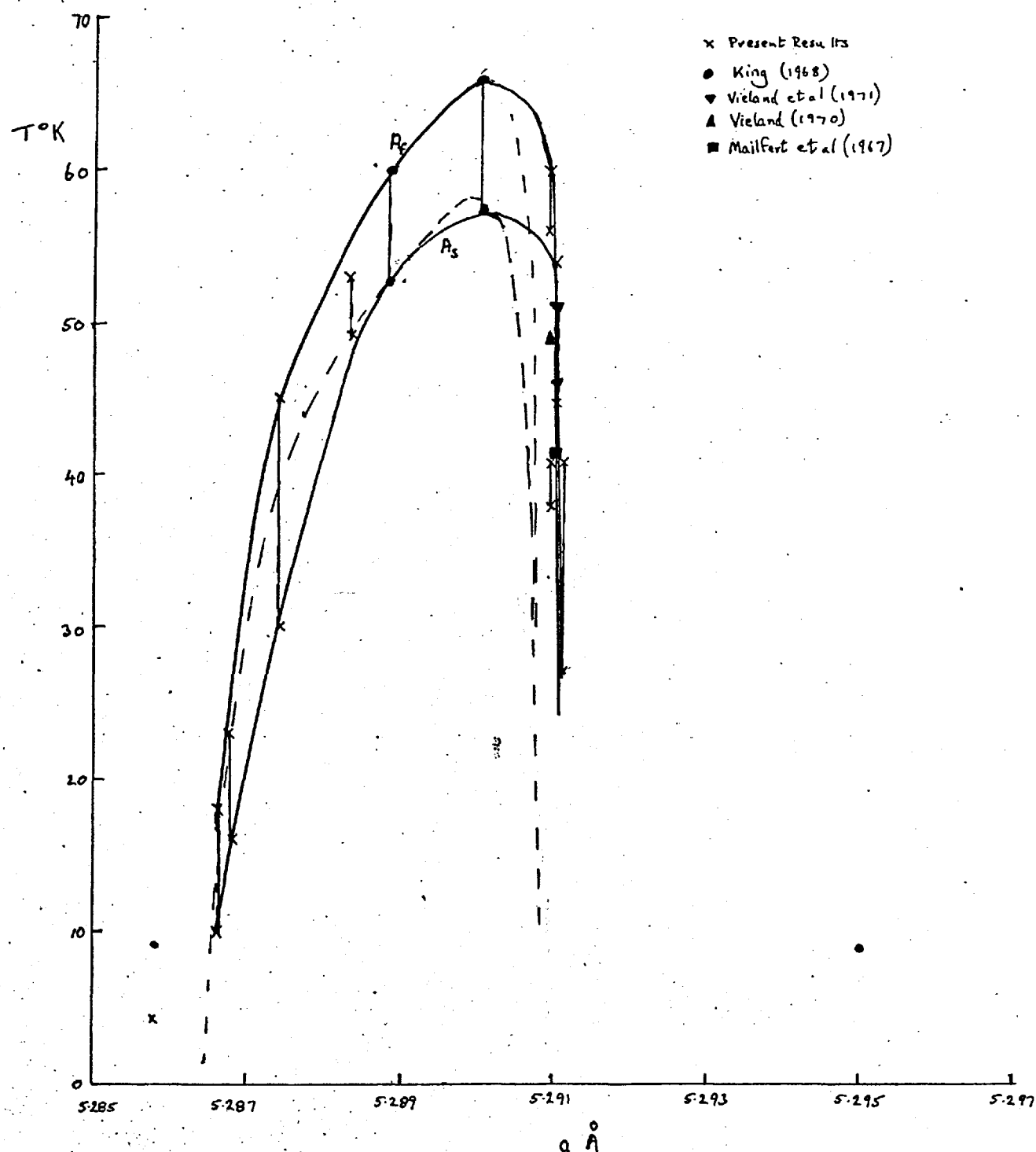


Figure 4.25. The dependence of the A_s and A_f temperatures upon lattice parameter of Nb-Sn.

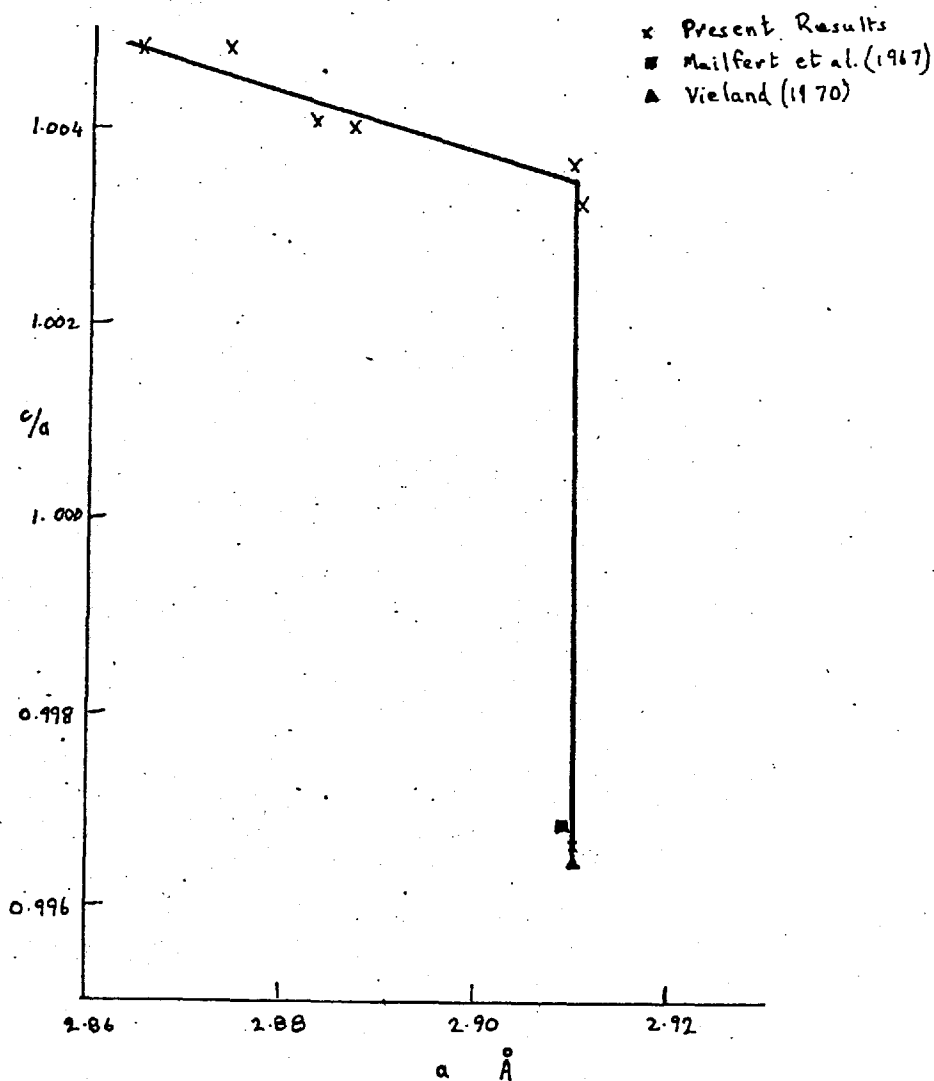


Figure 4.26. The axial ratio of the martensitic phase of Nb-Sn. as a function of lattice parameter.

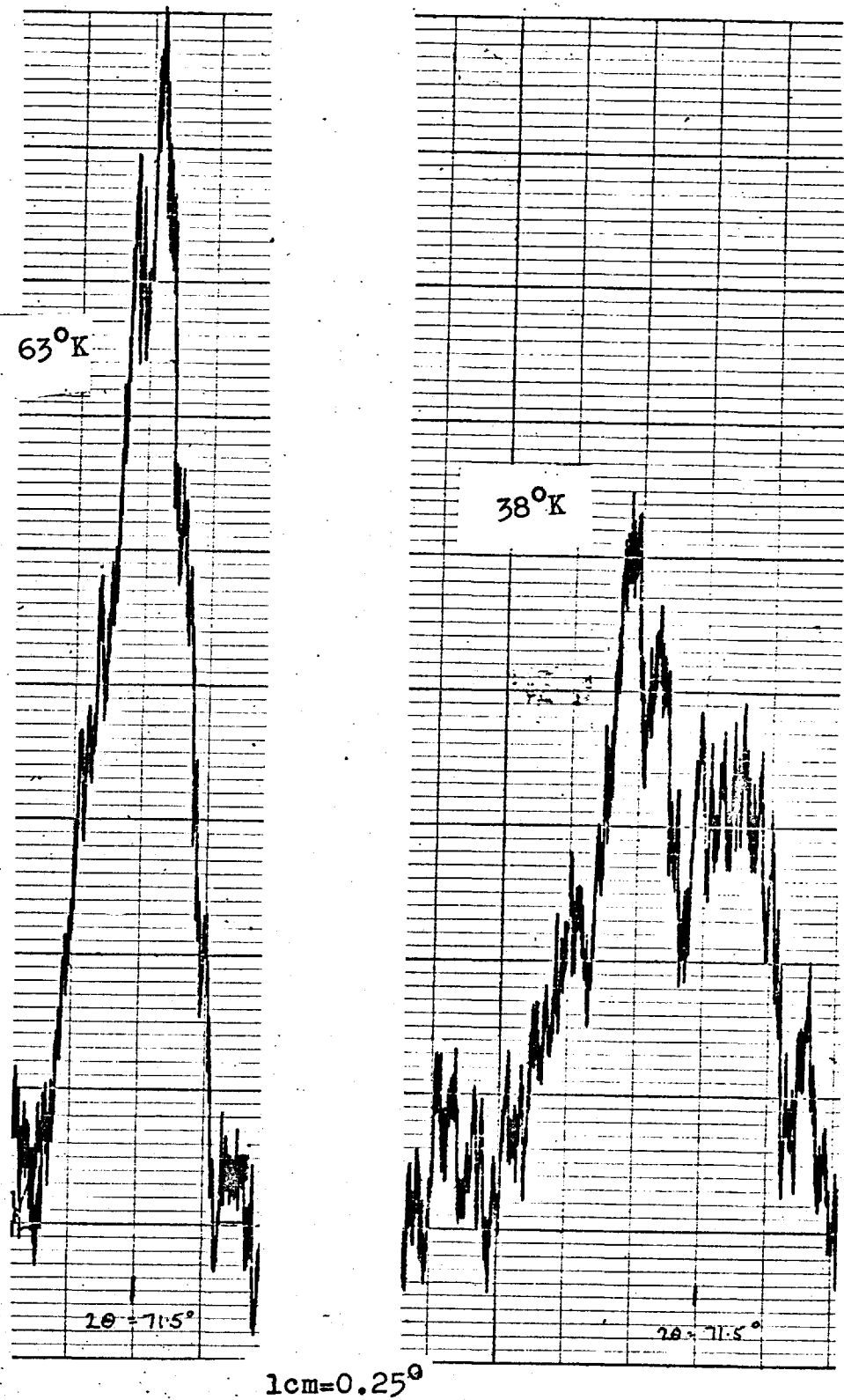


Figure 4.27. The splitting of the 400 line of Nb-Sn(12).

Room
Temperature.

15°K

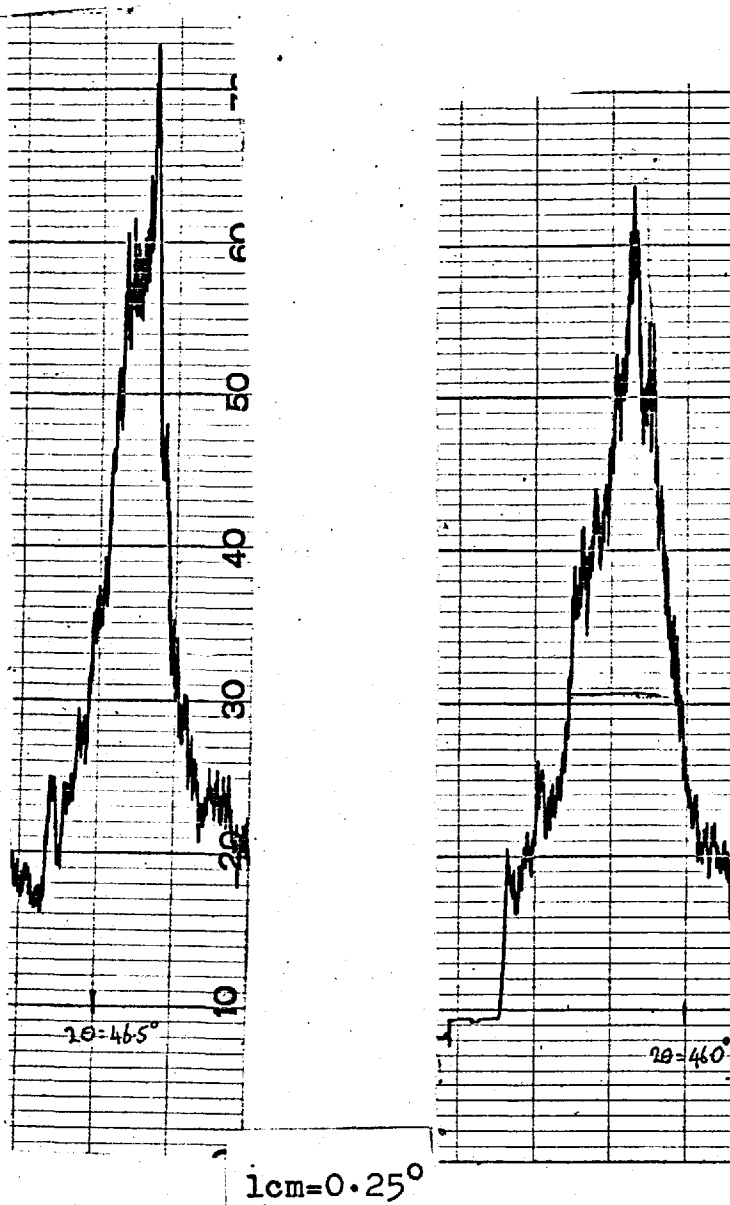


Figure 4.28. The splitting of the 211 line of V-Ga(2).

transformation was observed in any of the present powdered samples of V-Si, which was surprising in view of the observations of a transformation, both in powders and single crystals reported in the literature. Line broadening in V-Si powders has been reported by Batterman and Barrett (1964, 1965) and by King et al. (1967), but in the former case the line broadening was not clear enough for quantitative measurements and single crystal work was undertaken. The sample used by the second authors was recooled as V-Si (8a) and a further sample (taken from the single crystal used by Pollock (1966) for optical microscopy at low temperatures) was cooled as V-Si (8b). In neither case was a transformation observed as can be seen in figure 4.29, where the peak at 4.2° K for V-Si (8b) is shown. The implication of this measurement is that the broadening observed by King et al. (1967) was due to misalignment. The absence of a transformation in the V-Si samples will be discussed in chapter six. That a low enough temperature had not been reached by the specimen is improbable, however, as the linearity of the thermometer calibration curve indicated that the specimen block as a whole was at the temperature recorded. Further, the results for Nb-Sn agree with those of King (1968) (measured on the same alloys but with a different experimental arrangement), indicating that a temperature gradient across the specimen mount is unlikely to be of the order of 12° K. which would be the gradient necessary for the specimen surface to be at a temperature above the critical temperature of the sample when the thermometer indicated a temperature of 4.2° K. This appears even more unlikely when it is noted that no hysteresis was observed. Moreover, McKinnon (1970) has indicated that, as a result of the geometry of the specimen holder and the path taken by the liquid helium, in general the specimen is likely to be colder than the thermometer rather than the reverse.

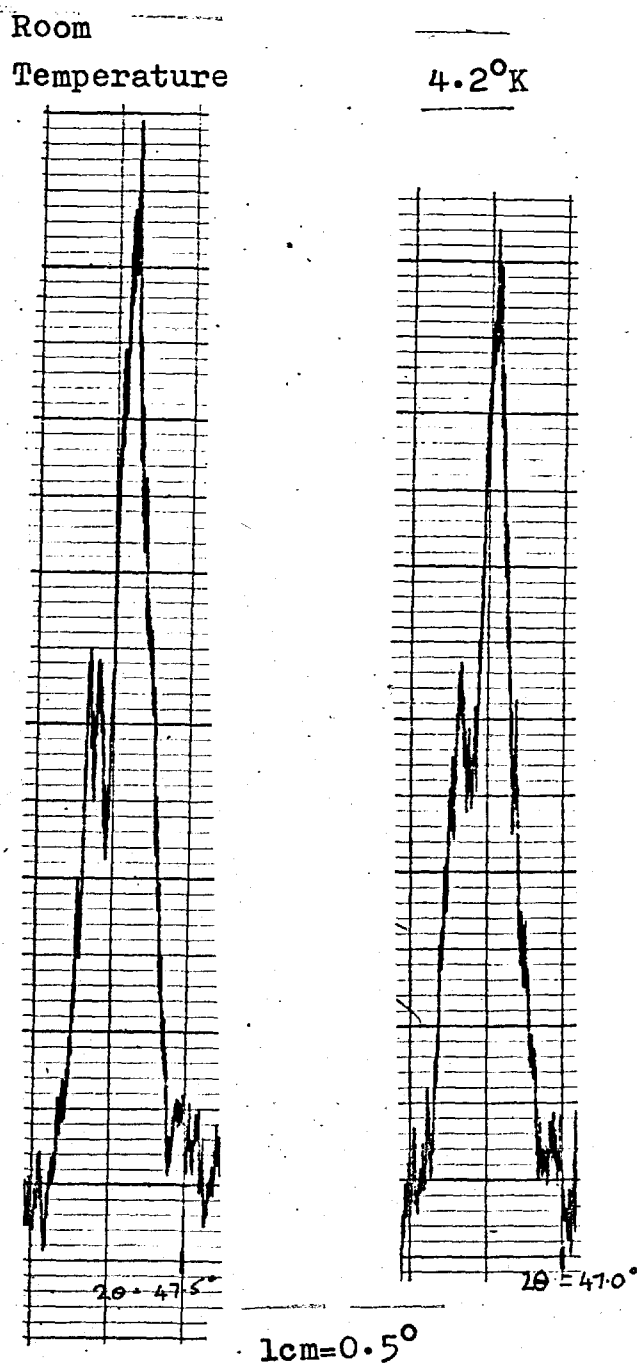


Figure 4.29. The 211 line of V-Si(8) at room temperature and at 4.2°K.

4.5 Superconducting Transition Temperatures

The superconducting transition temperatures of the samples were measured using the method described in section 3.6. The values measured are given in Table 4.6 with the room temperature lattice parameters and these are plotted in figure 4.30 and 4.31. The lines in the figures represent the relationship between the critical temperature and the lattice parameter taken from figures 2.23 and 2.24. The value for the single crystal V-Si (8) is taken from Pollock (1966). Because a thermocouple was used to measure the temperature, the errors are larger than usually found in transition temperature measurements when a more accurate thermometer, e.g. a Ge thermometer, is used. However, as explained in section 3.6c, the error bars not only represent the error in measurement but also indicate the breadth of the transitions. Except in the case of Nb-Sn (11) these breadths seem to be of a similar size ($\pm 0.5^\circ \text{K}$) for all compositions. In the Nb-Sn system, the samples were not all the same as those used for the low temperature X-ray measurements and the breadth of the transition does not appear to be related to the lattice parameter but implies a lack of homogeneity in some of the sintered samples. (None of the samples used for the low temperature diffractometry showed broad X-ray peaks which would indicate this lack of homogeneity). Nb-Al (1) and Nb-Al (2) both showed second transitions due to the second phase present.

The initial intention was to measure the T_c 's of the high temperature X-ray camera samples both before and after the series of measurements in that camera. As this was not possible because of the small specimen size and the fracture of specimens in the camera, the bulk samples on which the transition temperatures were measured, corresponding to those samples investigated in the high temperature camera, were subjected to a heat treatment summarised in table 4.7a. The values of T_c before and after the treatment are given in table 4.7b. Of the V-Si samples all those with high T_c 's before heat treatment

Table 4.6.

Superconducting Critical Temperatures.

Sample No.	T_c °K	δT_c K°	a_{RT} Å
Nb-Sn 1	18.18	0.48	5.2950
Nb-Sn 5	15.38	0.43	5.2856
Nb-Sn 6	13.65	0.43	5.2865
Nb-Sn 7	11.90	1.25	5.2875
Nb-Sn 11	14.79	2.50	5.2868
Nb-Sn 12	17.19	0.46	5.2909
Nb-Al 1	5.65	0.20	5.1862
Nb-Al 2	16.03	0.48	5.1871
Nb-Al 3	15.25	0.71	5.1893
Nb-Al 4	16.82	0.47	5.1914
Nb-Al 5	11.49	0.84	5.1942
V-Si 1	16.89	0.55	4.7241
V-Si 2	16.91	0.53	4.7242
V-Si 3	17.56	0.46	4.7245
V-Si 4	16.72	0.51	4.7245
V-Si 5	17.49	0.47	4.7246
V-Si 6	16.89	0.45	4.7246
V-Si 7	17.25	0.46	4.7247
V-Si 8	16.90	0.20	4.7248
V-Si 9	12.80	1.02	4.7295
V-Si 10	11.32	1.25	4.7327
V-Si 11	9.76	0.34	4.7333
V-Si 12	10.65	0.68	4.7352
V-Ga 1	14.89	0.43	4.8172
V-Ga 2	15.00	0.66	4.8166
V-Ga 3	7.54	0.42	4.8183
V-Ga 4	7.63	0.31	4.8192
V-Ga 5	13.91	0.42	4.8200
V-Ga 6	10.59	0.85	4.8202
V-Ga 7	7.32	0.31	4.8191
V-Ga 8	8.91	0.34	4.8183
V-Ga 9	7.44	0.41	4.8187

δT_c is calculated as the combined effect of the transformation width, the error in measurement and the error in the thermocouple calibration curve (see appendix 4E).

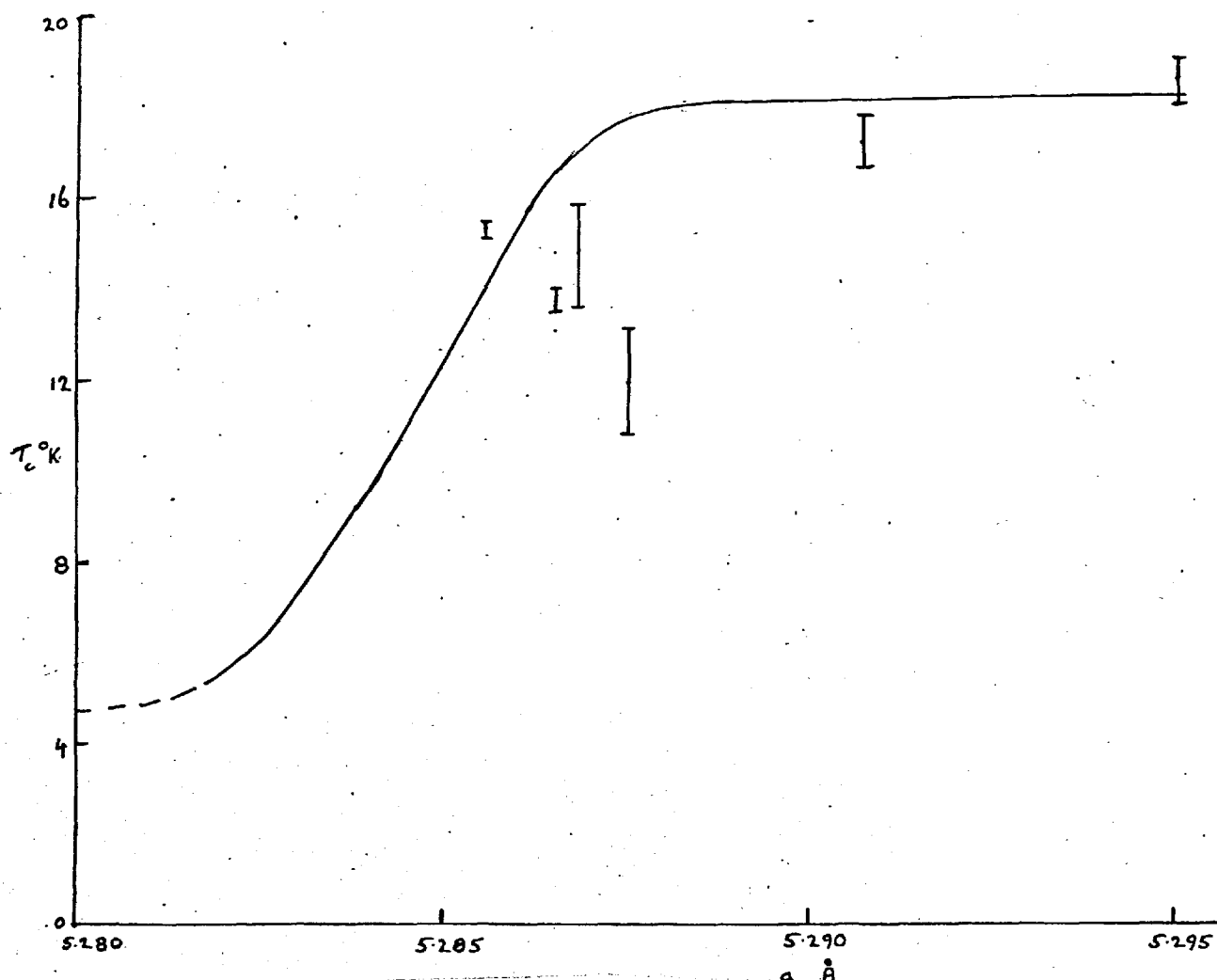


Figure 4.30a. The dependence of T_c on lattice parameter for Nb-Sn.

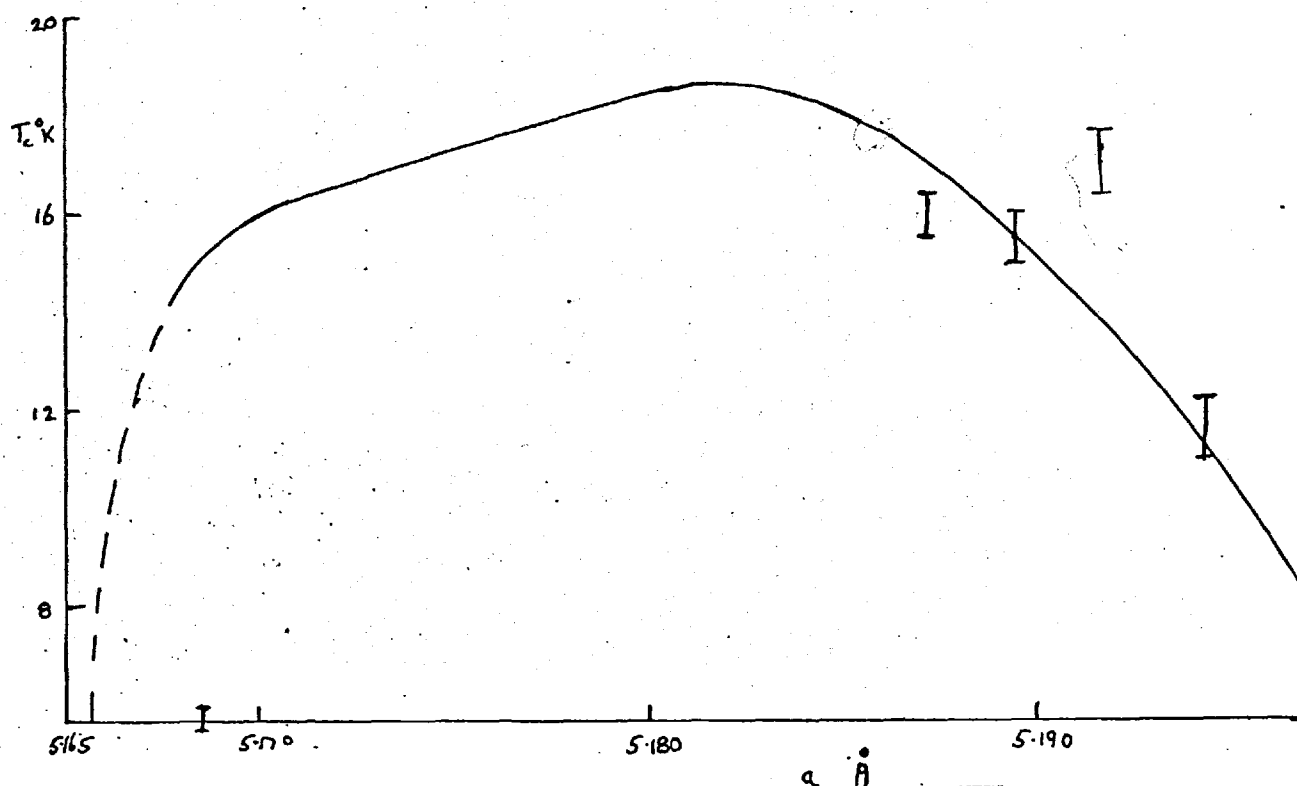


Figure 4.30b. The dependence of T_c on lattice parameter for Nb-Al.

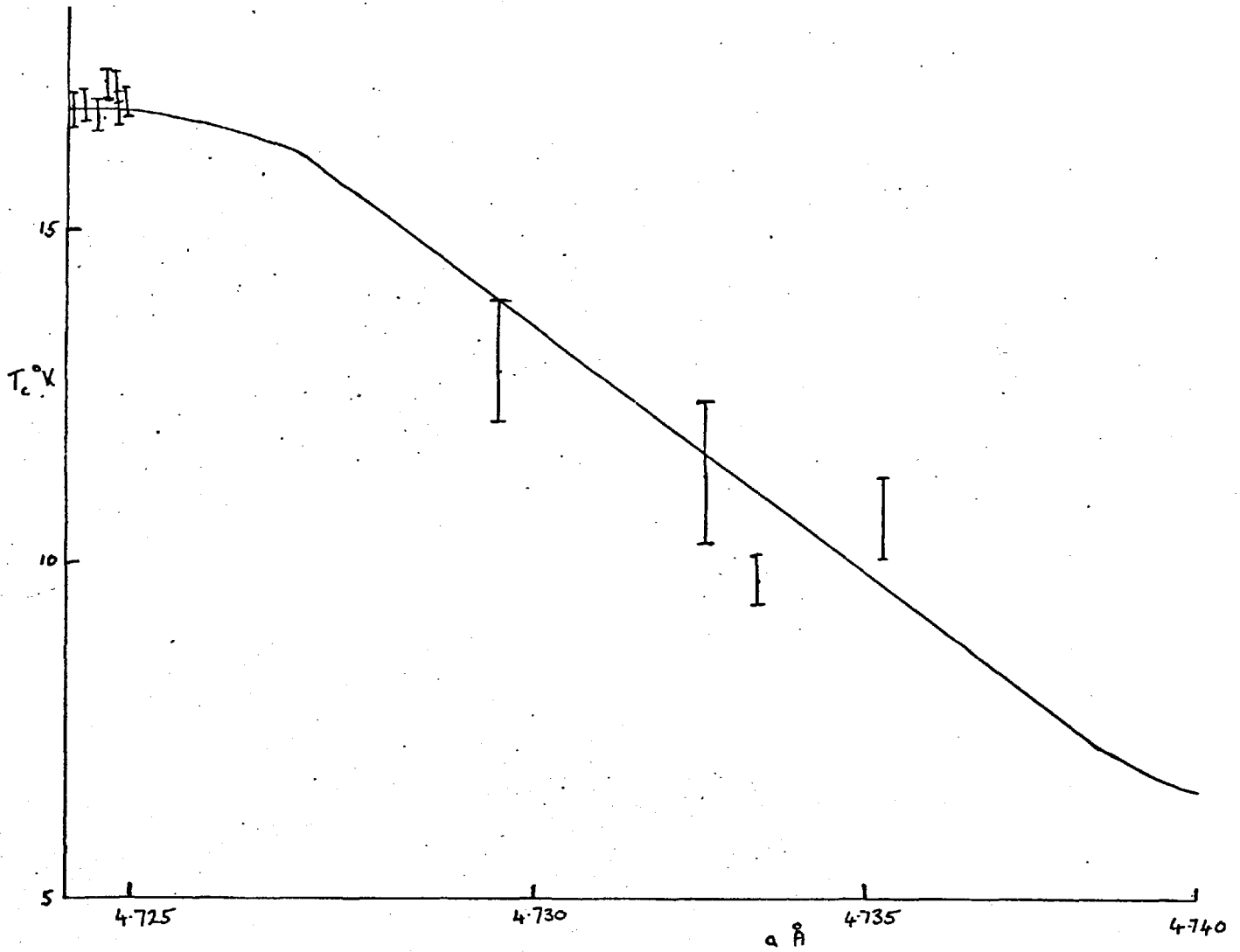


Figure 4.31a. The dependence of T_c on lattice parameter for V-Si.

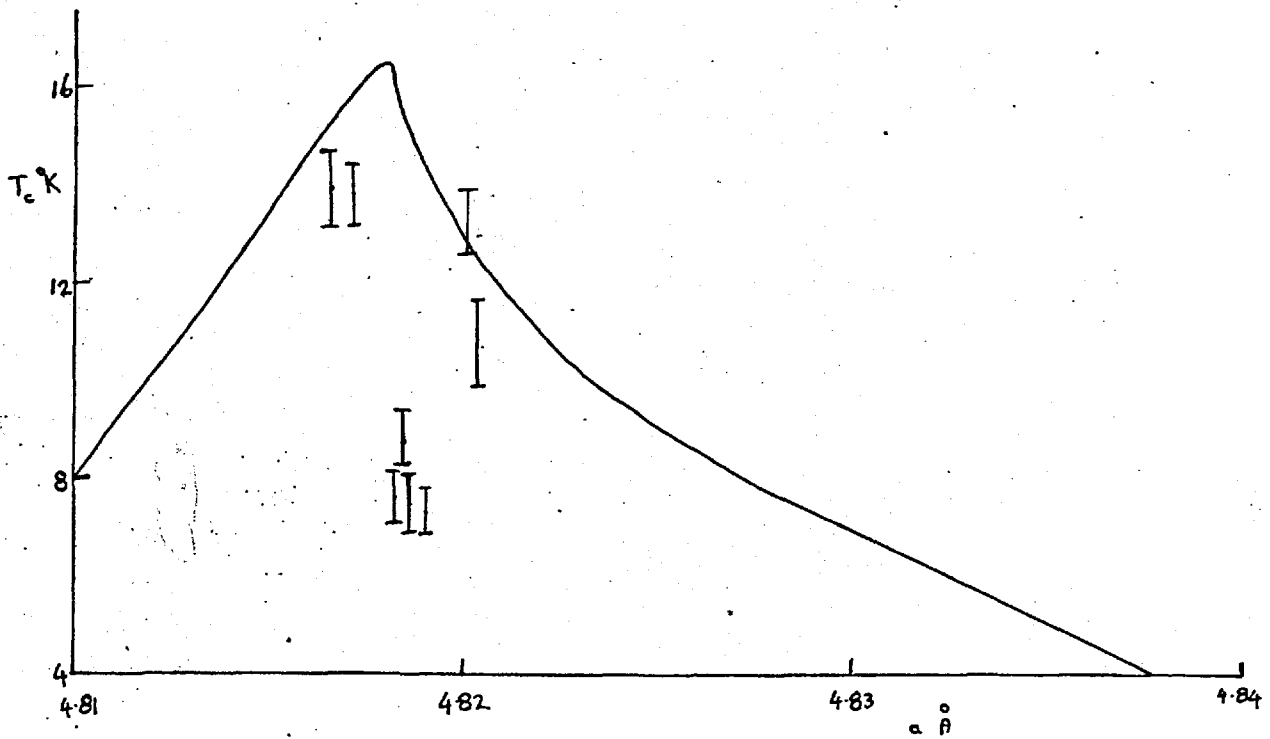


Figure 4.31b. The dependence of T_c on lattice parameter for V-Ga.

Table 4.7a

Summary of Heat Treatment.

Temperature °C	Time hours
402	24
620	24
810	24
910	24
800	24
520	24

Table 4.7b.

Superconducting Critical
Temperatures
before and after Heat Treatment

Sample No.	Initial T_c °K	Final T_c °K
Nb-Sn 1	18.18	16.83
Nb-Al 2	16.03	17.77
Nb-Al 5	11.49	11.36
V-Si 2	16.91	16.34
V-Si 3	17.56	16.55
V-Si 4	16.72	16.59
V-Si 9	12.80	14.03
V-Si 10	11.32	14.28
V-Si 11	9.76	12.25
V-Si 12	10.65	13.77
V-Ga 1	14.89	14.68
V-Ga 6	10.59	12.55

showed a drop in T_c after the treatment and those low T_c 's before the treatment showed a rise in T_c after it. A similar effect was observed in the V-Ga and Nb-Al systems, though only two samples were investigated in each system. The implication of these results is that there is a change in composition. The Nb-Sn (1) sample showed a drop in T_c also, but this sample was a single crystal of the material with the high lattice parameter and, therefore, not a typical case. It was not possible to measure the transition temperature of Nb-Sn (2) because it was only available in powder form. The correlation of the transition temperatures with composition and the variations with heat treatment will be discussed in chapter six.

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Chapter Five

Ordering in Non-Stoichiometric Compounds

"We must speak next in order concerning the quality of each class individually, and show from what composition of numbers each was formed".

- Plato (The Timaeus)

5.1 Interchange and Vacancy Disorder

The interpretation of order-disorder in the β -W compounds and in any non-stoichiometric compound, is complicated because the disorder can be either of an interchange or a vacancy type, or a mixture of the two. Interchange disorder refers to the structure in which atoms of one type are situated on sites normally occupied by the other type of atom. At the stoichiometric composition, this corresponds to the classic situation analysed by Bragg and Williams (1934) and even when the composition deviates from stoichiometry all sites are assumed to be occupied. This is the situation analysed by Bradley and Jay (1932) for FeAl and Van Reuth and Waterstraat (1968) have applied the method to the A₁₅ compounds with some slight differences in the mathematics (section 2.4). Vacancy disorder, as the name implies, refers to a situation in which either type of site becomes vacant on disordering, particularly in non-stoichiometric alloys. This situation usually arises as a result of large differences in atomic size, so that it is impossible for an atom to be on a "wrong" site without grossly distorting the surrounding lattice. For this reason vacancies tend only to be on one type of site. Bachner and Gatos (1966) have calculated the X-ray intensities from vacancy distributions on the A sites in an A₃B β -W type lattice (section 2.4).

5.2 The Ordering Model

Since it is possible that interchange and vacancy disorder exist together in the same compound and, as density measurements are meaningless because of the presence of second phase, it has been found necessary to develop the Bachner-Gatos (vacancy) model further to take account of interchange disorder. This model is general to any binary compound with two types of lattice site and does not apply to the β -W compounds alone.

The following quantities are, therefore, defined:

Y_A = fraction of total sites that are A atom sites

Y_B = fraction of total sites that are B atom sites

X_A and X_B = fractions of A and B atoms

f_A and f_B = atomic scattering factors of A and B atoms
(corrected for anomalous dispersion)

r_A and w_B = fractions of A and B sites occupied by A atoms

r_B and w_A = fractions of B and A sites occupied by B atoms

T_A and T_B = geometrical terms, functions of hkl , multiplying f_A and f_B in the structure factor equation.

The expression for the structure factor for the line hkl in a fully ordered alloy is:

$$F = f_A T_A + f_B T_B \quad (5.1)$$

For a disordered alloy this can be written:

$$F = (r_A f_A + w_A f_B) T_A + (r_B f_B + w_B f_A) T_B \quad (5.2)$$

If this is now multiplied by $Y_A + Y_B = 1$ and the multiplying factors of T_A and T_B considered separately, then the factor associated with T_A becomes:

$$r_A f_A Y_A + r_A f_A Y_B + w_A f_B Y_B + w_A f_B Y_A$$

Adding and subtracting the terms $(w_B f_A + r_B f_B) Y_B$ leads to an expression:

$$(r_A - w_B) f_A Y_B + (r_A Y_A + w_B Y_B) f_A + (w_A - r_B) f_B Y_B + (r_B Y_B + w_A f_A) f_B$$

By definition, the following identities hold:

$$Y_A r_A + Y_B w_B = X_A, \quad Y_B r_B + Y_A w_A = X_B$$

and if the order parameters S_A and S_B are defined as:-

$$S_A = r_A - w_B, \quad S_B = r_B - w_A$$

then the multiplying factor for T_A can be written as:

$$S_A f_A Y_B + X_A f_A - S_B f_B Y_B + f_B X_B$$

Similarly, adding and subtracting the term $(f_A f_A + w_A f_B) Y_A$ to the multiplying factor for T_B and collecting terms leads to the expression:

$$X_A f_A - S_A f_A Y_A + S_B f_B Y_A + X_B f_B$$

To apply this analysis to the β -W structure, Y_A , Y_B , T_A and T_B must be given the correct values for the structure, which are:

$$Y_A = \frac{1}{4}, \quad Y_B = \frac{1}{4}.$$

$$T_A = 2\{\cos\pi(k+1) \cdot \cos(\pi l/2) + \cos\pi(l+h) \cdot \cos(\pi h/2) + \cos\pi(h+k) \cdot \cos(\pi k/2)\}$$

$$T_B = 1 + \cos\pi(h+k+1)$$

The expression for the structure factor of the hkl line of the β -W structure then becomes:

$$F = (X_A f_A + f_B X_B)(T_A + T_B) + \frac{1}{4}(S_A f_A - S_B f_B)(T_A - 3T_B) \quad (5.3)$$

This expression can be shown to be equivalent to the vacancy model of Bachner and Gatos (1966), if the condition for vacancies on A sites as the only form of disorder, $S_B = 4X_B$, is introduced. Equation 5.3 then reduces to equation 2.3. To show the equivalence of this model with that of Van Reuth and Waterstraat in the case of pure interchange disorder, it is necessary to define those authors' order parameters, denoted here by S'_A and S'_B , in terms of the parameters defined above. These become:

$$S'_A = \frac{r_A - X_A}{1 - X_A} = \frac{r_A - w_B}{4(1-X_A)} = \frac{S_A}{4(1-X_A)} \quad (5.4a)$$

$$S'_B = \frac{r_B - X_B}{1 - X_B} = \frac{3(r_B - w_A)}{4(1-X_B)} = \frac{3S_B}{4(1-X_B)} \quad (5.4b)$$

It can be seen that for a stoichiometric alloy with no vacancies the Bragg-Williams order parameter S is equal to S_A , S_B , S'_A and S'_B , while for a non-stoichiometric

alloy, still without vacancies, S'_A and S'_B can be related to a single order parameter S' because $X_A + X_B = 1$. If, however, there are vacancies present S'_A and S'_B cannot be simply related as now $X_A + X_B + X_V = 1$, where X_V is the proportion of vacancies, and S_A , S_B , X_A and X_B must be treated as separate quantities.

5.3 Determination of Order Parameters and Composition from X-Ray Intensity Data

To obtain the values of X_A , X_B , S_A and S_B from equation 5.3, in the general case a minimum of five diffraction lines are necessary, since only relative intensities are measured. This number can be reduced to four if the intensity arising from thermal diffuse scattering is known to sufficient accuracy for it to be used as a scaling factor (see Appendix 3). Alternatively, if the composition of the alloy is known, the ratio X_A/X_B can be determined and the minimum number of lines to be measured reduced to three, providing the correct lines are chosen for reasons which will be explained in section 5.4.

To explore the applicability of the last approach, the theoretical intensities of the 222, 320 321 and 400 diffraction lines of the four A.15 structures studied were calculated from equation 5.3, corrected for multiplicities and scaled to the intensity of the 400 line. This was done using computer programme ORDER (Appendix 4f). The atomic scattering factors were taken from Mirkin (1964) and the International Tables for X-ray Crystallography (1962) and the anomalous dispersion corrections from Warren (1969). The mean $\sin\theta/\lambda$ was taken for the four lines for each system, the errors in the atomic scattering factors involved in this approximation being less than those involved in using scattering factors derived by different methods. The values used were calculated from Fermi-Thomas method, but a comparison was carried out for V-Si and V-Ga with the scattering factors derived from Hartree-Fock self-consistent field

theory and the variation in the intensity ratios was of the order of 2-3%.

These theoretical intensity ratios, I_{222}/I_{400} , I_{320}/I_{400} , I_{321}/I_{400} for the A.15 phase of V-Si are plotted in figure 5.1 against composition for various degrees of disorder. This gives a chart for each reflection on which the solid lines (one for each reflection) refer to pure vacancy disorder i.e. all A atoms are on A sites and B atoms on B sites, but not all sites are occupied. If the following terms are defined the other lines on the charts can be explained:

AA = percentage of A atoms on A sites

AB = percentage of A atoms on B sites

BA = percentage of B atoms on A sites

BB = percentage of B atoms on B sites.

The lines in the charts can now be characterised by a pair of indices (AB, BA). The pure vacancy disorder line is defined as (AB, BA) = (0, 0) and the dotted lines parallel to it represent (AB, 0) or (BA, 0) depending upon which side of the (0, 0) line they lie. General values of (AB, BA) can be derived by drawing lines parallel to the (0, 0) line such that the spacing measured from (0, 0) line is given by the difference between the (AB, 0) spacing and the (0, BA) spacing. The point X, for example, in figure 5.1 is a distance 3.0 from the (0, 0) line, the (AB, 0) spacing is 7.5 and the (0, BA) spacing 6.0. If (n_1, n_2) are the indices of the line through X then

$$n_1 \cdot 7.5 - n_2 \cdot 6.0 = 3.0$$

To find the values of n_1 and n_2 a table similar to table 5.1 can be constructed, only the near diagonal terms being necessary as the distance from the nearest (AB, 0) or (0, BA) line can be measured. The nearest value to the intercept can be chosen and the indices read off. In the present example (n_1, n_2) can (2, 2) or (6, 7) or possible higher values.

Once these values have been determined with a knowledge of the composition, all the other parameters can be determined from the computed tables used to plot

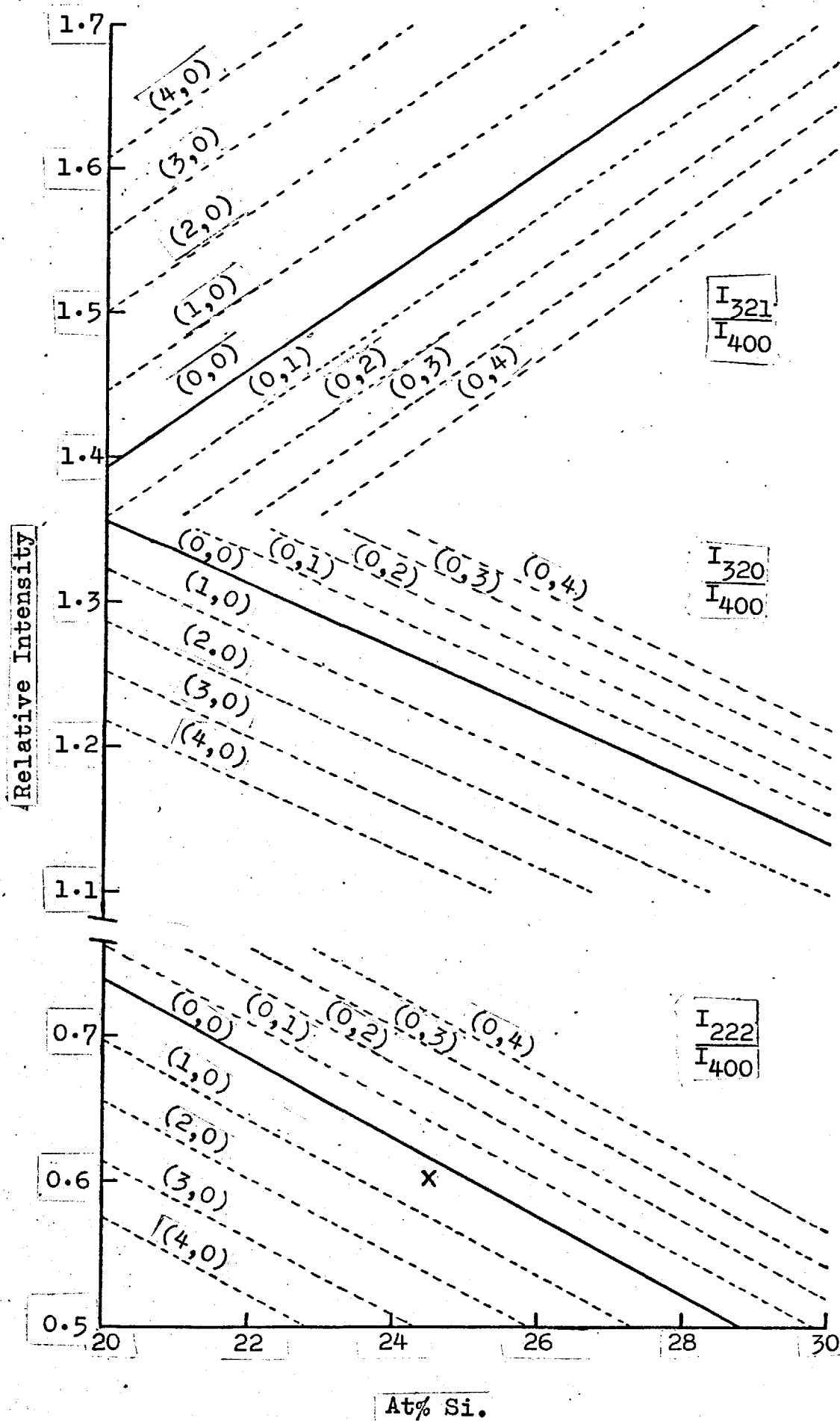


Figure 5.1.

Theoretical Intensity Charts for the V-Si System.

Table 5.1.

Table for use in determining (AB,BA)

	1	2	3	4	5	6	7	8	9	n_1
1	1.5									
2	-4.5	3.0								
3		-3.0	4.5							
4			-1.5	6.0						
5			-7.5	0	7.5					
6				-6.0	1.5					
7					-4.5	3.0				
8						-3.0	4.5			
9							-1.5	6.0		
10								0	7.5	

n'
2

the charts. An example of these is given in Table 5.2.

5.4 The Fitting of Experimental Data to the Charts

In the previous section the method of determining the degree of order once the position of the point X in figure 5.1 is known has been described. In theory it should be possible to plot the point X from the relative intensity I_{hkl}/I_{400} for a specified composition, but in practice both the composition and the intensities may not be known to sufficient accuracy and, hence, the three measured intensity ratios are plotted on a strip of graph paper which is then moved horizontally and possibly vertically until the degree of order is the same for all three Bragg reflections. The degree of order is then calculated as explained in the previous section. The composition may also be read off the chart and compared with the given value, in the present case inferred from room temperature lattice parameter plots. It is possible to carry out the fitting procedure with only two intensity ratios, particularly if they respond in opposite senses to changes of order, as do the ratios I_{321}/I_{400} and I_{320}/I_{400} for the β -W structure, but the third ratio is necessary if the composition is to be found.

5.5 Applications and Limitations of the Method

The degeneracy referred to at the end of section 5.3 is inherent in equation 5.3 and its occurrence will depend on the atomic scattering factors of the constituent atoms. This limits the application of the model, therefore as it is not always possible to distinguish between the types of order, particularly in a stoichiometric alloy. It is, however, possible to distinguish between interchange disorder and vacancy disorder in a non-stoichiometric alloy, for in an A-rich non-stoichiometric alloy either the excess A atoms will go to B sites or vacancies will be created on B sites. One mechanism will probably be preferred because of the relative sizes and valencies of the constituent atoms. If vacancies are created on B sites the

V-SI SYSTEM
DISORDER

SA	SB	XA	XB	I12/I16	I13/I16	I14/I16	YA	YB	AA	AB	BB	BA
100.	100.	75.	25.	0.6047	1.2446	1.5643	75.	25.	75.	0.	25.	0.
100.	96.	75.	24.	0.6246	1.2610	1.5384	76.	24.	75.	0.	24.	0.
96.	96.	76.	24.	0.5909	1.2332	1.5825	76.	24.	75.	1.	24.	0.
100.	92.	75.	23.	0.6451	1.2778	1.5125	77.	23.	75.	0.	23.	0.
96.	92.	76.	23.	0.6104	1.2493	1.5568	77.	23.	75.	1.	23.	0.
92.	92.	77.	23.	0.5774	1.2219	1.6007	77.	23.	75.	2.	23.	0.
100.	88.	75.	22.	0.6662	1.2948	1.4864	77.	23.	75.	0.	22.	0.
96.	88.	76.	22.	0.6305	1.2659	1.5309	78.	22.	75.	1.	22.	0.
92.	88.	77.	22.	0.5965	1.2379	1.5750	78.	22.	75.	2.	22.	0.
88.	88.	78.	22.	0.5642	1.2108	1.6188	78.	22.	75.	3.	22.	0.
100.	84.	75.	21.	0.6880	1.3123	1.4602	78.	22.	75.	0.	21.	0.
96.	84.	76.	21.	0.6512	1.2827	1.5049	78.	22.	75.	1.	21.	0.
92.	84.	77.	21.	0.6162	1.2541	1.5492	79.	21.	75.	2.	21.	0.
88.	84.	78.	21.	0.5830	1.2265	1.5932	79.	21.	75.	3.	21.	0.
84.	84.	79.	21.	0.5513	1.1998	1.6368	79.	21.	75.	4.	21.	0.
99.	100.	74.	25.	0.5981	1.2391	1.5730	75.	25.	74.	0.	25.	0.
99.	99.	74.	26.	0.6019	1.2423	1.5679	74.	26.	74.	0.	25.	1.
99.	96.	74.	24.	0.6180	1.2556	1.5468	76.	24.	74.	0.	24.	0.
99.	95.	74.	25.	0.6219	1.2588	1.5419	75.	25.	74.	0.	24.	1.
95.	96.	75.	24.	0.5843	1.2276	1.5914	76.	24.	74.	1.	24.	0.
95.	95.	75.	25.	0.5882	1.2309	1.5862	75.	25.	74.	1.	24.	1.
99.	92.	74.	23.	0.6386	1.2725	1.5206	76.	24.	74.	0.	23.	0.
99.	91.	74.	24.	0.6424	1.2756	1.5158	76.	24.	74.	0.	23.	1.
95.	92.	75.	23.	0.6038	1.2439	1.5654	77.	23.	74.	1.	23.	0.
95.	91.	75.	24.	0.6077	1.2471	1.5603	76.	24.	74.	1.	23.	1.
91.	92.	76.	23.	0.5707	1.2163	1.6098	77.	23.	74.	2.	23.	0.
91.	91.	76.	24.	0.5747	1.2196	1.6044	76.	24.	74.	2.	23.	1.
99.	88.	74.	22.	0.6599	1.2897	1.4942	77.	23.	74.	0.	22.	0.
99.	87.	74.	23.	0.6636	1.2927	1.4896	76.	24.	74.	0.	22.	1.

Table 5.2. Order parameters, site occupations and Intensities for V-Si.

intensity ratio will be on the (0, 0) line. If the excess A atoms go to B sites then the intensity ratio will have a value different from the (0, 0) line. In both cases it would be unlikely for thermodynamic reasons that B atoms would enter A sites, in an A-rich alloy, particularly in a material which retains its order to high temperatures as the β -W compounds appear to do, for the intensity ratios do not alter significantly with temperature. It can therefore be assumed that if A atoms enter B sites, or vice-versa in a B-rich alloy, then interchange disorder predominates, and if vacancies are produced then vacancy disorder is the predominating mode.

Three distinct types of behaviour can now be distinguished:-

1. Vacancy disorder on one side of stoichiometry only with interchange disorder on the other side.
2. Vacancy disorder on both sides of stoichiometry.
3. Interchange disorder on both sides of stoichiometry.

For type 1 behaviour one type of atom (A) cannot enter the opposite type of site (B), but B atoms can enter site A, or vice versa. At stoichiometry, therefore, perfect order is to be expected. On the opposite side of stoichiometry the excess B atoms will enter A sites creating interchange disorder. For type 2 behaviour neither type of atom can enter the opposite type of site and again perfect order or an equal number of vacancies on each type of site, an indistinguishable situation, is expected at the stoichiometric composition. Only for the third type of behaviour is disorder probable at stoichiometry. In theory the intensity ratio could lie on the (0, 0) line for all compositions, so that this behaviour could not be distinguished from type 2 behaviour. It seems likely, however, that because both types of atom can be on both types of site, the disorder and, therefore, the intensity ratio will vary with composition. If such behaviour occurred in β -W compounds the implied equivalence of the two types of atom, would suggest that a classical order-disorder transformation

should take place. As the β -W compounds appear to be ordered at high temperatures, no change in intensities being observable on heating, such behaviour in these alloys seems improbable.

It can be concluded, therefore, that although the method described in this chapter has its limitations in deriving quantitative results, particularly for stoichiometric alloys, it can be an important aid to the study of the variations in ordering in non-stoichiometric alloys. From such variations an indication of the behaviour of the stoichiometric alloys can be deduced.

5.6 Order in the β -W Alloys

It is now possible to interpret the intensity measurements on the β -W alloys in terms of the arguments in the preceding sections. As the changes in intensity with temperature were always associated with lattice parameter changes, these were attributed to changes in composition, as will be discussed in chapter six. Only the order in the alloys at room temperature was therefore calculated.

While it was not always possible to obtain perfect agreement between the results from the three intensity ratios of one alloy for the site occupation parameters, reasonable results were obtained by using the 320/400 and 321/400 ratios. The small multiplicities of both the 222 and 400 lines meant that for these two lines harmonic effects, the errors in recording the intensity and the errors in intensity measurement were proportionally greater than for the 320 and 321 lines and the different result from the 222/400 ratio was not, therefore, unexpected. It was, however, usually in qualitative agreement with the other two i.e. it indicated the same mode of disorder, if not the same degree of disorder. Because of this scatter in the results, no interpolation between the (0, BA) and (AB, 0) lines was carried out, the values of the nearest of these lines being sufficient to characterise the dis-

Table 5.3.Site Occupation in β -W Compounds.

Sample No.	Composition	AB	BA
Nb-Sn 1	29 at % Sn	0	9
Nb-Sn 2	26 at % Sn	0	4
V-Si 2	25 at % Si	0	3
V-Si 3	25 at % Si	0	0
V-Si 4	25 at % Si	0	2
V-Si 9	22 at % Si	2	0
V-Si 10	20 at % Si	2	0
V-Si 11	20 at % Si	4	0
V-Si 12	19 at % Si	5	0
V-Ga 1	26 at % Ga	0	2
V-Ga 6	28 at % Ga	0	5
Nb-Al 2	21 at % Al	3	0
Nb-Al 5	16 at % Al	5	0

For definitions of AB and BA, see section 5.3.

order mode in the non-stoichiometric alloys.

The results are given in table 5.3, and the predominant mode of disorder in the non-stoichiometric alloys is interchange i.e. the atoms of the type in excess enter the other atom sites. This is true particularly of Nb-Sn (1) and accounts for its anomalously high lattice parameter. At the stoichiometric composition of V-Si there is evidence that a certain amount of interchange disorder is present, in agreement with van Reuth and Waterstraat (1966) but the exact amount is difficult to determine for the reasons given above. The implications of the behaviour will be discussed in chapter six, but the present results indicate that the predominant disordering mode in a non-stoichiometric alloy can be determined using the method described in this chapter.

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Chapter Six

Discussion of Results

"If the world were good
for nothing else, it is a fine
subject for speculation".

- William Hazlitt

6.1 Introduction

Up to this point in the thesis, the work has been considered in terms of the different measurements made on the materials studied. In this discussion chapter, the four systems Nb-Sn, V-Si, V-Ga and Nb-Al will be discussed with reference to both previous work and the results reported in chapters four and five. A final section will be devoted to a comparison of the experimental results with the current theories.

6.2 The Niobium-Tin System

6.2a The Structure at Low Temperatures

The existence of a structural transformation in the Nb-Sn system at a temperature a little higher than the superconducting transition temperature has been reported in the literature and confirmed by the present results. That the transformation temperature T_m is a function of composition is also evident from these results, in agreement with King (1968), who made measurements, during heating only, on some of these alloys. However, from measurements made on other alloys and the results of Vieland (1970) and Vieland and Wicklund (1971), together with the replotted composition/lattice parameter relationship given in figure 2.7, it appears that the Sn-rich boundary of the phase lies at about 26 at % Sn ($a = 5.2911 \text{ \AA}$) i.e. at a higher Sn concentration than that proposed by King (1968). From figure 2.6 it can be seen that this concentration is in fact the equilibrium Sn-rich boundary of the parent β -W phase. The low Sn concentration boundary of the martensitic phase, however, occurs at $5.2866 \text{ \AA}$ which corresponds to a composition of approximately 23 at % Sn, which does not coincide with the low Sn boundary of the β -W phase, which occurs at approximately 18 at % Sn, and hence only alloys which contain more than 23 at % Sn in the β -W phase transform martensitically on cooling.

No hysteresis was observed in the transformation at any composition, in agreement with Vieland et al. (1971) (who only measured a stoichiometric alloy), and hence, as noted in chapter four, the M_s and A_f temperatures can be identified as can the M_f and A_s temperatures. The dotted M_s line proposed by King (1968) on the basis of the single point of Mailfert et al. (1967) is, therefore, in error.

For all compositions the transformation took place over a fixed range of temperature, regardless of the cooling or heating rate. The low temperature tetragonal structure is thus an equilibrium structure. This, however, does not contravene the phase rule, which is usually interpreted as giving a single transformation in a one component (or constant composition) system. This interpretation arises because in normal diffusion controlled transformations, any effects of pressure or stress can be relieved continuously and the phase rule is written $P + F = C + 1$ (P is the number of phases, C the number of components and F the resulting number of degrees of freedom). In a martensitic transformation, however, the pressure created by the volume difference (even though they may be small) and the stresses caused by the maintenance of a coherent interface cannot be relieved and hence the full phase rule must be written in its original form $P + F = C + 2$, which allows related temperature and pressure variations for a transformation at a fixed composition.

There are several possible reasons for the transformation taking place over a range of temperatures. Firstly, there may be differences in composition among the grains making up the powder, a likely explanation as in a single crystal Mailfert et al. (1967) found a single transformation temperature. Secondly, even within the crystallites there may be composition gradients, as found by Batterman and Barrett (1965) in a single crystal of V-Si only some sections of which transformed. Thirdly, there is the variation in crystallite size, for in general M_s is known to be a function of particle size (Reed and

Breedis 1966).

The order of the transformation has been the subject of much discussion in the literature but the paper by Vieland et al. (1971) shows that the transition in a stoichiometric material is of the first order because of the spontaneous strain observed (figure 2.22a). The results reported in this thesis confirm this and show that it is the case for all compositions. The spontaneous strain was deduced from the axial ratio which was measured from the diffraction line splitting at $M_f(A_s)$, and it decreases with increasing tin content up to the stoichiometric value, beyond which the axial ratio becomes inverted, indicating that the direction, but not the value, of the tetragonal strain is reversed. Although, at first sight, this may appear anomalous, it is not unreasonable since the strain involved in introducing excess Nb atoms into large Sn sites is quite different from the situation beyond stoichiometry where the large Sn atoms must be fitted into the much smaller Nb atom sites, as can be seen from the anomalously high lattice parameter of Nb-Sn (1), the diffusion prepared sample which has Sn atoms on Nb sites. Since the reversal in c/a is abrupt it is possible that alloys such as Nb-Sn(9) may have areas of both tetragonalities, positive and negative, as can be seen from the chart record of the 400 diffraction peak at 27° K in figure 6.1. A similar result for $Nb_3(Sn_x, Sb_{1-x})$ was found by Vieland (1970) and the reasons for this will be similar, although the presence of a third atom type complicates the situation.

The original argument that the phase was of the second order was based on the apparent absence of a volume change. The measurements of King et al. (1967) indicate that a small volume change does occur, but even if this were not the case, the absence of a volume change would not invalidate the statement that the phase change is of the first order, for a change in free energy arises from the stress-strain term due to the shape change. The lack of a latent heat has also been explained, by Vieland et al. (1971). As the transformation occurs over a range of temperature, some regions of the material will be

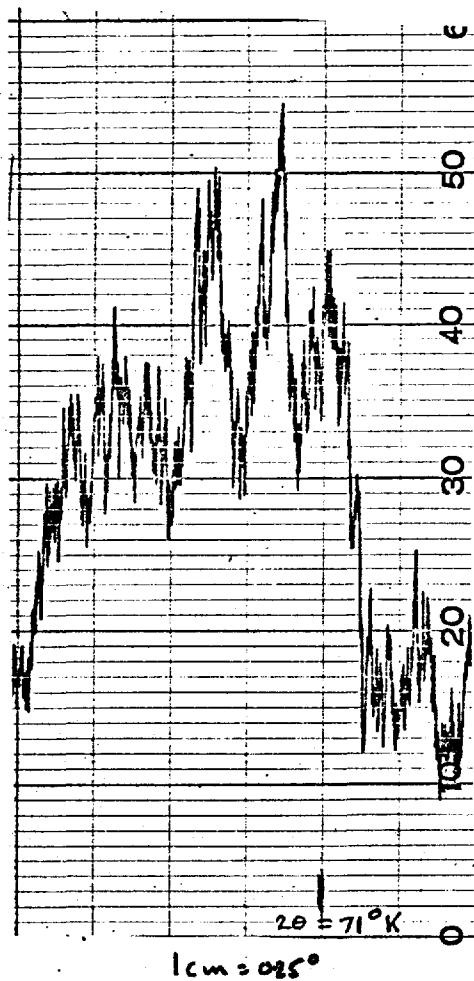


Figure 6.1. The 400 line of Nb-Sn(9) at 27₀ K.

unstable with respect to a tetragonal distortion at a slightly higher temperature than others, for reasons discussed above, and at $M_s(A_f)$ a slight broadening of certain X-ray peaks will be produced, as is observed. The bulk of the crystal will not soften until the temperature denoted as $M_f(A_s)$ is reached. Between M_s and M_f the first material to transform will, however, not be able to relieve completely the stress by achieving the full tetragonal strain as it will be clamped by the untransformed material. This is why slight broadening in the X-ray peaks and a blurring of the specific heat discontinuity is observed.

The effects of the surrounding material on crystallites which are unstable to a tetragonal strain are even more important in V-Si and will, therefore, be discussed further in section 6.3a and, with reference to the theory, in section 6.6a.

6.2b The Superconducting Properties

The critical temperatures measured for the Nb-Sn alloys (figure 4.30) show a certain amount of scatter about the line taken from other data but the general trend is similar, an increase in T_c towards the stoichiometric composition. The high value at this composition can be attributed to the electron to atom ratio coming at a peak in the Matthias plot (Figure 1.10a) but although the fall is due partly to the change in this ratio with composition, the strain in the lattice due to the departure from stoichiometry may be a more important parameter. Testardi (1971) has calculated the dependence of T_c on strain for the V-based systems but similar data are not available for Nb-Sn, though it is expected that a similar result would be obtained.

No magnetisation measurements were made during the present work but it is interesting to consider published work of Potapov (1967, 1969), whose results have been replotted in figure 6.2. The resemblance between these curves and the low temperature phase ^{diagram} is striking. Potapov

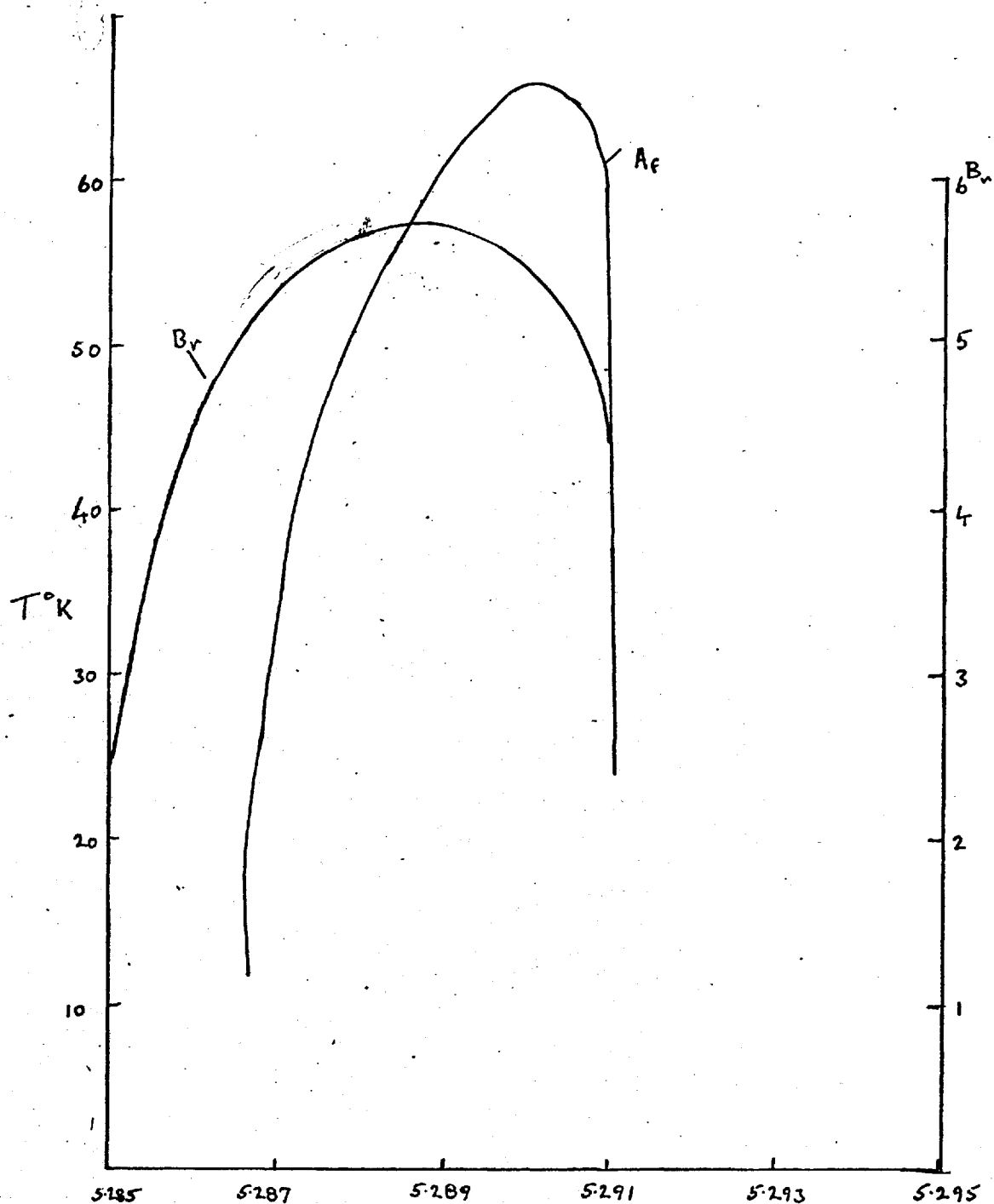


Figure 6.2. The remanent flux (Potapov 1969) and the A_f temperature (from figure 4.25) as a function of lattice parameter.

attributes the flux pinning to the factor S , the area of the grain boundaries in the specimen, which changes with composition. Normally, however, heat treatment will alter the grain size of a material and thus at one composition a variation in S could be obtained. That the microstructure of V-Si is sensitive to heat treatment can be seen from the micrographs in figure 4.2. and similar behaviour would again be expected for Nb-Sn. If the flux pinning is a function of grain boundary area, then it can be assumed that heat treatment will move the curve of the variation in S parallel to the ordinate axis. The size of crystallites in an alloy is then a function of composition reaching a peak near the stoichiometric value.

An alternative flux pinning mechanism is the presence of dislocations arising from the structural transformation. Maximum flux pinning (as indicated by B_r) occurs at the same composition as the highest value of the transformation temperature and the density of dislocation tangles arising from the stresses involved in the transformation of grains which are randomly oriented, particularly in a polycrystalline material, are also likely to be at a maximum at this composition, for the stresses appear to be related to a degree of cooling below the transformation temperature, increasing as the temperature is lowered. Such a model will be discussed further in terms of the V-Si system where flux pinning and lattice softening occur but no transformation.

6.2c The Effects of Heat Treatment

The effects of heat treatment on Nb-Sn alloys have been observed in several different ways. The range of observations have, however, been limited to an almost stoichiometric alloy obtained after heat treatment of a diffusion prepared sample. The thermal expansion and ordering results have been shown in figure 4.3, 4.13 and 4.14. Nb-Sn (1) is the as-cast material and Nb-Sn (2) the material after heat treatment. The effect of heating

the as-cast material in the high temperature camera was to reduce its lattice parameter and heating the already heat-treated material produced no apparent change in lattice parameter (Figure 4.3 is in error for the reasons given in section 4.3 as is shown by a direct comparison of the room temperature films before and after heating). No change in order is apparent for this sample either, all the variations in the intensity plot in figure 4.14 being within experimental error.

The change in lattice parameter of Nb-Sn (1) appears to have taken place between 800 and 900° C as would be expected from the annealing treatment. The evidence all indicates that this lowering of the lattice parameter was due to the evolution of Sn and not of hydrogen. Firstly Mailfert et al. (1967) observed a 2% weight loss on heating and King (1971) observed the deposition of Sn on a cold surface in the pumping line. Secondly the treatment of Nb-Sn with acid (section 4.1) produced not only a change in lattice parameter but also a large strain, which was not observed in the freshly prepared diffusion alloys. Thirdly, the ordering measurements indicate that there are Sn atoms on Nb sites and at 600° C (nearly twice the melting point of Sn) a change in the intensity ratios is observed corresponding to a change in composition towards stoichiometry.

It is therefore concluded that the high lattice parameter in the diffusion prepared sample is due to the presence of Sn atoms on Nb sites. As the alloy composition lies outside the normal limits of the phase it is likely that this is due to the effects of the high pressure of formation. As no changes were observed in the degree of order of the stoichiometric alloy it can also be concluded that the changes in order are due solely to changes in composition in the direction either of stoichiometry or of greater homogeneity, rather than to a change in the degree of long range order. One problem which is still outstanding, however, is the high values of T_c for the

diffusion prepared sample for the presence of Sn atoms on Nb sites should cause degradation of the superconducting properties.

6.3 The Vanadium Silicon Structure

6.3a The Structure at Low Temperatures

From a study of the literature (section 2.5) it is clear that a cubic to tetragonal structural transformation takes place in single crystals of the V-Si β -W phase. That this only occurs over a very narrow composition range also appears from a closer study. Batterman and Barrett (1965) report that only some of the crystals taken from the same bar underwent a change to the low temperature tetragonal structure and Testardi et al. (1971) describe the details of crystallisation (section 2.8) such that a sample which has a higher transformation temperature (T_m) has a lower superconducting critical temperature (T_c). Testardi attributes this to the strain due to the structural transformation but it appears more likely that the drop in T_c is due to a change in composition, which is also a strain effect as Testardi, himself, indicates as the amount of second phase increases with the drop in T_c . From these observations it seems probable that the tetragonal phase of V-Si is very narrow and does not include the stoichiometric value.

The only firm evidence of a transformation in a powdered sample in the literature is that of King et al. (1967) and the present work shows that this result must be considered as doubtful. Batterman and Barrett (1965) observed broadening in powder lines but it was not clear enough for quantitative measurements to be made. The absence of a transformation in the samples studied in the present work is attributable to any of the four causes assuming that the sample was at the temperature measured, which, for the reasons explained in chapter four, is almost certain. Firstly the grain size of the powders may be too small for nucleation.

An approximate calculation from the micrographs, however, shows that the average grain size was 10-60 μm . and as the particle size was $<100 \mu\text{m}$, many of the particles contained more than one grain, and as can be seen from the X-ray peaks of V-Si (8), (figure 4.29) no broadening due to particle size effects could be observed. In view of this, it is concluded that such a mechanism is not responsible for the absence of a transformation.

Secondly, the range of composition of the low temperature tetragonal form of V-Si is very narrow as seems clear from the evidence described above as well as from the lattice softening measurements of Finlayson (1968), (figure 2.20). A simple explanation for the absence of a transformation in the samples studied in the present work is that no sample falling within the tetragonal structure composition range was prepared. As many samples around the stoichiometric value were studied this does not seem very likely. A third possible explanation, that impurities present in the β -W phase possibly due to the easy oxidation of vanadium, suppress the transformation also seems unlikely as such impurities would be expected to reduce the superconducting T_c , an effect which was not observed.

A fourth explanation seems the most likely. The samples, as can be seen from the micrographs in figure 4.2, were not single phase and probably, as in the Nb-Sn samples, a certain range of composition existed amongst the grains of the β -W phase. From a study of the transformation in Nb-Sn it appears probable that the tetragonality of some crystallites is at least partially suppressed by the pressure of the untransformed crystallites, and in V-Si the strain involved is smaller by a factor of 2.5, (Mailfert et al. 1967), so that the pressure of untransformed material, both β -W and second phase, could be sufficient to completely suppress the transformation. Indeed, Kunzler et al. (1966) have shown that pressure will suppress the specific heat anomaly, due to the transformation in a single crystal of V-Si. Therefore, unless

a powder sample is very homogeneous and of the correct composition, it will not transform to a tetragonal form at low temperatures. This arises from a combination of two factors, the small tetragonal strain in V-Si and the narrow composition range of the tetragonal phase. The cause of the narrowness of the martensitic phase may be due to the bulk strain arising from the deviation from stoichiometry, and this will be discussed more fully in section 6.6. The presence of such a strain is, however, implied by the lattice parameter variation across the phase and the associated variation in the atomic site occupation, V atoms being situated on Si sites in the low Si content alloys.

6.3b The Superconducting Properties

The critical temperatures of the V-Si alloys studied in the present work show a distribution with composition in agreement with that derived from the published data. As with Nb-Sn the T_c decreases as the alloy becomes less stoichiometric, Testardi (1971) has derived a dependence of T_c on the hydrostatic strain in V-alloys produced by increasing non-stoichiometry and his results together with experimental points for binary and pseudo-binary alloys are shown in figure 6.3. It appears from this result that this strain factor has a more marked effect on T_c than does the variation in the electron to atom ratio which is only varying slowly across the β -W phase range. What the mechanism of this effect is will be considered in section 6.6.

Consideration of the results of Finlayson (1968) in figures 2.20 and 2.25 shows a relationship between the lattice softening and the flux pinning composition dependences for V-Si, very similar to the relationship between the structural transformation temperature and the flux pinning for Nb-Sn, although the peak is sharper. The peak in lattice softening implies a similar phase diagram for V-Si to that found for Nb-Sn, but although a phase transformation has not been observed in these polycrystalline materials (Finlayson's sample showing maximum lattice softening is V-Si (1)), the stresses arising from the

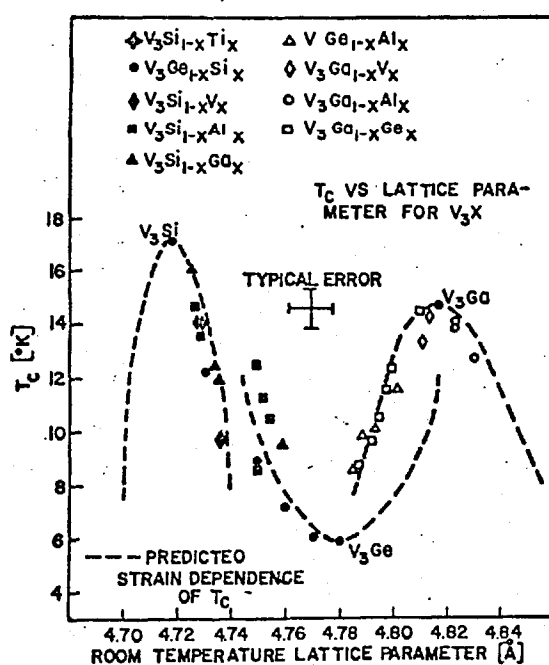


Figure 6.3. The strain dependence of T_c in the V-based β -W alloys. (Testardi 1971)

suppression of a transformation will, nonetheless, increase with the degree of supercooling below T_m . If the narrowness of the phase predicted in the previous section is correct, then the flux pinning curve will take the form found by Finlayson (1968), except for the somewhat less steep decline towards the lower Si contents. As the lattice softening and flux pinning curves have the same form here the stresses will still be present but the transformation temperature will be below the superconducting T_c and no transformation will take place as the different density of states at the Fermi surface below T_c will stabilise the cubic phase, as discussed by Labbe (1968). It was not possible to determine with any accuracy the area of the grain boundaries in Finlayson's alloys but there appears to be a decrease in the amount of second phase as stoichiometry is approached. This makes it appear unlikely that second phase is responsible for the flux pinning, as suggested by Finlayson (1968).

6.3c The Effects of Heat Treatment

A more detailed study of the effects of heat treatment was made on the V-Si system than on the Nb-Sn system and the results of the high temperature X-ray measurements were shown in figures 4.4 to 4.10 and 4.15 to 4.21. The thermal expansion curves are approximately linear except for anomalous points at certain temperatures and, if the intensity ratios are considered at these temperatures an anomaly is also found, indicating a change in composition. The change in lattice parameter due to a change in ordering would be of the same magnitude as the experimental error and it can therefore be concluded that, in general, heat treatment has the effect of changing the lattice parameter and hence the composition. Consideration of the micrographs confirms this, for heat treatment at different temperatures produces different grain structures due to the interaction of the β -W phase with the second phase present. Such an interaction will almost certainly produce a change in composition of the β -W phase. This result confirms those for Nb-Sn of Maier (1969)

and Vieland (1964). Further evidence comes from the superconducting T_c 's before and after heat treatment. high T_c 's tend to be reduced and low T_c 's enhanced implying that the composition of the β -W phase has tended to move towards the centre of its range and the alloy as a whole become more homogeneous.

6.4 The Vanadium-Gallium System

6.4a The Low Temperature Structure

Only one report of a transformation to a tetragonal structure in the V-Ga system has appeared in the literature, that by Nembach et al. (1970). These authors observed the transformation in an electron microscope specimen prepared by the interdiffusion of adjacent V and Ga layers. Broadening of the lines of the β -W phase at about 50° K was attributed to a possible phase transformation. The possible transformation observed in the present work occurred at 15° K, a temperature the same as the superconducting critical temperature of the sample. As this was the sample with the highest T_c measured and was within the error of measurement, stoichiometric, the data available for Nb-Sn and V-Si indicate that this sample was the most likely to transform. No single crystals have been prepared of V_3Ga and no evidence is available, therefore, for comparison with the powder work. If this sample did transform, then the range of composition of the martensitic phase in V-Ga is of the same order as that in V-Si and the axial ratio (1.0005) is of the same order as that of the V-Si martensite. If, however, the temperature measured by Nembach et al. is correct then a much broader range of composition would be expected for the tetragonal phase and probably a higher axial ratio, in which case a transformation would be expected in others of the samples examined. As reported in chapter four no such effect was found but a transformation could have been suppressed for the same reasons as in the V-Si system. The result of Gossard (1966) that no broadening

was observed in the n.m.r. spectrum of V_3Ga indicates that if a transformation does take place the composition range of the tetragonal phase is narrow and does not include the stoichiometric value. No lattice softening measurements as a function of composition have been reported for this system, but the high value of the softening at the stoichiometric composition indicates that a transformation is likely but suppressed.

6.4b Superconducting Properties

Apart from the low values of T_c for some of the alloys near stoichiometry, which may be due to disorder in the lattice, the measured values of T_c show good correspondence with the line taken from previously published results. The curve, as for V-Si, follows that predicted by Testardi (1971) shown in figure 6.3 and as for the previous system the strain is a more important factor than the variation in the electron to atom ratio.

The upper critical field for V-Ga is limited by the high normal state paramagnetic limiting (Clogston 1962 and Chandrasekar 1962) but the results of Foner et al. (1970) shown in figure 2.26c imply that V-Ga has a peak at the stoichiometric composition in the value of H_{c2} and, hence, in the value of κ and the amount of flux pinning. If this is so, then the behaviour described for Nb-Sn and V-Si is also typical of V-Ga and is further evidence for the low temperature phase diagram suggested in the previous section. An alternative explanation is that with the drop in T_c the drop in H_{c2} is automatic following the relation derived by Clogston (1962):

$$H_{c2} = k T_c \quad (6.1)$$

where k is a constant equal to $18.4 \text{ K-gauss}/^\circ \text{K}$. However, as it is the bulk hydrostatic strain which reduced T_c , and in the other systems the variations in pinning and lattice softening are related, it seems probable that the same relationship will hold for the V-Ga system.

6.4c The Effect of Heat Treatment

Levinstein et al. (1965) show a plot of lattice parameter against annealing temperature for a sample of composition 2 V:Ga (figure 6.4) and the lattice parameter/composition relationship shows that this is due to a change in composition. The present specimens show a slightly different behaviour. The thermal expansion curves (figure 4.11) of the two alloys studied by X-rays at high temperature, one with 26 at % Ga (V-Ga1) the other with 28 at % Ga (V-Ga6), are linear except for the measurements on the alloy after heating to a temperature above 1000° C. Above this temperature the phase range of the "Cs-Cl" structure phase, is entered, as was clear from the presence of additional peaks in the powder pattern. The intensity ratios (figures 4.22 and 4.23) are also virtually constant until this higher temperature is approached. Changes on heating and cooling in V-Ga (6) were within the experimental error and it was concluded that no changes in composition or order took place. From the measurements of the T_c 's of the samples before and after the heat treatment described in section 4.5 it was concluded that the composition of V-Ga (6) had moved towards the stoichiometric, an increase of 2° K in the T_c being observed. Changes of composition, therefore, are related to the temperature of heat treatment, as can be confirmed by examination of the micrographs in figure 4.2. It is clear then that the behaviour of the V-Ga system is similar to that of the other two systems considered.

6.5 The Niobium-Aluminium System

No evidence of a transformation to a tetragonal structure was observed in any of the Nb-Al alloys cooled. The peaks used were broad even at room temperature and showed no sign of broadening further on cooling. This is in agreement with the results of Willens et al. (1969) using n.m.r. techniques. It is interesting to note, however, that these authors observed an increase

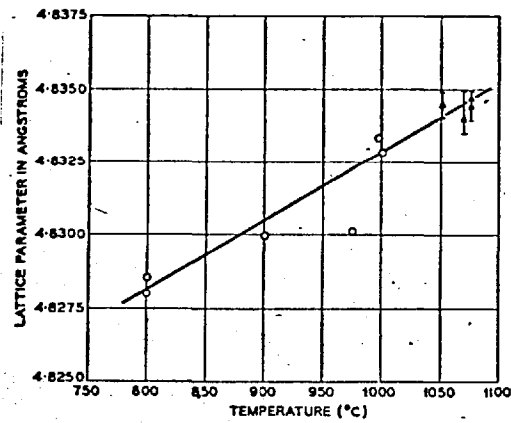


Figure 6.4. The dependence of lattice parameter on heat treatment temperature in V-Ga. (Levinstein et al. 1965)

in superconducting critical temperature after heat treatment, a result implying that a change of composition had taken place during such treatment. No such change of composition is referred to by the authors nor, indeed, is composition referred to at all, a rather strange omission in view of the wealth of literature referring to the composition ranges of the β -W structure materials! That no transformation can take place is by no means certain. In V-Si, a T_c lower than the maximum is observed for the alloy which transforms (Testardi et al. 1971) and it does not seem unlikely that a similar effect occurs in Nb-Al. Moreover, lattice softening is observed as for the other three systems studied (figure 2.17a). Willens et al. however, present further data for Nb-Al indicating that in many of its physical properties, e.g. the electronic specific heat and the temperature dependence of the magnetic susceptibility, it differs radically from the other three compounds. This implies that the Fermi level does not lie near a peak in the density of states and that no transformation is, therefore, possible.

As noted above, heat treatment alters the composition of an alloy and this can be seen clearly from the high temperature X-ray results (figures 4.12 and 4.24). The sample with the higher Al content has a virtually linear thermal expansion curve and constant intensity ratios up to 1000°C which is to be expected as it lies within the β -W phase the whole time. Above this temperature there is a change in both the intensity ratio and the thermal expansion curve, indicating that a composition change has taken place. The sample with the lower Al content, moreover, after reaching a temperature of 1000°C undergoes a complete phase change. At this composition (≈ 16 at % Al) this is to be expected as the stable structure is now the α -Nb solid solution. Heat treatment, therefore, has a similar effect in this system to that observed in the other three and no classical order-disorder transformation is observed.

6.6 Comparison of the Experimental Results with The Theoretical Predictions

6.6a Composition Dependence of the Structural Properties

As described in section 2.7, there are two band theories of the β -W compounds, one by Labbé, Friedel and Barišić and the other by Cody, Cohen and Halloran (subsequently referred to as LFB and CCH). Both of these are based on a model in which the Fermi level lies near a discontinuity in the density of states, such that a temperature change causes the Fermi level to go from a peak in density of states to a trough, and the tetragonal instability is produced. Both derive these results from a consideration of the Helmholtz free energy, predict the transformation to be of the first order and derive the correct variation of the elastic constants. CCH (1968) derive the curve shown in figure 2.29d for the tetragonal distortion, in good agreement with the later work of Vieland et al. (1971) while LFB (Labbé 1967) obtain the dependence on the sub-band filling (figures 2.28a) of the point at which the shear modulus goes to zero (figure 2.28c). Vieland et al. (1971) have since demonstrated that because the structural transformation takes place the shear modulus does not go to zero. The derivation is, none the less, valid as the temperature difference between the transformation temperature and the point at which the extrapolated shear modulus/temperature curve goes to zero is very small (figure 2.22b).

The numerical value of the sub-band filling, defined by the ratio Q/Q_0 , was calculated by LFB from the maximum value of the transformation temperature then known and the sign of the tetragonal strain. If

$$Q/Q_0 < \frac{8a^2A}{M^1} \quad (6.2)$$

where a is the lattice parameter, M^1 the lattice contribution to the shear modulus and A includes constants of the band structure, then the tetragonal strain is positive.

If however,

$$Q/Q_0 < \frac{16}{3} \frac{a^2 A}{M^1} \quad (6.3)$$

then, the tetragonal strain is negative. The present work shows that at or very near the stoichiometric composition, the sign of the tetragonality for Nb-Sn is reversed so that for a Sn content of less than 25 at % $c/a > 1$, as is the case for V-Si where the alloys which transform have less than 25 at % Si. For the V-Ga alloy which may have transformed (section 4.4) $c/a > 1$, but, because of the scatter in the composition/lattice parameter plot it is not possible to say on which side of stoichiometry the alloy lies. As the limiting values of Q/Q_0 are functions of the lattice parameter, which varies with composition, a change in the sign of the tetragonal strain is not impossible within the terms of the theory.

Both the CCH theory and the LFB theory are concerned with electronic effects only, i.e. they deal with the Helmholtz free energy, $F = U - TS$, rather than the Gibbs free energy $G = U - TS + PV$. It can be seen from the results discussed in the earlier parts of this chapter that while this may be adequate for stoichiometric alloys it is an incomplete approach for a non-stoichiometric alloy, for the hydrostatic strain produced by the deviations from stoichiometry appears to have at least as important an effect on the structural properties as do the electronic variations. The effect on T_c of such a stress has been shown by Testardi (1971), but no analysis has been carried out of the effect on the structural transformation. As the stress term will alter not only the free energy of the electrons but also the shape of the density of states curve, band structure calculations are very complex. The effects of strain will therefore be considered in qualitative terms.

It is general experience (Reed and Breedis 1966) that hydrostatic stress can suppress first order phase transformations and Kunzler et al. (1966) have shown that an externally applied hydrostatic stress will suppress

the transformation in a V-Si single crystal and, therefore, it is reasonable to assume that a hydrostatic strain within the crystal (indistinguishable from one produced by external stress) will also tend to suppress the transformation even if lattice softening occurs. In this case as lattice parameter and ordering results demonstrate that the hydrostatic strain increases away from stoichiometry, the narrowness of the martensite phase in V-Si will be due to the suppression of the transformation due to hydrostatic strain. Eventually a similar effect will occur in Nb-Sn, but in Nb-Sn the spontaneous tetragonal strain is larger. It can be deduced from this that the driving force for the transformation is larger and, therefore, the hydrostatic strain must be larger before the transformation is totally suppressed. The phase field is, therefore, wider than that for V-Si. If the measured c/a ratio for V-Ga is correct then the phase field of the transformation in that system is expected to be even narrower than for V-Si. From these arguments the low temperatures phase diagram of Nb-Sn should appear as shown in figure 6.5, which does not contradict the experimental results. The results of Potapov (1969), however, indicate a fall in flux pinning before stoichiometry as shown in the low temperature phase diagram in figure 4.25. If the peak is where it is shown in figure 4.25, then the situation is similar to that for V-Si where the fall in the transformation temperature occurs before the stoichiometric value is reached, i.e. at a value of less hydrostatic strain than at the peak. This may be due to the electronic effect derived by LFB which can be seen in figure 2.8 where the drop in T_m is very sharp at values of Q/Q_0 near to unity.

The reversal of the tetragonal strain at stoichiometry in Nb-Sn can be simply interpreted in terms of these arguments, as arising from the greater strains involved in introducing Sn atoms into Nb sites.

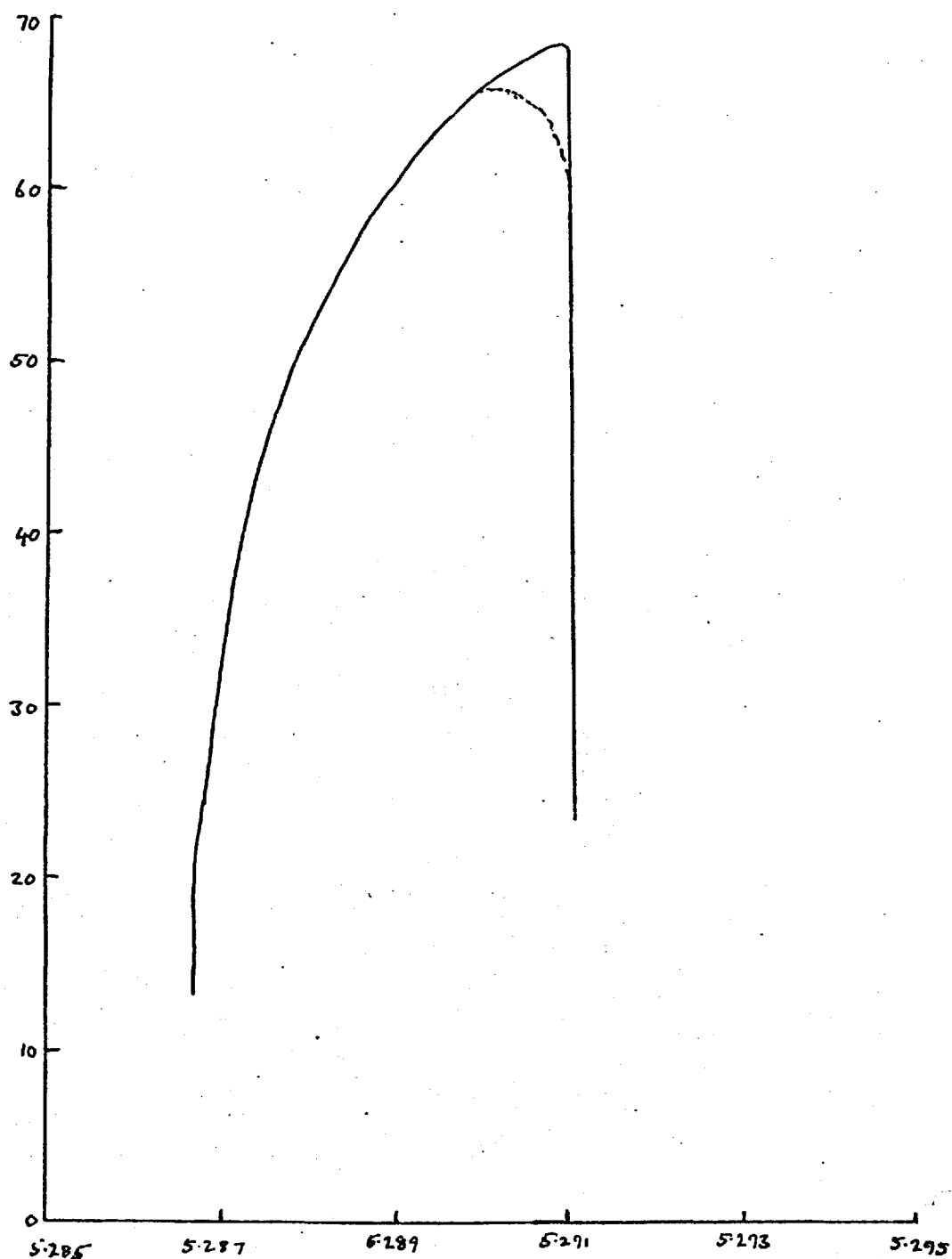


Figure 6.5. Possible forms of the composition dependence of the A_f temperature in Nb-Sn.

6.6b The Superconducting Properties

The dependence of T_c upon composition has been calculated by LFB (1967) and the curves shown in figure 6.6. They make the assumption that because the isotope effect is small in the β -W structure alloys ($\alpha \approx 0.1$ in equation 1.58) then the high value of T_c is determined by the high value of $N(0)$, the density of states at the Fermi surface, and not by the narrowness of the phonon density of states. The work of McMillan (1958) and Hopfield (1969), however, indicates that this not so and that it is the variations in θ_D which govern the T_c . Hopfield (1969) has calculated λ , the electron phonon coupling constant as

$$\lambda = \frac{1}{M\omega^2} \left(\frac{dH}{dx} \right)^2 \frac{N_P(0) N_D(0)}{N(0)} \quad (6.4)$$

where M is the atomic mass, ω the mean phonon frequency, $N_P(0)$ and $N_D(0)$ the density of states of the P and D bands and $N(0)$ the overall density of states. The differential term represents the perturbation potential. The correspondence between the theoretical values and the measured values is reasonable as shown below.

	<u>T_c (calc) $^{\circ}$ K</u>	<u>T_c (measured) $^{\circ}$ K</u>
V_3Si	17.6	17.1
V_3Ge	2.1	6.0
V_3Ga	13.5	16.5
V_3Au	0.7	0.7

The low isotope effect, however, is not explained by this treatment and, indeed, as Hopfield points out, it is difficult to determine accurately the variation in the phonon modes with the variations in the density of states at the Fermi surface. If, however, the interaction is not by means of the phonon but by means of the Frohlich acoustic plasmons, the lack of isotope effect is immediately explained by Rothwarf (1970), for the plasmon frequencies do not depend on the mass of the ions. The decline in the value

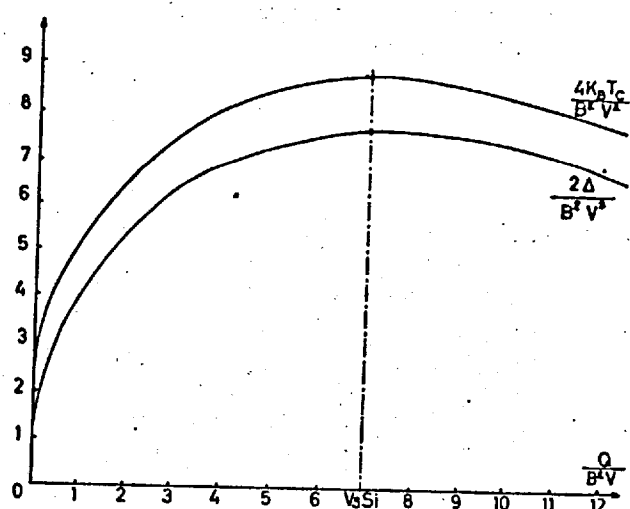


Figure 6.6. The dependence of the superconducting critical temperature and the energy gap on the small number of electrons Q in the d-sub-band. (Labbé et al. 1967)

of T_c away from stoichiometry can also be explained in terms of the effect of strain on the density of states curve which will be smoothed out so that the high peaks suggested by LFB will be broadened. That this occurs is predicted by the hydrostatic strain effect on the martensite formation and such a change will undoubtedly alter the plasmon spectrum which will alter T_c . Evidence for this is given by Rothwarf (1970) in that the plasmon modes are very sensitive to the variations in the physical properties. A further point in favour of this theory is that apart from the Pauling theory, which could equally be applied to the acoustic plasmons as to phonons, it is the only theory which explains the Matthias plot of T_c against the electron to atom ratio satisfactorily, (figure 1.10a).

The variations in flux pinning and in the upper critical field H_{c2} with composition can be explained in terms of the hydrostatic strain as has been described in the sections dealing with the Nb-Sn and V-Si systems. That a high critical field exists is due to the high κ value of these alloys, which can be explained partly in terms of the dislocations produced by strains in the material and partly by the density of states itself, in terms of the electronic specific heat constant. The superconducting properties, as well as the structural properties, are, thus, functions of both electron behaviour and strain.

6.7 Summary and Conclusions

A survey of the literature has shown that the values ^{of the} superconducting parameters for the β -W materials are higher than those for other materials and that in some of these materials a structural instability is present at low temperatures. Both these superconducting properties and the structural effects appear to be functions of composition variations and, therefore, the relationship of superconductivity to the structure of the four β -W materials, Nb-Sn, V-Si, V-Ga and Nb-Al has been investigated. To this end, apparatus for X-ray measurements at

high and low temperatures, and for the measurement of superconducting critical temperatures was constructed. Measurements of the lattice parameter of the alloys at room temperature were first made and these were used to characterise the alloy compositions, to which all other measurements were related. These measurements were of the structural transformation temperature (if a transformation took place), of the superconducting critical temperature and of the change in properties on heat treatment, by X-ray and metallographic methods.

In order to interpret the X-ray intensities in terms of atomic disorder in the non-stoichiometric alloys a model was developed which is not limited in its applications to the β -W systems but can be applied to any binary alloy with two types of lattice site.

The results of this work and conclusions drawn therefrom can be summarised as follows:-

1. The room temperature lattice parameter of a β -W alloy is a function of its composition and the sign of the variation of this parameter away from the stoichiometric value is determined by the relative sizes of the constituent atoms.
2. The variations in superconducting T_c with composition are in agreement with the published data and these variations are accounted for in terms of the hydrostatic strain produced by the deviation from stoichiometry. The acoustic plasmon as the mode of interaction has been considered and found to explain certain otherwise unexplained facts.
3. The variation of the structural transformation temperature has been found to be a function of composition in the Nb-Sn system and deduced to be so in the V-Si and V-Ga systems. The absence of a transformation in the present V-Si samples and the width of the tetragonal phase is explained in terms of the hydrostatic strain due to non-stoichiometry.

The absence of a transformation in the Nb-Al system has been considered but not explained in terms of the present theory.

4. The absence of a transformation and the high lattice parameter in Nb-Sn (1) were found to be due to the presence of excess tin atoms on niobium sites, as a result of the high pressure of formation. The high T_c in this sample is, however, unexplained.
5. The sign of the tetragonal strain was found to be a function of the type of non-stoichiometry in a sample. In an A_3B type alloy, material on the A-rich side will have an axial ratio greater than unity, and B-rich material will have an axial ratio less than unity.
6. No changes in ordering were found to occur on heating the β -W alloys, except those attributable to changes in composition which occur by interdiffusion with the other phases present. The temperature of heat treatment, is, therefore, important in determining the composition and hence the properties of an alloy. Variations in order at room temperature are attributable to the effects of the type of atom in excess entering the other type of atom site.
7. In view of the above conclusions, knowledge of composition, or its equivalent, the room temperature lattice parameter of an alloy is vital if any attempt at explaining its properties is to be made.

6.8 Suggestions for Future Work

Suggestions for future work can be divided into three sections:- (a) The Development of Theory, (b) The Further Investigation of the Properties of the Materials, and (c) The Investigation of Materials for Practical Applications.

6.8a Development of the Theory

The extension of the band theories of the phase transformation and the superconducting properties to include the effects of pressure terms.

6.8b Further Properties of the Materials

1. The investigation of high temperature phase relations by use of hot-stage microscopy, so as to determine more accurately the changes in microstructure.
2. The investigation of a phase transformation in single crystals of V-Ga and Nb-Al, if they can be grown.
3. The investigation of the variations of lattice softening with composition in Nb-Sn, V-Ga and Nb-Al, using either single crystals or polycrystalline material.
4. The investigation of the compositional dependence of flux pinning in V-Ga and Nb-Al alloys.

By comparison of the results of these experiments, it should be possible to determine whether the mechanism discussed in this chapter is operational in all these β -W phases and hence verify the validity of the arguments in its favour.

6.8c Practical Applications

The investigation of the stresses in commercial superconducting tapes as a result of epitaxy and differential contraction between the superconductor and the substrate material, and the effect of these on the martensite, current carrying capacity and superconducting critical temperature.

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APPENDICES

Appendix 1Procedure for sealing capillaries under vacuum

The letters all refer to figure A1.1.

1. The supporting plate (A), the copper foil (B) and the silicon rubber (C) are removed from the underside of the base plate (G). (Two of the retaining screws are replaced by studding to facilitate replacement).
2. After the foil (B) has been cleaned and, if necessary to soften it, annealed, a capillary (D) is slid through the pin-hole in the foil and sealed in with "Araldite" epoxy resin.
3. The silicon rubber (C), the copper foil (B) and the supporting plate (A) are replaced (the silicon rubber, the underside of the base plate (G) and the O-ring in the support plate (A) having been cleaned), before the "Araldite" is set. The studding is used to locate the three components.
4. The glass funnel (E) is cleaned and replaced in the foil (F), bolted to the plate (M), "Araldite" again being used to join them. (This prevents the funnel lifting with the stopper).
5. The apparatus is left for 12 hours (overnight) for the "Araldite" to set.
6. The stopper (H) is placed in the funnel, the top end attached to the cantilever system to the shaft (K), the sieved powder placed in the funnel and the bell jar (L) and implosion shields (not shown in diagram) replaced.
7. The bell-jar (L) is evacuated to a pressure of 10^{-6} mm. Hg. and flushed with an inert gas. This is repeated four times and the system again evacuated.
8. By sliding down shaft (K), the stopper (H) is raised, so that the powder can fall into the capillary (D).
9. The capillary is sealed using an oxy-gas flame.

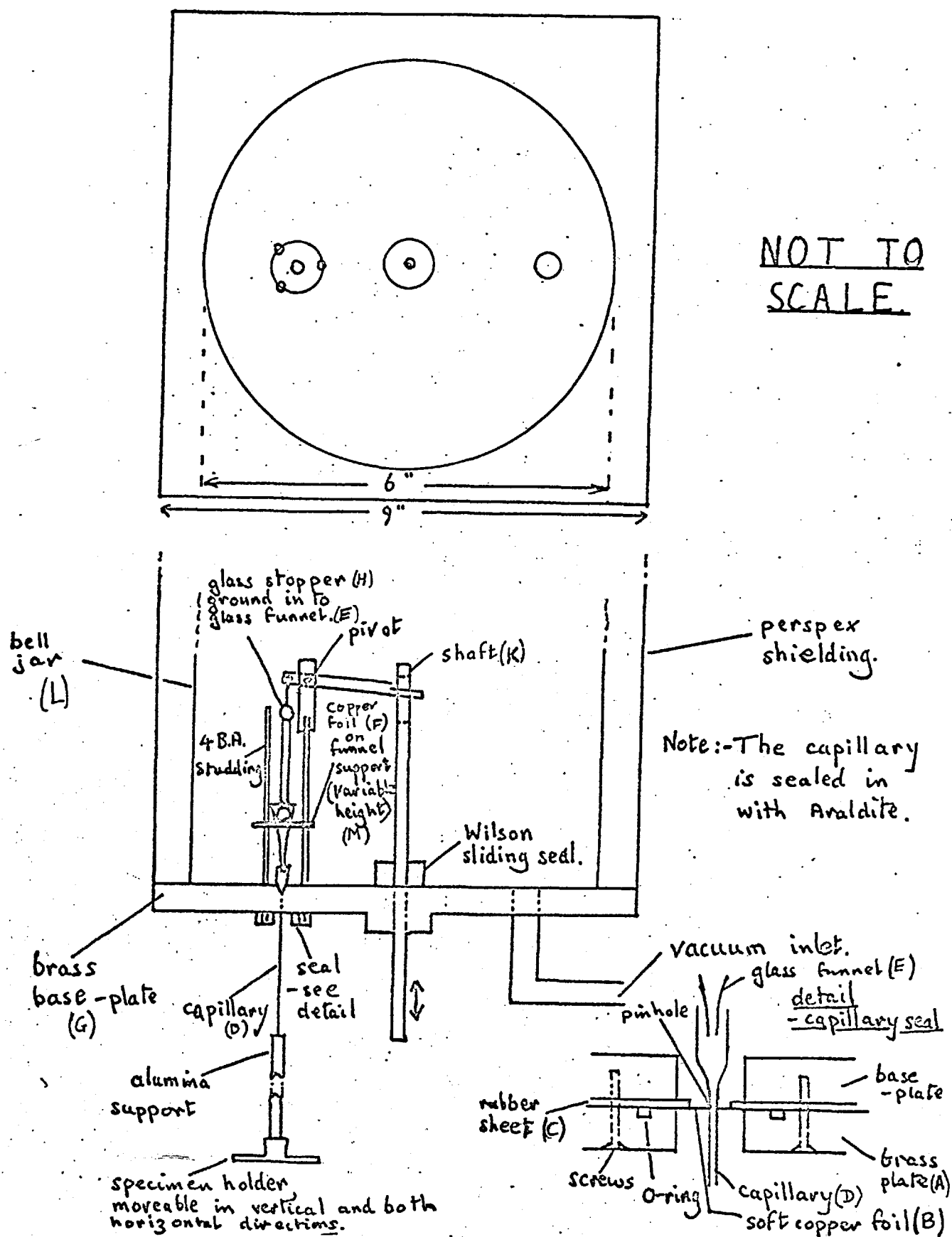


Figure A1.1. Apparatus for loading capillaries under vacuum.

Appendix 2

Use of the Continuous Flow Cryostat

A2a Cooling Procedure

The letters all refer to figure A2.1.

1. When the central section has been replaced, the main vacuum space is evacuated to a pressure of 40μ Hg. (for helium) or 10^{-6} mm. Hg. (for nitrogen) through tap (A).

2(a). If it is possible for the syphon to be introduced to the transport dewar after its other end has been connected to the cryostat, the syphon (D) should be placed in the cryostat, the needle valve (E) closed, and the system evacuated up to the needle valve (E). The needle valve (E) is then opened and the syphon (D) slowly introduced into the transport dewar. When it is at the required depth the top of the transport dewar is sealed in the normal way and the flow of cold gas or liquid controlled by valves (E), (F) and (G) and with the bladder (H).

2(b). If it is not possible for the syphon to be introduced to the transport dewar after its other end has been connected to the cryostat, the syphon (D) is flushed with helium gas and the sealing assembly (I) slid to near the end of the syphon (D). The syphon is then introduced to the transport dewar, the top of the dewar sealed and the syphon (D) slid through the seal (I) until it is possible to connect the other end of the syphon to the cryostat. This connection is made against a flow of helium gas flowing "backwards" through the cryostat. (When the needle valve (E) is closed this will be stopped. The pumping line is then disconnected from the helium gas supply and connected to the pump, and the system evacuated up to the needle valve (E) which is then opened and the syphon (D) lowered in the transport dewar to the required depth. The flow is controlled as in 2(a).

3. When the required temperature is reached the "speedi-valve" (G) is closed and the temperature controlled by the needle valves (E) and (F) and the heater.

4. At the completion of the experiment, needle valve (E) is closed and then needle valve (F). Needle valve (E) can then be opened and the syphon removed from both cryostat and transport dewar. On later models a helium gas line has been introduced so that warm gas can be admitted to the system, decreasing the time required for the return to room temperature.

A2b Preparation of Samples

The sample mount is a copper or gold plate, machined so that the specimen surface is in the same plane as the alignment slit, and it has a hole 1.5 x 1.0 cm. machined in it. It is placed with the specimen surface side (with the countersunk holes for the retaining screws) downwards on a sheet of thin "mylar" and secured. The powder, ground to 300 mesh in a pestle and mortar is sprinkled on to the "mylar" until the layer is no longer translucent. It can then be secured using acetone collodion and backed with copper powder to give good thermal conductivity or with vacuum grease which both acts as a fixative and a good conductor at low temperatures.

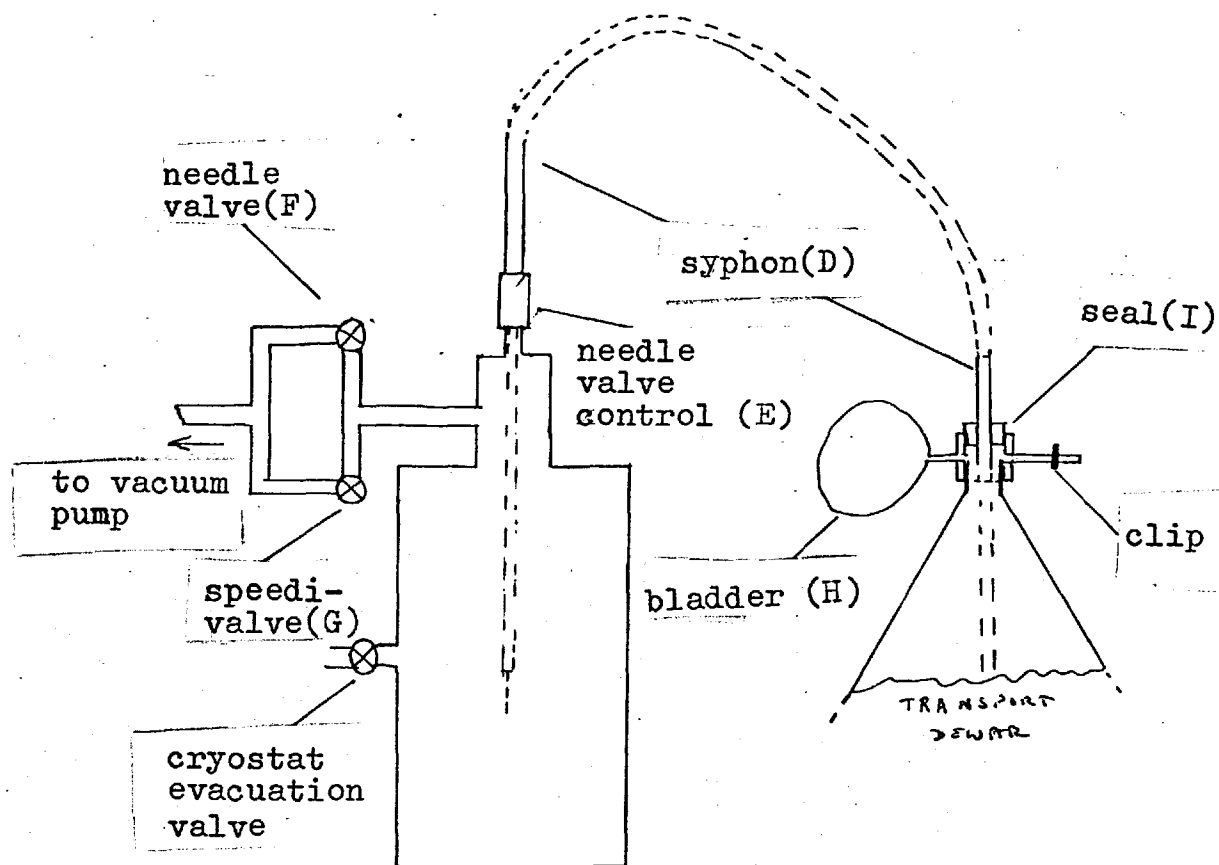


Figure 2.1. Schematic diagram of continuous flow cryostat to illustrate the operating procedure.

Appendix 3

A3 Alternative Treatment of X-Ray Intensities

The following analysis was developed to analyse the X-ray intensities and obtain both the Debye Temperatures and the degree of order of the material being examined. As explained in section 3.4g the data was found not to be accurate enough for this method to be applicable.

A3a Temperature and X-Ray Intensity

James (1948) has given an almost complete account of the influence of temperature on the diffraction of X-rays and derives an expression for the intensity scattered by a lattice:

$$\underline{I}(\underline{S}/\lambda) = |f_0|^2 e^{-2M} \underline{I}_0(\underline{S}/\lambda) + \underline{I}_2(\underline{S}/\lambda) \quad (\text{A3.1})$$

where f_0 is the atomic scattering factor for a lattice of one atom type, λ , the wave length of the radiation, $\underline{S} = \underline{s} - \underline{s}_0$, the difference between the unit reciprocal lattice vectors of the incident and scattered waves, and $M = 8\pi^2 \overline{u_s^2}(\sin^2\theta)/\lambda^2$ is a factor which arises from the vibrations of the lattice, $\overline{u_s^2}$ being the mean square elongation of any point of the lattice from its mean position in a direction parallel to $\underline{S}$. The term $\underline{I}_0(\underline{S}/\lambda)$ gives the intensity of ordinary diffraction maxima, and describes the intensity scattered by a lattice of points at rest. The intensity of these maxima are reduced by the thermal motion but they are not broadened. The second term $\underline{I}_2(\underline{S}/\lambda)$ gives the general scattering and can be written:

$$\underline{I}_2(\underline{S}/\lambda) = |f_0|^2 e^{-2M} \sigma \quad (\text{A3.2})$$

$$\text{where } \sigma = \frac{1}{2} \sum_{\underline{g}} G_{\underline{g}} \{ \underline{I}_0(\underline{S}/\lambda + \underline{g}) + \underline{I}_0(\underline{S}/\lambda) \} \quad (\text{A3.3})$$

This term arises from consideration of the lattice vibrations in terms of normal modes ($j = 1, 2, 3$) and is the sum over these modes and the lattice waves of wave vector $\underline{g}$. This term can be rewritten, giving an expression for the thermal diffuse scattering I_{TD}

$$I_{TD} = I_e f^2 e^{-2M} N^2 \sum_j (G_{gj})^2 \quad (A3.4)$$

$$\text{where } G_{gj} = \frac{2\pi h}{2mN} \frac{1}{\omega_{gj}} (\underline{R} \cdot \underline{e}_{gj})^2 \coth \left[\frac{h\omega_{gj}}{4\pi kT} \right] \quad (A3.5)$$

In these equations N is the number of atoms, f the atomic scattering factor, $2M$ the Debye factor referred to above, h is Planck's constant, m is the atomic mass, $\underline{R}$ ($=2\sin\theta/\lambda$) the diffraction vector from the origin of the reciprocal lattice to the point of measurement, $\underline{e}_{gj}$ a unit vector in one of the directions of vibrations of the lattice (j) and ω_{gj} is the circular frequency of the elastic wave g , k the Boltzmann constant and T the absolute temperature.

A3b Thermal Diffuse Scattering for Cubic Powder Patterns

To correct intensities for thermal diffuse scattering, an estimation of the value of the scattering can be made assuming that all the atoms vibrate independently. Warren (1953) showed that at high temperatures a better approximation is obtained if it is assumed that the velocities of all the elastic waves in the lattice are equal. Herbststein and Averbach (1955) follow Warren in this assumption and write $\omega_{gj} = 2\pi V|\underline{g}|$ where V is the velocity of these waves. The temperature diffuse scattering (from equations A3.4 and A3.5) now becomes:

$$I_{TD} = \frac{NI_e h f^2 e^{-2M}}{2mV|\underline{g}|} \coth \frac{hV}{2kT} \sum_j (\underline{R} \cdot \underline{e}_{gj})^2 \quad (A3.6)$$

If each Brillouin zone is replaced by a sphere of equal volume and $2M$ assumed to be small, A3.6 becomes:

$$I_{TD} = \frac{NI_e f^2 (1 - e^{-2M})}{6\{\phi(\chi)/\chi + \frac{1}{2}\}} \frac{g_{\max}}{g} \coth \left[\frac{\chi}{2} \frac{g}{g_{\max}} \right] \quad (A3.7)$$

where $\chi = \theta_D/T$ and $\phi(\chi)$ is the Debye Integral. $\sum_0 (\underline{R} \cdot \underline{e}_{gj})^2 = 1$ if all the waves have the same velocity and:

$$v = \frac{\omega_{\max}}{g_{\max}} = \frac{k\theta_D}{hg_{\max}} \quad (\text{A3.8})$$

$$\text{so that: } \frac{hV|g|}{2kT} = \frac{\chi}{2} \frac{g}{g_{\max}} \quad (\text{A3.9})$$

Equation A3.7 gives the intensity corresponding to a point in the Brillouin zone, hkl . For a particular value of $\sin\theta/\lambda$, the intensity on a powder pattern is given by averaging over all such points on the surface of a sphere of radius R . To do this it is necessary to average over the part of the sphere which falls in each Brillouin zone, summing over all zones transversed by the sphere and dividing by the area of the sphere $4\pi R^2$. For the β -W structure $g_{\max} = (6/\pi)^{1/3}/a$ where a is the lattice parameter. The intensity due to thermal diffuse scattering is thus given by:

$$I_{TD} = \frac{NI_e f^2 (1-e^{-2M}) (6/\pi)^{2/3}}{6\{\phi(\chi) + \frac{1}{2}\chi\}} \frac{1}{\chi} \times \sum_{hkl} \frac{j_{hkl}}{x_{hkl}} \ln \left[\frac{\sinh(\chi/2)}{\sinh[\frac{1}{2}\chi(\pi/6)^{1/3} |x - x_{hkl}|]} \right] \quad (\text{A3.10})$$

where j_{hkl} is the multiplicity of the hkl reflection, $x = 2a \sin\theta/\lambda$ and $x_{hkl} = 2a \sin\theta_{hkl}/\lambda$.

Equation A3.10 can be written as:

$I_{TD} = A \cdot I_{Th}$ where $A = NI_e$ and I_{Th} represent the other terms in the equation together with terms representing the absorption and Lorentz-polarisation corrections. I_{Th} can be calculated at a particular value of $\sin\theta/\lambda$, at a particular temperature, for a lattice of known composition and known Debye temperature, if weighted means are taken for the values of f and the atomic mass. The measured intensity at any point can then be represented by an equation:

$$I_m = A \cdot I_{Th} + B \cdot \theta + C + I_B \quad (\text{A3.11})$$

where I_B is the intensity of the Bragg reflection and $K\theta + C$ represents a trapezoidal background including the Compton scattering and any zero errors in the method of recording the intensities. Away from a Bragg peak $I_B = 0$ and the intensity is represented by the expression

$$I_m = A \cdot I_{Th} + K\theta + C \quad (A3.12)$$

If this function is now fitted to the measured background curve, the constants A , k and C can be found by a least squares method (Sparks and Borie 1962). If the value of the Debye temperature is not known, it can be varied in the calculation of I_{Th} until a minimum variance is found in the value of A (Gazzara 1960). The true Bragg intensities can then be found from equation A3.11.

The Bragg intensity of any reflection is also given, when corrected for temperature etc., by the expression:

$$I_B = NI_e \times (\text{expressions for the structure factors}) \quad (A3.13)$$

As $NI_e = A$ has been found from the least squares analysis, in theory, absolute intensities can be treated rather than relative intensities as is usually the practice.

A computer programme was written to carry out this analysis, and the inaccuracy of the data was found to be too great for this analysis to give significant results.

References

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- James R.W. (1948) "The Optical Principles of the Diffraction of X-Rays" (G. Bell & Sons).
- Sparks E.J. and Borie B.S. (1962) Adv. in X-Ray Analysis 6, 177.
- Warren B.E. (1953) Acta. Cryst. 6, 803.

Appendix 4Computer Programmes

All the computer programmes used in this work were written in Fortran IV and run either on the University of London C.D.C. 6600 and 6400 or the University College, London, IBM 360 computer. A printout of each programme, together with a brief description of its operation, is given.

A4A Programme D.S.L.P.

Programme D.S.L.P. calculates the lattice parameter of a cubic material from the line positions of a powder pattern on a Debye-Scherrer Straumanis mounted film. The film is placed on the film measuring device with $\theta = 0^\circ$ position to the left of the $\theta = 180^\circ$ position and the line positions read from left to right, such that the $\theta < 90^\circ$ values precede the $\theta > 90^\circ$ values.

The data read into the computer, together with the variable names assigned to them are as follows:-

WAVE(1+3) = Wave lengths of radiation used
 (1 $\equiv$ $k\alpha_1$, 2 $\equiv$ $k\alpha_2$, 3 $\equiv$ weighted mean, $k\alpha$)

NUM (1+4) = Numbers of lines on the different parts of the film as described at the beginning of the programme.

NDATA = Number of films.

THETA(I) = Line positions on film.

Z (I) = $h^2+k^2+l^2$ where hkl are the Laué indices.
 (It is assumed that the structure is known so that most of these values are correct).

LAM (I) = 1, 2 or 3 indicating the wave length which produced the line (1 $\equiv$ $k\alpha_1$, 2 $\equiv$ $k\alpha_2$ and 3 $\equiv$ $k\alpha$, i.e. an unresolved doublet).

The programme first calculates AVA and AVB, the $\theta = 0^\circ$ and $\theta = 180^\circ$ positions and if any measured line pair gives a value disagreeing with the mean by more than 0.10, the reflection is ignored in subsequent calculations and a message is printed to this effect. The Bragg angles

(0) XZ are then calculated, corrected for film shrinkage, and by standardising the values to the $k\alpha_1$ wavelength, a check in the indexing is carried out by comparing the values of $\sin^2\theta/(h^2+k^2+l^2)$. This is done by rejecting any line which differs from the average value by more than three standard deviations. Re-indexing is carried out by varying the value of $(h^2+k^2+l^2)$ and repeating the comparison. If a new index is found or the line rejected then a message is printed to this effect.

An approximate lattice parameter A_0 is then calculated from the highest angle line and the least squares analysis carried out as described in section 3.3.

The variable names are:-

AAO	= A	DDELTA	= $\frac{\partial \delta}{\partial \theta}$
GAMA	= γ		
DELTA	= δ	DGAMA	= $\frac{\partial \gamma}{\partial \theta}$
DRIF	= K		
DELK	= ΔK	FTHET	= $\frac{\partial F_0}{\partial \theta}$
DELA	= ΔA		
FO	= F_0	W(I)	= WEIGHTING FUNCTION

The analysis is repeated until $\Delta A/A_0 < 0.00005$. The standard deviation SDA in the result is then calculated and a further indexing check carried out by comparing values of θ calculated from the lattice parameter with the measured values. If any line is rejected or re-indexed, again a message is printed and the least squares analysis repeated, A check is also incorporated in case every line is rejected.

A4B Programme LSQ

Programme LSQ calculates the $\theta = 0$ position and the circumference of the film holder of the high temperature camera described in section 3.4. A least squares fit is made to the equation:

$$\text{THETR} = 2C(XA)/360 + A \quad (\text{A.1})$$

where THETR is the θ value of a line calculated from the lattice parameter, XA the measured position of the line (with an arbitrary zero), C the circumference of the film

holder and A , a constant representing the $\theta=0^\circ$ position. In the programme THETR is represented by Y, XA by Z, C by A, A by B and X/180 by X.

From the computed values of C and A and the measured knife edge positions the values of the knife edge positions were calculated.

A4C Programme H.T.L.P.

Programme H.T.L.P. calculates the lattice parameters of a cubic crystal from the line positions on the films from a 19 cm. camera. The true knife edge positions are known from previous calculations and the knife edge positions are read off the films. These are given the names ENKT and ENK respectively in the programme. The values of the line positions on the two films, THETR and THETL are read into the computer and their positions relative to the knife edge positions on the film calculated. A shrinkage correction using ENK and ENKT is included in the next stage which is to calculate the Bragg angles for each film from the true knife edge values. A mean of the values for the two films is then taken. The programme from this point is identical with programme D.S.L.P.

A4D Programme LATEXP

Programme LATEXP calculates the lattice expansion of cubic materials from four low angle line shifts, using equation 3.7. The data read into the computer together with the variable names assigned to them are as follows:-

ENKT (1+4)	= True knife edge positions.
NSYST	= Number of specimens.
NDATA	= Number of films per system.
AO	= Room temperature lattice parameter.
THETR, THETL	= Line positions on left and right films respectively.
T	= Temperature of exposure.

The Bragg angles XZ are first calculated as a mean of those calculated from the two films using the same method as that described for programme H.T.L.P. The mean

change in lattice parameter MADD, the coefficient of thermal expansion ALPHA, and the lattice parameter A at temperature T are then calculated. The standard deviations $\Delta a/a_0$ and that in ALPHA are also calculated. While the number of measurements (4) is not enough for statistical significance the value of the standard deviation gives an indication of the scatter among the measurements.

A4E Programme AI5TC

Programme AI5TC calculates the critical temperature of a sample from a series of values of thermocouple readings. The first stage, however, is to produce a calibration curve for the thermocouple. TCAL are the calibration temperatures and CALG the thermocouple readings for those temperatures. By a least squares method the constants A and B are calculated in the calibration equation.

$$TCAL = A \cdot CALG + B \quad (A4.2)$$

The errors in both A and B are also calculated.

The thermocouple readings for the transitions AMV are read into the computer and a mean value MGOL, and its standard deviation DOLS, computed. Then the temperature THETK is calculated using the equation:

$$THETK = (MGOL - B)/A \quad (A4.3)$$

The error DTHE in the T_c (THETK) is finally computed.

A4F Programme ORDER

Programme ORDER calculates the I_{hkl}/I_{400} X-ray intensity ratios from the site occupations for the systems V-Si, V-Ga, Nb-Sn and Nb-Al. The multiplicities AM for the four lines and the atomic scattering factors FA and FB are read by the computer and the site occupations as percentages AA, AB, BB and BA varied, where:

- AA = no. of A atoms on A sites
- AB = no. of A atoms on B sites
- BB = no. of B atoms on B sites
- BA = no. of B atoms on A sites.

The variations of these include the situations where vacancies are present and X_A and X_B are calculated as the fraction of A atoms and B atoms in the solid, where $X_A + X_B + X_V = 100$ and X_V (not used in the programme) is the number of vacancies. S_A and S_B are also calculated as described in Chapter 5 and the intensities S_{INT} and, hence, the intensity ratios $RELA$ calculated. Y_A and Y_B are also calculated as the chemical composition of the alloy ($Y_A + Y_B = 100$). The values of the various parameters are finally printed for the four systems. The values DFA , DFB , EFA and EFB are the anomalous dispersion correction terms $\Delta f'$ (DFA , DFB) and $\Delta f''$ (EFA , EFB) for the A and B atoms.

```

C   DEBYE=SCHEERER LATTICE PARAMETERS
C   CUBIC CRYSTALS
C   THETA IN CENTIMETRES FROM LEFT TO RIGHT, LOW ANGLES TO LEFT
C   NUM(1)=TOTAL NO. OF MEASUREMENTS (THETA VALUES)
C   NUM(2)=NO. TO LEFT OF EXIT HOLE
C   NUM(3)=NO. BETWEEN HOLES
C   NUM(4)=NO. TO RIGHT OF ENTRY HOLE
C   LAM=1 FOR K-ALPHA 1 LINES, WAVE 1
C   LAM=2 FOR K-ALPHA 2 LINES, WAVE 2
C   LAM=3 FOR K-ALPHA (WEIGHTED MEAN. LINES), WAVE 3
C   ORDER OF OF LAM AND N CORRESPONDS TO ORDER BETWEEN HOLES
C   STARTING AT LOW ANGLES. Z=N, HSQD+KSQD+LSQD.
      REAL THETA(80), Z(40), WAVE(3), SUMA(40), SUMB(40), DIFFA(40), BA(40),
      DDIFFB(40), BB(40), XA(40), XB(40), XC(40), XD(40), S(40), SS(40), SJ(40),
      DWAVEL(40), GAMMA(40), DELTA(40), ALPHA(40), DDELTA(40), DGAMA(40),
      DFTHET(40), W(40), DEML(40), FO(40), AL(40), DE(40), DL(40), AF(40),
      DDF(40), Q(40), SQXA(40), SOXA(40), AA(40), SXD(40), XZ(40), SQXJ(40)
      INTEGER NUM(4), LAM(40)
      READ(5,75) (WAVE(I), I=1,3)
75  FORMAT(3F8.5)
      WRITE(6,131) (WAVE(I), I=1,3)
131  FORMAT(15H WAVELENGTHS, 3F8.5)
      READ(5,181) NDATA
181  FORMAT(I2)
      DO 220 NFILM=1, NDATA
      WRITE(6,191) NFILM
191  FORMAT(12H FILM NO., I2)
      READ(5,171) (NUM(I), I=1,4)
171  FORMAT(4I4)
      WRITE(6,141) (NUM(I), I=1,4)
141  FORMAT(11H NUMBERS, 4I4)
      NUMA=NUM(1)
      NUMB=NUM(2)
      NUMC=NUM(3)
      NUMD=NUM(4)
      READ(5,16) (THETA(I), I=1, NUMA)
16  FORMAT(8F10.4)
      READ(5,99) (Z(I), I=1, NUMC)
99  FORMAT(20F4.0)
      READ(5,77) (LAM(I), I=1, NUMC)
77  FORMAT(40I2)
      WRITE(6,101)
101  FORMAT(15H MEASURED LINE)
      WRITE(6,111) (THETA(I), I=1, NUMA)
111  FORMAT(5F10.4)
      WRITE(6,121)
121  FORMAT(20H LINE N LAM)
      DO 230 I=1, NUMC
      WRITE(6,151) I, Z(I), LAM(I)
151  FORMAT(I4, XX, F4.0, XX, I4)
230  CONTINUE
      NXA=0
      NXB=0
      DO 10 K=1,2
      TOTA=0
      TOTB=0
98  DO 20 I=1, NUMB
      IF(Z(I)) 20,20,304
304  SUMA(I)=THETA(NUMB+I)+THETA(NUMB+1-I)
20  TOTA=TOTA+SUMA(I)
      DO 30 I=1, NUMD
      IS=NUMC-NUMD+I
      IF(Z(IS)) 30,30,306
306  SUMB(I)=THETA(NUMA+1-I)+THETA(NUMA-2*(NUMD)+I)
30  TOTB=TOTB+SUMB(I)

```

```

AVA=TOTA/(2.0*(FLOAT(NUM(2)-NXA)))
AVB=TOTB/(2.0*(FLOAT(NUM(4)-NXB)))
IF(K-2) 2,10,10
2 DO 40 I=1,NUMB
  IF(Z(I)) 40,40,305
305 DIFFA(I)=SUMA(I)-(AVA)*(2.0)
  BA(I)=ABS(DIFFA(I))-0.10
  IF(BA(I)) 40,40,4
4 NXA=NXA+1
  WRITE(6,91) I
91 FORMAT(12H SCRAP LINE ,I2)
  Z(I)=0
40 CONTINUE
  DO 50 I=1,NUMD
    IS=NUMC-NUMD+I
    IF(Z(IS)) 50,50,307
307 DIFFB(I)=SUMB(I)-(AVB)*(2.0)
    BB(I)=ABS(DIFFB(I))-0.10
    IF(BB(I)) 50,50,5
5 NXB=NXB+1
  WRITE(6,91) IS
  NC=NUM(3)-NUM(4)+I
  Z(NC)=0
50 CONTINUE
10 CONTINUE
  IF(NXA.EQ.NUMB) GO TO 220
  IF(NXB.EQ.NUMD) GO TO 220
C XZ=BRAGG ANGLE,THETA,CORRECTED FOR FILM SHRINKAGE
  DO 60 I=1,NUMB
60 XA(I)=(THETA(NUMB +I)-THETA(NUMB +1-I))*3.14159/((AVB-AVA)*4.0)
  DO 70 I=1,NUMD
  XB(I)=(THETA(NUMA +1-I)-THETA(NUMA -(2*(NUMD -I))+I))*3.14159/
  D((AVB-AVA)*4.0)
  IF(XB(I)) 6,6,7
6 XC(I)=XB(I)
  GO TO 88
7 XC(I)=(3.14159/2.0)-XB(I)
88 ND=NUM(3)-NUM(4)+I
70 XA(ND)=XC(I)
  IF((NUMB+NUMD).NE.(NUMC)) GO TO 8
  GO TO 9
8 NE=NUM(3)-NUM(4)-NUM(2)
  DO 80 I=1,NE
  NF=NUMB+I
80 XA(NF)=(THETA((2*(NUMB )+I)-AVA)*3.14159/((AVB-AVA)*2.0)
9 CONTINUE
  WRITE(6,73)
73 FORMAT(18H THETA N )
  DO 200 I=1,NUMC
  XZ(I)=(XA(I))
  WRITE(6,161)XZ(I),Z(I)
161 FORMAT( F10.4,XX,F4.0)
200 CONTINUE
  SUMS=0
  SUMSS=0
  DO 100 I=1,NUMC
  IF(Z(I)) 100,100,12
12 IF(LAM(I)-2) 24,25,26
26 SXD(I)=((SIN(XZ(I)))*(WAVE(1)))/(WAVE(3))
  GO TO 27
25 SXD(I)=((SIN(XZ(I)))*(WAVE(1)))/(WAVE(2))
  GO TO 27
24 SXD(I)=SIN(XZ(I))
27 XD(I)=ATAN(SQRT(((SXD(I))**2.0)/(1.0-((SXD(I))**2.0))))
  S(I)=((SIN(XD(I)))*2.0)/Z(I)

```

```

SUMS=SUMS +S(I)
100 CONTINUE
AVS=SUMS/(FLOAT(NUM(3)-NXA-NXB))
DO 110 I=1,NUMC
IF (Z(I)) 110,110,13
13 SS(I)=(ABS(S(I)-AVS))*2.0
SUMSS=SUMSS +SS(I)
110 CONTINUE
SSD=SQRT(SUMSS/(FLOAT(NUM(3)-NXA-NXB)))
DO 120 I=1,NUMC
IF (Z(I)) 120,120,14
14 IF ((ABS(S(I)-AVS))-3.0*(SSD)) 15,15,17
15 GO TO 18
C REINDEXING CYCLE(SIN SQ. THETA)/N
17 DO 130 J=1,NUMC
IF(Z(J)) 130,130,78
78 SJ(J)=((SIN(XD(I)))*(2.0))/Z(J)
IF ((ABS(SJ(J)-AVS))-3.0*(SSD)) 19,19,21
19 WRITE (6,22) XZ(I),Z(J)
22 FORMAT(13H FOR THETA = ,F7.5/11H NEW N = ,F2.0)
Z(I)=Z(J)
GO TO 120
21 IF (NUM(3)-J) 23,23,130
23 WRITE(6,91) I
Z(I)=0
130 CONTINUE
18 CONTINUE
120 CONTINUE
28 DO 140 I=1,NUMC
IF (LAM(I)-2) 29,31,32
29 WAVEL(I)=WAVE(1)
GO TO 33
31 WAVEL(I)=WAVE(2)
GO TO 33
32 WAVEL(I)=WAVE(3)
33 CONTINUE
140 CONTINUE
C CALCULATION OF FIRST AAO.
309 L=NUMC
DO 210 M=1,NUMC
IF(Z(L)) 34,34,49
34 L=L-1
210 CONTINUE
49 A0=(WAVEL(L))*(SQRT(Z(L)))/((SIN(XZ(L)))*(2.0))
AAO=1.0/((A0)*(2.0))
C LEAST SQUARES ANALYSIS
DRIF=0
39 ALSUM=0
DESUM=0
DLSUM=0
AFSUM=0
DFSUM=0
35 DO 150 I=1,NUMC
IF (Z(I)) 150,150,36
36 GAMA(I)=(2.0)*((SIN(XZ(I)))*(2.0))
DELTA(I)=((SIN(2.0*(XZ(I)))*(2.0))*((1.0/(SIN(XZ(I))))+
D(1.0/(XZ(I))))
ALPHA(I)=((WAVEL(I))*(2.0))*(Z(I))/(2.0)
DDELTA(I)=(SIN((2.0*(XZ(I))))*((4.0/(SIN(XZ(I))))-
D(8.0*(SIN(XZ(I))))+((4.0/(XZ(I)))-((8.0)*((SIN(XZ(I)))*(2.0)))/
D(XZ(I)))-((2.0)*((COS(XZ(I)))*(2.0))/(SIN(XZ(I))))
D-((SIN((2.0*(XZ(I))))/(XZ(I))*(2.0)))
DGAMA(I)=(2.0)*(SIN((2.0*(XZ(I))))
FTHET(I)=((DRIF)*(DDELTA(I)))-DGAMA(I)

```

```

W(I)=1.0/(ABS((DRIF)*((4.0)*(COS(XZ(I)))**3.0))
D=((8.0)*((SIN(XZ(I)))**2.0)*(COS(XZ(I))))
D+((2.0)*(SIN((4.0)*(XZ(I))))/(XZ(I)))
D-((SIN((2.0)*(XZ(I))))/(XZ(I)))**2.0)
D-((2.0)*(SIN((XZ(I))*(2.0))))**2.0
DEML(I)=((ABS(FTHET(I)))**2.0)/W(I)
FO(I)=((AAO)*(ALPHA(I)))+(DRIF)*(DELTA(I))-GAMA(I)
AL(I)=((ALPHA(I))**2.0)/(DEML(I))
ALSUM=ALSUM+AL(I)
DE(I)=((DELTA(I))**2.0)/(DEML(I))
DESUM=DESUM+DE(I)
DL(I)=((ALPHA(I))*(DELTA(I)))/(DEML(I))
DLSUM=DLSUM+DL(I)
AF(I)=((ALPHA(I))*(FO(I)))/(DEML(I))
AFSUM=AFSUM+AF(I)
DF(I)=((DELTA(I))*(FO(I)))/(DEML(I))
150 DFSUM=DFSUM+DF(I)
DELK=((AFSUM)*(DLSUM)-(DFSUM)*(ALSUM))/(((DLSUM)**2.0))
D=(ALSUM)*(DESUM)
DELA=((AFSUM)*(DESUM)-(DFSUM)*(DLSUM))/((ALSUM)*(DESUM) -
D((DLSUM)**2.0))
WRITE(6,38) AAO,DELA,DRIF,DELK
38 FORMAT(6H AAO= ,F8.7/11H DELTA A = ,F8.7/11H DRIFT K = ,F10.7/
D11H DELTA K = ,F10.7)
DRIF=DRIF-DELK
AAO=AAO-DELA
IF (((DELA)/(AAO)).LE.0.00005) GO TO 42
GO TO 39
42 AO=1.0/(SQRT(AAO))
SUMQ=0
QDIV=0
X=(DESUM)/((ALSUM)*(DESUM)-((DLSUM)**2.0))
DO 160 I=1,NUMC
IF(Z(I)) 160,160,43
43 Q(I)=(1.0/(DEML(I)))*((ABS(FO(I)))**2.0)
SUMQ=SUMQ+Q(I)
160 QDIV=QDIV+1.0
SDAA=SQRT(((SUMQ)*X)/((QDIV)-2.0))
SDA=(((AO)**3.0))*((SDAA)/(2.0))
SUMN=0
WRITE(6,54) AO,SDA
54 FORMAT(20H LATTICE PARAMETER=,F8.6/
D23H STANDARD DEVIATION = ,F8.6)
DO 170 I=1,NUMC
IF(Z(I)) 48,48,46
48 SUMN=SUMN+1
GO TO 170
46 SQXA(I)=(Z(I))*(((WAVEL(I))/(2.0)*(AO)))**2.0)
SOXA(I)=(SIN(XZ(I)))**2.0
IF(ABS(SQXA(I)-SOXA(I)).LE.0.004) GO TO 170
C REINDEXING CYCLE SIN SQUARED THETA(CALC-MEASURED)
DO 180 J=1,NUMC
SQXJ(J)=(Z(J))*(((WAVEL(I))/(2.0)*(AO)))**2.0)
IF(ABS(SQXJ(J)-SOXA(I)).LE.0.004) GO TO 45
GO TO 52
45 Z(I)=Z(J)
WRITE(6,44) XZ(I),Z(I)
44 FORMAT(13H FOR THETA = ,F7.5/11H NEW N = ,F2.0)
GO TO 170
52 IF (NUM(3)-J) 53,53,180
53 WRITE(6,91) I
Z(I)=0
XZ(I)=0
180 CONTINUE
170 CONTINUE

```

```
SUMM=0
DO 190 I=1,NUMC
  IF (Z(I)) 51,51,190
51 SUMM=SUMM+1
190 CONTINUE
  IF (SUMM.EQ.NUMC) GO TO 301
  IF (SUMM.EQ.(NUMC-1)) GO TO 303
  IF (SUMM-SUMN) 47,47,309
301 WRITE(6,302)
302 FORMAT(14H ALL Z = 0 )
  GO TO 47
303 WRITE(6,308)
308 FORMAT(22H .ALL Z BUT ONE = 0 .)
  GO TO 47
47 CONTINUE
220 CONTINUE
STOP
END
```

PROGRAMME H.T.L.P.

```

C HIGH TEMP., BRADLEY. LATTICE PARAMETERS
C CUBIC CRYSTALS
C NUMC=NO. OF LINES
C THETR AND THETL ARE LINE POSITIONS ON RIGHT AND LEFT FILMS.
C ENKT ARE CALIBRATED KNIFE EDGE ANGLES
C ENK ARE KNIFE EDGE POSITIONS
C FOR BOTH ENKT AND ENK NOS. 1 AND 2 ARE LOW AND HIGH ANGLES ON THE RIGHT
C AND NOS. 3 AND 4 ARE LOW AND HIGH ANGLES ON THE LEFT RESPECTIVELY
C ALL ARRAYS OF THE NO. OF LINES START AT LOW ANGLE.
REAL THETR(25), Z(25), WAVE(3), THETL(25), DIV(25), ENKT(4),
DWAVEL(25), GAMA(25), DELTA(25), ALPHA(25), ODELTA(25), DGAMA(25),
DFTHET(25), W(25), DEML(25), FO(25), AL(25), DE(25), DL(25), AF(25),
DDF(25), O(25), SQXA(25), SOXA(25), AA(25), SXD(25), XZ(25), SQXJ(25),
DENK(4), XD(25), S(25), SS(25), SJ(25), XA(25), XB(25), XH(25)
INTEGER LAM(25)
READ(5,75) (WAVE(I), I=1,3)
75 FORMAT(3F8.5)
WRITE(6,131) (WAVE(I), I=1,3)
131 FORMAT(15H WAVELENGTHS ,3F8.5)
READ(5,16) (ENKT(I), I=1,4)
16 FORMAT(4F10.6)
WRITE(6,141) (ENKT(I), I=1,4)
141 FORMAT ( 25H CALIBRATED KNIFE EDGES ,4F10.6)
READ(5,181) NDATA
181 FORMAT (I2)
DO 220 NFILM=1, NDATA
WRITE (6,191) NFILM
191 FORMAT (12H FILM NO. ,I2)
READ(5,151) NUMC, (ENK(I), I=1,4)
151 FORMAT(14,4F10.6)
WRITE(6,401) NUMC, (ENK(I), I=1,4)
401 FORMAT(10H NUMC = ,I4/20H FILM KNIFE EDGES ,4F10.6)
READ(5,171) (THETR(I), I=1, NUMC)
171 FORMAT (8F10.4)
READ(5,111) (THETL(I), I=1, NUMC)
111 FORMAT (8F10.4)
READ(5,99) (Z(I), I=1, NUMC)
99 FORMAT(20F4.0)
READ(5,77) (LAM(I), I=1, NUMC)
77 FORMAT(24I2)
NXA=0
WRITE(6,421)
421 FORMAT(20H XA XB )
DO 10 I=1, NUMC
XA(I)=ENKT(1)+(((ENKT(2)-ENKT(1))/(ENK(2)-ENK(1)))*(THETR(I)
D-ENK(1)))
XB(I)=ENKT(3)+(((ENKT(4)-ENKT(3))/(ENK(4)-ENK(3)))*(THETL(I)
D-ENK(3)))
WRITE(6,431) XA(I), XB(I)
431 FORMAT(2F10.6)
10 CONTINUE
DO 40 I=1, NUMC
IF(Z(I)) 40,40,305
305 DIV(I)=XA(I)/XB(I)
IF((ABS(DIV(I)-1.0)).LE.0.05) GO TO 40

```

```

      NXA=NXA+1
      WRITE(6,91) I
91  FORMAT(12H SCRAP LINE ,I2)
      Z(I)=0
40  CONTINUE
      IF (NXA.EQ.NUMC) GO TO 220
      DO 50 I=1,NUMC
      IF (Z(I)) 50,50,88
88  XZ(I)=(XA(I)+XB(I))/4.0
50  CONTINUE
      WRITE(6,411)
411 FORMAT(57H LINE      THETR      THETL      N      THETA(BRAGG)DEG LAM
D. )
      DO 200 I=1,NUMC
      XH(I)=180.0*XZ(I)/3.14159
      WRITE(6,161) I,THETR(I),THETL(I), Z(I),XH(I),LAM(I)
161 FORMAT(XX,I2,XX,F10.6,XX,F10.6,X,F4.0,XXX,F10.4,XXXXXXX,I2)
200 CONTINUE
      SUMS=0
      SUMSS=0
      DO 100 I=1,NUMC

```

From this point the programme is identical with programme D.S.L.P.

PROGRAMME LSQ.

```

C LEAST SQUARES PROGRAM
C Y=AX+B-----THETR=2C(XA)/360 +A
REAL X(40),Y(40),Z(40)
DO 20 J=1,6
  READ(5,1) N
  1 FORMAT(I4)
  READ(5,11) (Y(I),I=1,N)
  11 FORMAT(8F10,4)
  READ(5,21) (Z(I),I=1,N)
  21 FORMAT(8F10,6)
  WRITE(6,12)
  12 FORMAT(20H          Y          Z )
  M=FLOAT(N)
  SY=0
  SX=0
  SXX=0
  SXY=0
  DO 10 I=1,N
    X(I)=Z(I)/180.0
    WRITE(6,22) Y(I),Z(I)
  22 FORMAT(F10.4,F10.8)
    SXX=SXX+(X(I))**2.0
    SXY=SXY+(X(I))*(Y(I))
    SX=SX+X(I)
    SY=SY+Y(I)
  10 CONTINUE
  B=(SY*SXX-SX*SXY)/(M*SXX-(SX)**2.0)
  A=(M*SXY-SX*SY)/(M*SXX-(SX)**2.0)
  WRITE(6,2) A,B
  2 FORMAT(6H  A= ,F10.6/6H  B= ,F10.6)
  20 CONTINUE
  STOP
  END

```

```

C   LATTICE EXPANSION OF CUBIC MATERIALS MEASURED USING A BRADLEY
C   (GOLDSCMIDT) CAMERA
C   THETR AND THETL ARE LINE POSITIONS ON RIGHT LEFT FILMS.
C   ENKT ARE CALIBRATED KNIFE EDGE ANGLES
C   ENK ARE KNIFE EDGE POSITIONS
C   FOR BOTH ENKT AND ENK NOS.1 AND 2 ARE LOW AND HIGH ANGLES ON THE RIGHT
C   AND NOS.3 AND 4 ARE LOW AND HIGH ANGLES ON THE LEFT RESPECTIVELY
C   PROGRAM USES 4 LOW ANGLE LINE SHIFTS
REAL THETR(4,12),THETL(4,12),ENKT(4),ENK(4,12),T(12),SADD(12),
DXB(4,12),XZ(4,12),ADD(4,12),XA(4,12),MADD(12),ALPHA(12),SDELA(12),
DDELA(4,12),DEA(12),DEV(12),A(12)
READ(5,16) (ENKT(I),I=1,4)
16 FORMAT(4F10.6)
WRITE(6,141) (ENKT(I),I=1,4)
141 FORMAT ( 25H CALIBRATED KNIFE EDGES ,4F10.6)
READ(5,191) NSYST
191 FORMAT (I4)
DO 40 K=1,NSYST
WRITE(6,201) K
201 FORMAT (14H SYSTEM NO. ,I4)
READ(5,181) NDATA
181 FORMAT (I2)
READ(5,151) AO
151 FORMAT( F10.6)
WRITE(6,401) AO
401 FORMAT (6H AO= ,F10.6)
READ(5,171) ((THETR(I,J),I=1,4),J=1,NDATA)
171 FORMAT (8F10.4)
READ(5,111) ((THETL(I,J),I=1,4),J=1,NDATA)
111 FORMAT (8F10.4)
READ(5,1) ((ENK(I,J),I=1,4),J=1,NDATA)
1 FORMAT(8F10.4)
READ(5,11)(T(J),J=1,NDATA)
11 FORMAT(12F6.0)
DO 10 J=1,NDATA
SADD(J)=0
WRITE(6,411) J
411 FORMAT(10H FILM NO.,I2/67H LINE THETR THETL XA
D XB BRAGG THETA )
DO 20 I=1,4
XA(I,J)=ENKT(1)+(((ENKT(2)-ENKT(1))/(ENK(2,J)-ENK(1,J))))*
D(THETR(I,J)-ENK(1,J))
XB(I,J)=ENKT(3)+(((ENKT(4)-ENKT(3))/(ENK(4,J)-ENK(3,J))))*
D(THETL(I,J)-ENK(3,J))
XZ(I,J)=(XA(I,J)+XB(I,J))/4.0
ADD(I,J)=((SIN(XZ(I,J)))/(SIN(XZ(I,J))-1.0)
WRITE(6,131) I,THETR(I,J),THETL(I,J),XA(I,J),XB(I,J),XZ(I,J)
131 FORMAT(XX,I2,XXF10.5,XX,F10.6,XX,2F10.6,XXX,F10.6)
SADD(J)=SADD(J)+ADD(I,J)
20 CONTINUE
MADD(J)=SADD(J)/4.0
IF(T(J).EQ.T(1)) GO TO 17
ALPHA(J)=MADD(J)/(T(J)-T(1))
GO TO 18
17 ALPHA(J)=0
WRITE(6,21)
21 FORMAT(35H ROOM TEMPERATURE NO ALPHA )
18 A(J)=AO*(1.0+MADD(J))
WRITE(6,161) T(J),ALPHA(J),A(J),MADD(J)

```

```
161 FORMAT(5H T = ,F8.2,19H DEG K , ALPHA = ,F12.8, 7H A= ,F8.6,  
D27H ANGSTROMS DELTA/AO = ,F12.8)  
SDELA(J)=0  
DO 30 I=1,4  
DELA(I,J)=(ABS(ADD(I,J)-MADD(J)))*2.0  
SDELA(J)=SDELA(J)+DELA(I,J)  
30 CONTINUE  
IF(SDELA(J).EQ.0.) GO TO 32  
GO TO 33  
32 DEA(J)=0  
33 WRITE(6,211) DEA(J)  
211 FORMAT (27H ERROR IN DELTA/AO = ,F12.8)  
IF(T(J).EQ.T(1)) GO TO 10  
DEV(J)=DEA(J)/T(J)  
WRITE(6,301) DEV(J)  
301 FORMAT( 23H ERROR IN ALPHA = ,F10.8)  
10 CONTINUE  
40 CONTINUE  
STOP  
END
```

```

REAL CALG(5),TCAL(5),AMV(20),AK(20),GOLD(20) ,MGOL
READ(5,1) NSETS
1 FORMAT(I4)
READ(5,11) (CALG(J),J=1,5),(TCAL(J),J=1,5)
11 FORMAT(10F8.4)
SC=ST=SCT=STT=SDL=0
DO 20 J=1,5
SC=SC+CALG(J)
ST=ST+TCAL(J)
SCT=SCT+(TCAL(J))*(CALG(J))
STT=STT+(TCAL(J))**2.0
20 CONTINUE
A=(5.0*SCT-ST*SC)/(5.0*STT-ST**2.0)
B=(STT*SC-ST*SCT)/(5.0*STT-ST**2.0)
DO 60 K=1,5
DEL=A*TCAL(K)+B-CALG(K)
DSL=(ABS(DEL))**2.0
SDL=SDL+DSL
60 CONTINUE
DL=SDL/3.0
DLA=SQRT(5.0*DL/(5.0*STT-ST**2.0))
DLB=SQRT((DL*ST)/(5.0*STT-ST**2.0))
WRITE(6,2) (TCAL(J),J=1,5),(CALG(J),J=1,5),A,B,DLA,DLB
2 FORMAT(7H INPUT/8H T = ,5F8.3/8H MV = ,5F8.3/8H A = ,
DF10.6,8H B = ,F10.6/21H T DEG K V MV /19H ERROR IN A
D = ,F10.6/19H ERROR IN B = ,F10.6)
DO 30 J=1,20
K=J-1
AK(J)=FLOAT(K)
AMV(J)=B+A*AK(J)
WRITE(6,12) AK(J),AMV(J)
12 FORMAT(F8.2,3X,F6.3)
30 CONTINUE
DO 10 I=1,NSETS
READ(5,21) NR,(GOLD(J),J=1,NR)
21 FORMAT(I4/20F4.3)
SGOL=0
DO 40 J=1,NR
SGOL=SGOL+GOLD(J)
40 CONTINUE
MGOL=SGOL/(FLOAT(NR))
SDOL=0
DO 50 J=1,NR
DGOL=ABS(GOLD(J)-MGOL)
SDOL=SDOL+(DGOL)**2.0
50 CONTINUE
DOLS=SQRT(SDOL/(FLOAT(NR)))
THETK=(MGOL-B)/A
ERD=ABS(DOLS/A)
ERB=ABS(DLB/A)
ERA=(ABS(MGOL-B)/((ABS(A))**2.0))*DLA
SHK=ERD**2.0+ERA**2.0+ERB**2.0
DTHE=SQRT(SHK)
WRITE(6,32) I,MGOL,DOLS,THETK,DTHE
32 FORMAT(15H SPECIMEN NO.,I4/9H TC = ,F8.6,12H + OR - ,F8.6
n,10H MV. = ,F9.6,12H + OR - ,F8.6,11H DEG . K )
WRITE(6,42) (GOLD(J),J=1,NR)
42 FORMAT(25H THERMOCOUPLE READINGS /20F5.3)
10 CONTINUE
STOP
END

```

PROGRAMME ORDER.

```

COMMON TA(4),TB(4),SINT(4),RELA(3),AM(4)
READ(5,1) (TA(I),I=1,4),(TB(I),I=1,4)
1 FORMAT(8F4.0)
AM(1)=8.0
AM(2)=24.0
AM(3)=48.0
AM(4)=6.0
DO 20 L=1,2
DO 20 NE=1,4
IF(L.EQ.2.AND.NE.GT.2) GO TO 20
READ(5,11) FX,FY,DFA,DFB,EFA,EFB
WRITE(6,11) FX,FY,DFA,DFB,EFA,EFB
11 FORMAT(6F6.4)
FA=SQRT((FX+DFA)**2.0+EFA**2.0)
FB=SQRT((FY+DFB)**2.0+EFB**2.0)
IF(NE.EQ.1) WRITE(6,22)
IF(NE.EQ.2) WRITE(6,32)
IF(NE.EQ.3) WRITE(6,42)
IF(NE.EQ.4) WRITE(6,52)
22 FORMAT (17H V-SI SYSTEM )
32 FORMAT (17H V-GA SYSTEM )
42 FORMAT (17H NB-SN SYSTEM )
52 FORMAT (17H NB-AL SYSTEM )
WRITE(6,2)
2 FORMAT(25H DISORDER //56H SA SB XA XB
D 112/116 113/116 114/116 ,43H YA YB AA A
DB BB BA )
AA=76.0
DO 10 I=1,5
AA=AA-1.0
BB=26.0
DO 10 J=1,5
BB=BB-1.0
AB=-1.0
DO 10 K=1,5
AB=AB+1.0
BA=-1.0
DO 10 M=1,5
BA=BA+1.0
IF(BA+AA.GT.75.0.OR.AB+BB.GT.25.0) GO TO 10
XA=AA+AB
XB=BA+BB
SA=AA*4.0/3.0-AB*4.0
SB=BB*4.0-BA*4.0/3.0
YB=XB*100.0/(XA+XB)
YA=XA*100.0/(XA+XB)
DO 80 IA=1,4
SINT(IA)=(SA*FA-SB*FB)*(TA(IA)-3.0*TB(IA))/4.0 +(XA*FA+XB*FB)*
D(TA(IA)+TB(IA))
80 CONTINUE
DO 90 IA=1,3
RELA(IA)=(ABS(SINT(IA)/SINT(4)))**2.0
RELA(IA)=RELA(IA)*AM(IA)/AM(4)
90 CONTINUE
WRITE(6,12) SA,SB,XA,XB,RELA(1),RELA(2),RELA(3),YA,YB,AA,AB,BB,BA
12 FORMAT(4(2X,F4.0),2X,3(F8.4,2X),6(2X,F4.0))
10 CONTINUE
20 CONTINUE
STOP
END

```