

ABSTRACT OF THESIS

submitted for the degree of Doctor of Philosophy in the University of London by G.G. Fletcher, B.Sc., A.R.C.S., D.I.C. in April, 1953.

Density of States for 3d Electrons in Nickel and Application to the Theory of Ferromagnetic Anisotropy.

The first part of this work consists of a calculation of the energy density of electronic states $N(E)$ per atom for the 3d electrons in nickel, using the tight binding approximation. The importance of such a calculation to the theory of metals is indicated in Chapter I. The tight binding approximation was used as it was considered superior and easier to handle than other methods, notably the cellular method; this opinion was supported by the final results. The first calculation made contained a deliberate approximation, which was then dropped and a more accurate calculation carried out. This method was quicker and more useful than a direct approach to the problem. From the final $N(E)$ curve several physical results were deduced, notably the low temperature electronic heat coefficient, which agreed well with experiment.

The second part of this work consists of an application of Part I to Brooks' collective electronic theory of ferromagnetic anisotropy and related topics. This served to test the calculations of Part I as well as to clarify Brooks' theory and carry it to a quantitative stage for the first time. This also involved the consideration of theories of the gyromagnetic splitting ratio g' and ferromagnetic resonance (spectroscopic splitting factor g). It proved possible to extend Brooks' theory formally to remove one crude approximation but numerical values of g , g' and K for nickel could only be obtained

by use of Brooks' original formulae owing to the computational labour involved. These values, although of the right order of magnitude, cannot be said to agree very well with experiment; sufficiently well, however, to suggest that the calculations of Part I were quite accurate.

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DENSITY OF STATES FOR 3d ELECTRONS IN NICKEL AND APPLICATION
TO THE THEORY OF FERROMAGNETIC ANISOTROPY.

By
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Preface.

The transition metals are of particular interest in the theory of metals, since they display anomalous electronic properties, which are only explicable on the assumption that the energy density of electronic states $N(E)$ for certain critical values of energy E is much larger than for other metals. Previous quantitative work on relevant $N(E)$ curves has been very meagre and always based on the cellular method of calculation, giving results in poor agreement generally with experiment. Use of the tight binding approximation has been restricted to very roughly quantitative work at the best. On Professor's Jones suggestion, therefore, an attempt was made to calculate an $N(E)$ curve for the 3d electrons in nickel, using the tight binding approximation, which was considered superior to the cellular method and easier to handle, an opinion supported by the final results. Every attempt was made to make as few approximations and assumptions as possible, consistent with keeping the computational labour involved within reasonable bounds. The effects of all unavoidable approximations were closely examined. A particular approximation, which has been made by previous workers, was made at the start in order to obtain a complete $N(E)$ curve fairly easily and quickly. This approximation was then dropped and, using the results of the approximate calculation as a guide, a more accurate solution of the problem was obtained. Only part of the $N(E)$ curve for higher energies was calculated in this case owing to the computational labour involved and the relative unimportance of the rest of the curve. Among results of physical interest obtained are a bandwidth

of 2.7_e ev, degeneracy temperature of $1.4 \times 10^3 K$, and low temperature electronic heat coefficient γ of 1.6×10^{-3} cal/mol. deg.⁻² (compared with the experimental value of 1.74×10^{-3}). In general it is considered that the general shape of the curve has been well established and that the bandwidth obtained here is much nearer the truth than any previous result. As a first reasonably accurate application of the tight binding theory of metals it can be regarded as quite satisfactory.

As a further test of the accuracy of the calculations of Part I it was decided on Dr. Wohlfarth's suggestion to utilize them in a quantitative investigation of the collective electron theory of ferromagnetic anisotropy and allied topics propounded by Brooks in 1940. In the course of this work attempts have been made to clarify this theory and the assumptions involved, a few minor errors in Brooks' original derivation being corrected also. It has also been possible to extend the theory formally to remove what is probably its crudest approximation but the quantitative evaluation of the formulae involved proves quite prohibitively laborious. Although this is not true of Brooks' original formulae, even their evaluation involves difficulties, all of which have not yet been satisfactorily overcome. The numerical results for the gyromagnetic ratio g' and spectroscopic splitting factor g for nickel are in fair agreement with experiment, viz. 1.81 and 2.13 respectively as compared with 1.93 and 2.19-2.42. No suggestion arises as to the reason for the observed difference between $g-2$ and $2-g'$. The value of -3.22×10^5 ergs/c.c. obtained for the first anisotropy coefficient K , for

nickel is of the right sign but about 100 times too large. This is not regarded as particularly significant, however, owing to various approximations involved and on the whole the results of Part II can be said to confirm that the results of Part I, i.e. the $H(E)$ curve for nickel, are probably quite accurate.

The early part of this work was carried out at Imperial College, where the author was a research student from October 1949 to October 1950. For the remainder of the time, October 1950 to December 1952, the author has been on the staff of the University College of the South West, Exeter.

The results of the approximate calculation of Part I were published in a joint letter to the Philosophical Magazine (42, 106, 1951) with Dr. Wehlfarth. Apart from composing the letter, Dr. Wehlfarth's only contributions to this part of the work were purely of an advisory nature. The remainder of Part I was published by the author in fuller form in the Proceedings of the Physical Society (A65, 192, 1952). Copies of these publications are included at the end of this thesis.

Finally the author would like to express his thanks to Professor H. Jones and Professor V.G.A. Ferraro for their supervision of this work, Professor Jones and Dr. E.P. Wehlfarth for their help in carrying it through, Professor H. Brooks and the Library of Harvard University in making available a copy of Professor Brooks' Ph.D. thesis, and the University of London for the provision of a Postgraduate Studentship for the first year of this work.

(Chapters I-VI of Part I were submitted in July 1950 as a thesis for the Diploma of Imperial College.)

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Part 1. Calculation of Density of States Curve for 3d electron

in Nickel.

Chapter I.

Properties of Transition Metals Related to their d Energy Bands.

(a) Electrical Properties.

Electrical conduction of metals is considered to be effected mainly by the nearly-free s electrons travelling through the lattice, the resistance being caused by scattering of these electrons by the atoms when displaced from their mean positions by thermal vibrations and by scattering from impurity centres. This accounts satisfactorily for the noble metals Cu, Ag and Au, which have one s electron per atom and for which the d band is full. The transition metals, e.g. Ni, Pd, Pt could accommodate all their 10 outermost electrons in the d band but then they would be almost perfect insulators, certainly at very low temperatures. Other electronic properties indicate, however, that owing to band overlap they have ~ 5 s electrons per atom and a corresponding number of holes in the d band. (When two bands overlap, e.g. s and d, one cannot really refer to s and d electrons or s and d states as the two bands should be considered as one and each state is described by a mixture of s and d wave functions. For convenience, however, we shall refer to an electron whose wave function is predominantly s with some admixture of d as an s electron and so on.) However, the conductivities of Ni, Pd, Pt are much less than half those of the noble metals (Seitz 1940, p.10), even though there is an additional contribution to the current in the former case from

the d electrons (very small). Mott (1936a; 1936b) suggested that this decrease in conductivity might be due to scattering of the s electrons into vacant states in the d band as well as into other s states. This idea was able to account qualitatively for a number of features such as (i) the temperature variation of resistance of ferromagnetics and of paramagnetics at high temperatures (ii) the zero temperature coefficient of resistance of alloys such as constantan and (iii) the thermoelectric powers of the paramagnetics. Wilson (1938), however, carried out a more detailed investigation, showing that only certain s-d transitions are possible, thereby reducing their importance in accounting for abnormal conduction properties. For Mott's model to be applicable surfaces of the same constant energy constructed for the s and d bands in momentum space must intersect each other or lie close together at a number of points. Manning (1943) has examined this point in the case of body-centred cubic (b.c.c.) Fe and found that all corresponding points for different bands differ much too greatly in energy so that either Mott's model is inapplicable or the condition discussed by Wilson is not valid, as suggested by Seitz (1940, p. 540). The present calculation provides a basis for a similar test to be made in the case of Ni (face-centred cubic; f.c.c.) or for the future testing of any new theory

(b) Magnetic Properties.

Experimental work on the gyromagnetic effect has indicated that the ferromagnetism of the transition metals is largely due to electron spin and that their orbital motion has little effect (Stoner 1948; also Part II of this thesis). Associated with each

spin is a magnetic moment and it was suggested that this must be quantized, either parallel or antiparallel to the direction of a magnetic field (Debye, Sommerfeld 1916, see Stoner op.cit.). Slater (1930) pointed out that a necessary condition for ferromagnetism appeared to be the possession by the atoms concerned of an incomplete inner shell of electrons, capable therefore of taking on a magnetic moment by proper orientation of their spins, e.g. the transition metals. In a non-magnetic state the spins must just balance each other by setting themselves in antiparallel pairs. In changing to a magnetic state some electrons must change the direction of their spins so that there are more in one direction ($+\uparrow$) than the other ($-\uparrow$). These electrons must be raised to higher energy states, however, as all the lower states of positive spin are already full (a result of the exclusion principle) so that the change causes an increase of Fermi energy. To compensate for this, however, there is an increase in the number of exchange integrals between electrons of parallel spin, causing a decrease in exchange energy if these integrals are negative. Thus under certain conditions the ferromagnetic state may be the stable one, i.e. of lower total energy than the non-magnetic one. For the transition metals the d band corresponds to the incomplete inner electron shell of the free atom and, from certain results of Slater (1936), Greene and Manning (1943) show that ferromagnetism is more likely the higher the density of states $N(E)$ in the d bands at the Fermi surface (the height to which the band is filled at absolute zero). They are therefore able to explain why b.c.c. Fe is ferromagnetic rather than f.c.c.

Slater (1936) attacked the problem quantitatively and showed that Ni should be ferromagnetic but his estimate of the point in the iron group of elements, at which ferromagnetism should disappear, was very approximate as he had to extrapolate from the known energy bands of Cu to obtain those of Ni, Co and Fe. Slater's calculation is open to serious criticism since his exchange integral refers mainly to exchange between the outer electrons and the core of the same atom, thereby ignoring the concept of ferromagnetism as a cooperative phenomenon (Wohlfarth 1949b; 1953; see also Part II). The present calculation, however, may be extended, in principle, to enable an estimate to be made of the exchange energy using tight-binding wave functions and it may then be possible to ascertain more precisely the essential conditions for ferromagnetism.

Stoner (1935; 1936a) applied his collective electron treatment first to the problem of the magnitude and temperature variation of paramagnetism and obtained an expression for the magnetic susceptibility, χ_e , due to electron spin. From this it appears that χ_e will be high if the density of states $N(E)$ is high near the Fermi limit and in any case the shape of the $N(E)$ curve in this region is of paramount importance in testing Stoner's theory. The present calculation, besides giving the d band shape for Ni, should indicate the general shape for any metal with f.c.c. structure, to which the tight-binding approximation may be applied so that it should prove of assistance with this problem. Stoner (1936a; 1938a) has also considered the temperature variation of ferromagnetism, assuming, as in the

treatment of spin paramagnetism, a "standard band" form $N(E) \propto (E_{\text{max}} - E)^{1/2}$ an assumption not borne out by the present work. Wohlfarth has continued Stoner's work on collective electron ferromagnetism, considering Ni and Ni-Cu alloys (1949c), Ni-Co and related alloys (1949a) and Ni-Pd alloys (1948). The treatment is vitally dependent on the band form assumed for the metal or alloy and in the second paper Wohlfarth attributes discrepancies between theory and experiment to deviation of the band form from that assumed. In a further paper (1951) he has repeated much of Stoner's work on the assumption of a "rectangular band" ($N(E)$ constant) but obtains similar discrepancies with experiment. The application of the present work is obvious.

Brooks (1940) has applied the collective electron treatment to the problem of ferromagnetic anisotropy and shown that it is related to the divergence of the spectroscopic splitting factor g from 2. Other related topics are the gyromagnetic ratio g' and the problem of magnetostriiction. For none of these problems is the band shape explicitly required but a band calculation of the type made here is essential to any quantitative estimates of the quantities involved and Part II of this thesis is devoted to their consideration.

(c) Electronic Specific Heat.

The electrons in a metal can contribute to its specific heat by jumping to excited states, thereby absorbing energy. It can be shown (e.g. Mott and Jones 1936) that ~~this~~ electronic heat is proportional to the density of states $N(E)$, at the Fermi surface for the metal and for most metals it is negligible

compared with that due to the lattice vibrations except at very low temperatures. The transition metals, however, have comparatively large excess specific heats (above the ordinary classical value) at all temperatures and it has been suggested that these may be attributed to an electronic contribution. This is understandable if the Fermi surface occurs in a region, where $N(E)$ is large. Stoner (1936a; 1936b) applied his collective electron treatment to the problem and to the relation between the electronic heat and spin paramagnetism originally pointed out by Mott (1935). In a later paper (1936b) Stoner points out that variation of the electronic heat over the whole temperature range can be treated only on the basis of a completely specified band form and he assumes the same "standard" form as in his work on spin paramagnetism and ferromagnetism. Wohlfarth (1931) has also considered various thermal properties from the point of view of a rectangular band but considerable discrepancies with experiment occur on either assumption. The present calculation should improve the position. Electronic specific heat is, in fact, the most favourable electronic property to consider in seeking experimental confirmation of a d band calculation since, once $N(E)$ has been estimated theoretically, its value is immediately calculable without further complication (such as exchange effects). In fact good agreement with experiment is obtained in the present work.

(4) X-Ray Emission and Absorption.

If an atom becomes ionized by loss of an electron from a complete inner shell, an outer electron may jump down into the

vacant state with the emission of λ -radiation. In a metal the discrete energy levels of the free atom are broadened into bands and hence the emission spectrum consists of a continuum. Jones, Mott and Skinner (1934) gave a detailed theory of the emission showing that the intensity $I(E)$ of the emission band should be proportional to the density of states at the upper level and the probability of transition to the lower level. The emission bands of metals with filled or partly-filled d bands should therefore largely be due to transitions from the d band, assuming the density of states there to be much higher than in the s-p band. From consideration of experimental work Seitz (1940; p.440) concludes that the d band shifts in passing from Cu to Hf and that one-electron approximations are not very accurate when applied to d electrons. This is an important point, which the present work may help to clarify.

When a metal is bombarded with x-rays, some of the radiation is absorbed by inner electrons, which are thereby excited sufficiently to leave the atom. In addition, however, a fine structure occurs in the absorption spectrum for the metal, which Kronig (1931, 1932) attributes to electrons making transitions from the deep-lying K and L levels to empty levels lying above the Fermi limit as occur in the transition metals. Mott and Jones (1935, pp.151, 192) point out that the most direct evidence for the hypothesis that in these metals there are empty d states with very large $N(E)$ is provided by Veldkamp's work on the x-ray absorption spectra of Ta and W. The present work confirms this hypothesis. Jones and Mott (1937) have shown that such transitions

are unlikely except for transition metals.

Experimental work on the K and L emission and absorption bands of Ni has been carried out by a number of workers (see Canchois 1948, 1953 for refs.). The latest measurements are by Canchois (1953) on the L bands of Ni; in particular she considers the L emission bands, corresponding to transitions to 2p states, should be closely related to the structure of the 3s and 3d bands. Her deduction of a high, narrow peak in the 3d band near its upper limit agrees with the results obtained here; any quantitative agreement depends very much on the theory of x-ray emission and absorption adopted.

(c) Cohesion.

Seitz (1940, p. 271) suggests that the forces binding a solid together may be classified as electrostatic ones between bound charge distributions and others ultimately connected with the presence of "free" electrons, the latter being of primary importance in metals. It has generally been assumed that for a metal the binding is closely related to the covalent or electron-pair bond, so that only the relatively free s and p electrons make any great contribution to the binding energy. The transition metals, however, exhibit larger cohesive energies than the monovalent metals, which they precede in the periodic table. Mott interprets this qualitatively as due to differences in the way, in which the energy levels are filled (Seitz 1940, p. 428) while Seitz and Johnson (1937) suggest that at least part of the binding energy of the transition metals is related to a lowering of the centre of gravity of the occupied d levels in passing

from the free atom to the solid. Pauling (1938) has suggested, however, that the d electrons may contribute significantly to the cohesive forces in metals. His suggestion is that the d wave functions combine with the s-p functions to form a scheme of levels, in which there are a larger number of valence electrons per atom than the one s-p function per atom suggested by Krutter's band scheme for Cu. In principle this means a splitting of the five d zones into two separate systems, one responsible for the large cohesive energy of the transition metals and the other for their magnetic properties. Such a splitting may be derived from a group-theoretical treatment of crystalline wave functions; similarly the $N(E)$ curve exhibits two high peaks but it would seem to be the higher energy peak which is responsible for both types of phenomenon. The energy levels determined experimentally from X-ray work do not seem to agree with Pauling's assumption.

(f) Conclusion.

It has been the purpose of this chapter to discuss very briefly these physical properties of transition metals, which depend on the properties of the electronic d energy band, and to point out where the present and future related calculations may be of value. Apart from the main d band calculation it appears that in many cases further problems peculiar to particular electronic properties should be considered since few advances have been made in their elucidation over the last 15 years. The present work having been carried to a reasonably successful conclusion, it will be of interest to reconsider these more specialized topics in the light of the results obtained as has in fact been done in one case in Part II.

Chapter II.

Previous Band Calculations.

The various methods of band calculation in current use will first be indicated, followed by a summary of previous work on the f.c.c. lattice and d bands.

(a) Free Electrons.

The wave function ψ representing a free electron of mass m , moving in a field, in which its potential energy is V and its total energy is E , obeys Schrödinger's equation:-

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad 2.1$$

If V is spherically symmetrical, then separable solutions may be obtained in the form:-

$$\psi = f(r) S_l(\theta, \phi)$$

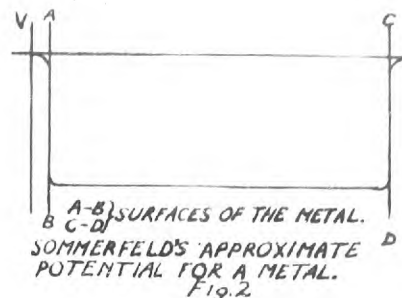
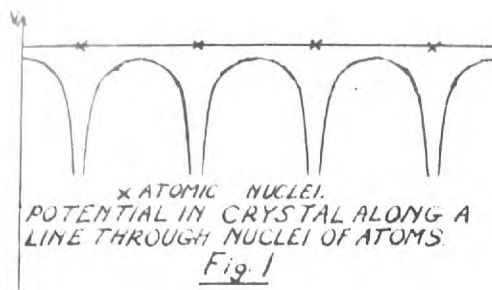
where (r, θ, ϕ) are spherical polar coordinates and $S_l(\theta, \phi)$ is a spherical harmonic of order l . The solutions for $l = 2$, for example, correspond to d states of the electron, the function S_l taking any of the linearly independent forms:-

$$\frac{yz}{r^2} ; \frac{zx}{r^2} ; \frac{xy}{r^2} ; \frac{x^2 - y^2}{r^2} ; \frac{3z^2 - r^2}{r^2}$$

each of which has two nodal planes passing through the centre of force.

A metal contains electrons, which are comparatively free to move through the metal, e.g. under the influence of an electric field. The potential, in which they move, depends on their interaction with each other and with the ions, from which they have been stripped. In a crystalline metal, in which the ions are at rest in their equilibrium positions, V is clearly periodic with the period of the crystal lattice. Along a line through the

nuclei of atoms, which are nearest neighbours, V must vary somewhat in the manner indicated in Fig.1.



For simplicity in the first treatment of the problem Sommerfeld (1928) assumed that the average field acting on an electron at a given point is zero, i.e. V is constant within a metal as shown above in Fig.2. If V is assumed zero within a cube of metal of side L , increasing suddenly to some finite value at the boundaries then ψ must satisfy:-

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \quad 2.2$$

where $\psi = 0$ at $x, y, z = 0$ and L . The solutions of 2.2 are:-

$$\psi = \sin \frac{\pi l_1 x}{L} \sin \frac{\pi l_2 y}{L} \sin \frac{\pi l_3 z}{L}$$

where l_1, l_2, l_3 are integers and:-

$$E = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} (l_1^2 + l_2^2 + l_3^2)$$

This model is not accurate for any real metal and Bloch (1928), assuming a periodic potential as in Fig.1, showed that the solutions of 2.1 must be of the form:-

$$\psi = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(x, y, z)$$

where $u_{\mathbf{k}}$ is a function, dependent in general on the wave vector $\mathbf{k}$ and periodic in x, y, z with the period of V , i.e. of the crystal lattice. ψ then represents a wave of wavelength $\frac{2\pi}{k}$ travelling

in the direction of $\underline{k}$.

(b) Approximation of Nearly-Free Electrons.

In this case V is assumed to be numerically small everywhere in comparison with the average K.E. of the electrons. For a simple cubic lattice with nearest neighbours a distance a apart a Fourier expansion of ψ gives for the wave function:-

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{n}} A_{\mathbf{n}} e^{i\mathbf{n}\cdot\mathbf{r}/a}$$

where $\mathbf{n}$ represents the integers (n_1, n_2, n_3) and the summation is over all positive and negative values of these integers. If the electrons are nearly free, it may be shown (Mott and Jones 1936, p.59) that $A_{\mathbf{n}} \ll A_0$ unless:-

$$k^2 \approx (\underline{k} - 2\pi\mathbf{n}/a)^2$$

in which case:- $E = \frac{1}{2} [E_0 + E_{\mathbf{n}} \pm \sqrt{\{E_0 - E_{\mathbf{n}}\}^2 + 4V_{\mathbf{n}}V_{\mathbf{n}}^*}]$

where:-

$$E_0 = \frac{\hbar^2 k^2}{2m}$$

$$E_{\mathbf{n}} = \frac{\hbar^2 (\underline{k} - 2\pi\mathbf{n}/a)^2}{2m}$$

$$V_{\mathbf{n}} = \iiint e^{2\pi i \mathbf{n} \cdot \mathbf{r}/a} V dxdydz / \iiint dxdydz$$

integrations being over unit cell of the lattice. Since $E \approx E_0$, it is easily shown that E must be discontinuous at the planes in $\underline{k}$ -space given by:-

$$k^2 = (\underline{k} - 2\pi\mathbf{n}/a)^2$$

i.e. there are certain forbidden ranges of energy for the electrons. Thus the discrete energy levels of the free electron have now broadened into zones of allowed energies, separated in general by forbidden zones.

(c) Approximation of Tight Binding.

This corresponds to the assumption that the atoms in the metal are comparatively far apart so that interaction between them is small and the discrete energy levels are therefore not

broadened as much as in (b). This will be dealt with fully in Chapter III.

(d) Method of Wigner and Seitz.

The case intermediate between (b) and (c), applicable to most metals, can be treated by a method due to Wigner and Seitz (1933, 1934). Their original method gives fairly accurately the wave function corresponding to the state of lowest energy in a metal, for which the field of the ion is known, but it has been extended by later workers to states of higher energy. Wigner and Seitz show that for a crystal with a high degree of rotational symmetry there is a large domain about each nucleus in which the field may be replaced by a spherically symmetrical one. The lattice is therefore partitioned into a set of space-filling polyhedra centred on the nuclei, the field being chosen to be spherically symmetrical within each. Then within each such cell Schrödinger's equation 2.1 must be considered, having solutions of the type:-

$$\psi = \frac{f_l(r, E)}{r} \Theta_m^l(\theta, \phi) \quad 2.3$$

where $f_l(r, E)$ satisfies:-

$$-\frac{\hbar^2}{2m} \frac{d^2 f}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] f = E f$$

and $\Theta_m^l(\theta, \phi)$ is a surface spherical harmonic. Bloch functions may be constructed from functions of type 2.3 by forming series of those associated with the same value of E :-

$$\psi_k(r) = \sum_{l,m} b_{l,m}^k f_l[r, E(k)] \Theta_m^l(\theta, \phi) \quad 2.4$$

The coefficients b are determined by appropriate boundary conditions.

For monoatomic crystals the most convenient cell is the

polyhedron, whose plane faces bisect orthogonally the lines joining an atom to its nearest neighbours, while similar cells containing more than one atom are constructed for polyatomic crystals. The boundary conditions for determining the $b_{\underline{k}}^{l,m}$ are that

- (i) $\psi_{\underline{k}}$ and its first derivative must be continuous at the boundaries between neighbouring cells and
- (ii) $\psi_{\underline{k}}$ must satisfy the Bloch condition:-

$$\psi_{\underline{k}}(\underline{r} + \underline{\tau}) = \psi_{\underline{k}} e^{i \underline{k} \cdot \underline{\tau}}$$

where $\underline{\tau}$ is a translation vector of the lattice. It follows that these conditions can only be satisfied for discrete values of $\underline{k}$ for a given $\underline{k}$, the permissible solutions providing the desired relationship between $\underline{k}$ and $\underline{k}$. It has not proved feasible to satisfy (i) and (ii) at all points on the boundaries of the polyhedra. Instead all but a finite number of the terms in 2.4 are discarded and boundary conditions imposed at just enough points to determine the coefficients of these terms. This is only justified if 2.4 converges rapidly, as it should do for small $\underline{k}$, since then the wavelength of the Bloch function is large compared with the dimensions of the cell.

Wigner and Seitz originally considered only the lowest electron level, for which the wave function is periodic with the periodicity of the lattice anyway. They then approximated to the actual cell by using a spherical one of the same volume, making the radial derivative of the wave function zero on the surface of the sphere. They calculated the energy as a function of inter-nuclear distance, showing a minimum near the observed distance.

In order to calculate excited energy levels Slater (1934)

extended Wigner and Seitz' method by considering a wave modulated in the crystal by the plane wave function $e^{ik \cdot r}$. Then by Bloch's theorem, if $\underline{r}$ is the vector from the nucleus of one cell to that of an adjacent one, conditions (i) and (ii) become as follows.

- (i) In passing from a point on the surface of a cell to the point perpendicularly opposite on the surface the wave function ψ is multiplied by the factor $e^{ik \cdot \underline{r}}$ and
- (ii) the derivative normal to the surface, ψ' , is multiplied by $-e^{ik \cdot \underline{r}}$ (since the outward normal at one point is the inward normal at the other).

If the wave function u is the sum of an even part u_g unchanged by such a translation, and an odd part, whose sign changes, then Slater shows that, if u_g and $\underline{k}$ are real, the odd part must be imaginary, i.e. $i u_o$. This is deduced from conditions (i) and (ii).

The spherical harmonics chosen for the component terms of u_g and u_o are those of lowest order, which will satisfy the boundary and symmetry conditions (Slater 1934) although von der Lage and Bethe (1947) have succeeded in introducing harmonics with much higher values of ℓ . In order to calculate the radial parts of the components some particular potential function must be assumed. When the boundary conditions are written down for the chosen points on the cell boundaries the equations contain as many arbitrary constants $b_{\ell, m}$ as there are equations. These linear, simultaneous equations have a non-zero solution only if the determinant of the coefficients of the $b_{\ell, m}$ is zero. These coefficients involve tangent factors T , e.g. $\tan \frac{r}{2k} (k_x + k_y + k_z)$ etc., and radial wave functions s, p , etc. calculated at the points

considered. This gives one relation between the T 's and others arise because the T 's are derived from only three independent quantities k_x, k_y , and k_z . Energy bands arise as follows. The radial wave functions depend on the energy and the T 's on the momentum. If the momentum in a certain direction is real, waves can be propagated and the corresponding energies are allowed. Complex values of momentum correspond to forbidden ranges of energy. The limits of the bands in momentum space correspond to simple relations between the radial wave functions, e.g. $a < 0; b \leq 0$.

It proves too difficult to solve the determinantal equation except for special directions of propagation, when the determinant can be reduced by simple algebra or group theory. This may result in one more condition than before and Slater avoided this by dividing the $b_{\frac{1}{2}}^{l,m}$ into two sets, one of which is taken as zero. Thus two classes of solution arise, depending on which set is taken as zero. The energy may then be plotted as a function of momentum for different directions of propagation and to derive surfaces of constant energy in momentum space some form of interpolation must be used. Sets of surfaces are constructed for each band, i.e. each solution of the determinantal equation.

Actual calculations of interest to the present work will now be considered.

Krutter's work on Cu (1935) is of interest since Cu has a f.c.c. lattice, is the next element to Ni in the periodic table and his results have been used in a number of practical applications. He applies the boundary conditions at the points midway between the atom and its nearest neighbours (12) giving 12

conditions. In forming his approximate wave function he employs the twelve wave functions of the free atom, which involve the lowest order spherical harmonics, i.e. one s, three p, five d and three of the possible seven f functions, hoping thereby to reproduce most correctly the energy bands originating from the s, p and d levels of the free atom. In order to calculate the 4s, 4p and higher wave bands he uses the Cu^+ field given by Hartree (without exchange). For the 3d band he modifies this field, effectively substituting a 4s for a 3d electron. Then the wave functions are calculated by numerical integration of the Schrodinger equation for a set of energy values. His results, shown as a graph of energy E plotted against internuclear distance R for a given direction of $\underline{k}$ (see Fig. 3) indicate that at normal separation (A) the 3d and 4s bands overlap considerably

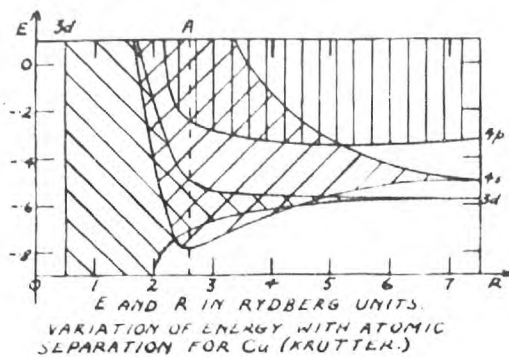


Fig. 3

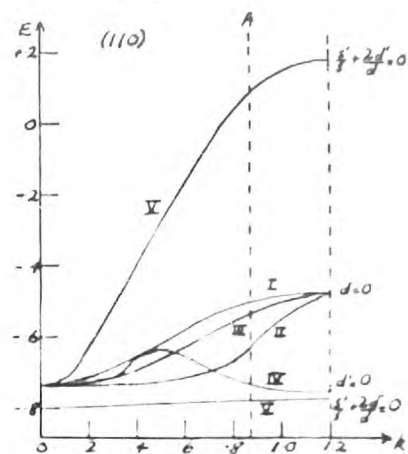


Fig. 4

E is also plotted as a function of momentum for various directions in k -space for the various classes of solution of the Schrödinger equation, e.g. the (110) direction is shown in Fig. 4. From these curves Krutter estimates the constant energy contours for the conduction electron in the $k_z = 0$ plane of the first Brillouin zone (B.Z.), using some unspecified form of interpolation.

Shackley (1937a) extended Krutter's treatment of the f.c.c. lattice, including more special directions and planes in k -space. Tibbs (1938) sets out the case of the (111) direction fully, using Hartree's unmodified cu^+ field throughout as he is only interested in the conduction electron. None of the twelve boundary points considered by Krutter occurs on this direction and Tibbs therefore uses different boundary conditions, thereby reducing the energy of the highest state of the first band and increasing the width of the first energy gap but his results do not seem to agree very well with experiment.

Manning and Greene's calculations for Fe are of interest since Fe is a ferromagnetic of the same group of elements in the periodic table as Ni. Manning (1943), in considering b.c.c. Fe, takes for his wave function within the atomic polyhedron the sum of 14 terms, viz. one s, three p, five d, four f and one g atomic wave functions. He then applies boundary conditions at the points midway between an atom and its nearest neighbours (8) and next-nearest neighbours (6). In determining the effective field for the metal he assumes the charge densities for the 1s to 3p electrons to be the same as found for the Fe atom by Manning and Goldberg (1938). The charge densities for the 3d and 4s electrons

are renormalized to the volume of the atomic sphere in metallic Fe, i.e. the sphere of volume equal to that of the atomic polyhedron. With this field the radial wave functions are found by numerical integration as in the Hartree self-consistent field method for atoms. Hence the values of the functions and their radial derivatives at the relevant 14 points are found and used to calculate the coefficients in the equations relating ϵ and k . Six density of states curves are thus obtained; bands I and II are full so that they cannot contribute to electrical conductivity or ferromagnetism. Band VI is a wide one with considerable admixture of s functions and probably accounts for most of the conductivity. Bands III, IV and V are narrow with high densities of states and are therefore important in connection with ferromagnetism.

Greene and Manning (1943) consider f.c.c. Fe, using for their wave function the sum of twelve terms, the same as Krutter used. Boundary conditions are then imposed at the same points as used by Krutter and the potential field is the same as that used by Manning for b.c.c. Fe. Bands I, II and VI prove to be almost the same as in the b.c.c. case but III and IV are broader and V has a very sharp peak. It is pointed out that band VI is very similar to band VI for Cu.

Calculations of energy bands by the Wigner-Seitz-Slater method are very laborious, to say the least. The restriction of imposing boundary conditions at a limited number of points may lead to serious error. Shockley (1937b) devised an "empty lattice" test of the cellular method, showing that, although quite accurate

in the first B.Z., it may be in error by a factor of 2 in the 2nd. Thus calculations of occupied levels in Li and Na are probably quite good, but for Cu and Fe the error will be larger. He also shows that the accuracy of the method improves only very slowly with an increasing number of boundary conditions. Howarth and Jones (1952) have recently extended von der Lage and Bethe's method, itself a great improvement on that of Slater, in the case of Na; they have also devised a method of correcting the eigenvalues so obtained by means of a surface integral, which also provides a much more general test of results than the empty lattice test. They find errors of $\sim 5\%$ but again this is for the 1st B.Z. only. Finally in all applications of the cellular method only special points, lines and planes in $\underline{k}$ -space are amenable to solution and therefore some extremely hazardous interpolation is necessary to obtain the constant energy surfaces (which it will be seen later are often very complex) and hence the $N(E)$ curve. This curve may thus be seriously in error as is indicated in most cases by calculations of the electronic heat (see Chapter VII).

Use of the tight-binding approximation removes these three objections. The calculations are relatively simple, boundary conditions are automatically satisfied if tight-binding wave functions are used and all points in $\underline{k}$ -space may be covered, not only special ones. Various objections, which in turn may be raised against the method, are considered in the next chapter.

Chapter III.

Theory of the Tight-Binding Approximation.

(a) Degenerate Level Theory for d Bands.

The form of the potential function for an electron in a crystal has already been indicated in Fig.1, the potential V becoming infinite at each nucleus. In the theory of tight binding a field of this form is considered, in which the atoms are relatively far apart so that the behaviour of an electron in the neighbourhood of any one atom is influenced only to a small extent by the field of the other atoms. With this assumption, if $\underline{r}$ denotes the position vector of any point and $\underline{r}_l$ the position of any atom in the crystal, the wave function of an electron in its neighbourhood will be approximately $\phi(\underline{r}-\underline{r}_l)$, the unperturbed wave function for an isolated atom with its centre at $\underline{r}_l$. By Bloch's theorem the wave function of the electron in an infinite crystal must be of the form $e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$, where $u_{\mathbf{k}}(\mathbf{r})$ is a function with the periodicity of the crystal lattice. If the function is assumed to be of the form:-

$$\psi = \sum_l c_l \phi(\underline{r}-\underline{r}_l) \quad 3.1$$

where the summation is over all lattice points of the crystal, then the coefficients c_l may be determined from Bloch's theorem, i.e.:-

$$c_l = e^{i\mathbf{k}\cdot\mathbf{r}_l}$$

so that for a state $\underline{k}$:-

$$\psi_{\underline{k}} = \sum_l e^{i\mathbf{k}\cdot\mathbf{r}_l} \phi(\underline{r}-\underline{r}_l) \quad 3.2$$

This is not exactly of the required form but is the best approximation to it of the form 3.1.

Now consider atomic d states, which are fivefold degenerate

in the isolated atom. The five independent d wave functions may be chosen in the Cartesian form:-

$$\left. \begin{aligned} \phi_1(r) &= \sqrt{\frac{15}{4\pi}} \frac{yz}{r^2} f(r) \\ \phi_2(r) &= \sqrt{\frac{15}{4\pi}} \frac{zx}{r^2} f(r) \\ \phi_3(r) &= \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2} f(r) \\ \phi_4(r) &= \sqrt{\frac{15}{16\pi}} \frac{x^2-y^2}{r^2} f(r) \\ \phi_5(r) &= \sqrt{\frac{5}{16\pi}} \frac{3z^2-r^2}{r^2} f(r) \end{aligned} \right\} \quad 3.3$$

where x, y, z , are Cartesian coordinates, $r = \sqrt{x^2 + y^2 + z^2}$ and $f(r)$ is the radial wave function. The angular functions correspond to the more usual spherical harmonics expressed in spherical polar coordinates, i.e. $\sin\theta\cos\theta\sin\phi$, $\sin\theta\cos\theta\cos\phi$, $\sin^2\theta\sin\phi\cos\phi$, $\sin^2\theta\cos 2\phi$ and $(3\cos^2\theta - 1)$. The numerical factors are normalising factors for the angular parts of the wave functions; the radial part is normalised separately as will be discussed later.

Wave functions are then formed as in 3.2:-

$$\psi_{\underline{n}} = \sum_{\underline{\ell}} e^{i\underline{\ell} \cdot \underline{r}} \phi_{\underline{n}}(\underline{r} - \underline{a}\underline{\ell}) \quad (n=1,2,3,4,5) \quad 3.4$$

where $\underline{r}$ is for convenience replaced by $\underline{a}\underline{\ell}$, $\underline{a}$ being a lattice constant for the crystal and $\underline{\ell} = (\ell_1, \ell_2, \ell_3)$, where ℓ_1, ℓ_2, ℓ_3 are integral or half-integral numbers. The wave function for an electron in the whole crystal is now assumed to be a linear combination of the functions 3.4:-

$$\Psi_{\underline{n}}(\underline{r}; \underline{\ell}) = \sum_{\underline{m}} a_{\underline{m}}(\underline{\ell}) \psi_{\underline{m}}(\underline{r}) \quad 3.5$$

If $H = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r})$ denotes the Hamiltonian for the electron in the crystal and E the energy, then $\Psi_{\underline{n}}$ must satisfy:-

$$(H - E) \Psi_{\underline{n}} = 0 \quad 3.6$$

Multiply 3.6 by $\psi_{\underline{p}}^*(\underline{r})$ and integrate over all space:-

$$\sum_{\underline{m}} a_{\underline{m}}(\underline{\ell}) \int \psi_{\underline{p}}^*(\underline{r}) (H - E) \psi_{\underline{m}}(\underline{r}) d\tau = 0 \quad 3.7$$

If it is assumed that the ψ_{nh} are orthogonal to one another, an assumption to be discussed later, then for the case of $p=1$, say, this reduces to:-

$$a_{n1}\alpha_1^2(H_{n1}-E) + a_{n2}\alpha_1\alpha_2 H_{n2} + a_{n3}\alpha_1\alpha_3 H_{n3} + a_{n4}\alpha_1\alpha_4 H_{n4} + a_{n5}\alpha_1\alpha_5 H_{n5} = 0 \quad 3.8$$

where:-
$$H_{nm} = \frac{\int \psi_{nh}^* H \psi_{nh} d\tau}{\alpha_n \alpha_m} ; \quad \alpha_n^2 = \int \psi_{nh}^* \psi_{nh} d\tau$$

Five equations of type 3.8 are obtained by letting p take the values 1,2,3,4,5 in turn and, eliminating $a_{n1}, a_{n2}, a_{n3}, a_{n4}, a_{n5}$ between them, the following equation results:-

$$|(H_{nm} - E\delta_{nm})\alpha_n\alpha_m| = 0$$

The α_n can be removed as factors, giving finally the secular determinantal equation:-

$$|H_{nm} - E\delta_{nm}| = 0 \quad 3.9$$

To evaluate the H_{nm} let H_L be the Hamiltonian and E_0 the energy of a d electron in the field of an isolated atom at $\underline{r}=\underline{aL}$, so that:-

$$H_L = -\frac{\hbar^2}{2m} \nabla^2 + U(\underline{r}-\underline{aL})$$

Then:-
$$H_L \phi_m(\underline{r}-\underline{aL}) = E_0 \phi_m(\underline{r}-\underline{aL})$$

and:-
$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) = H_L - U(\underline{r}-\underline{aL}) + V(\underline{r})$$

$$\therefore \alpha_n \alpha_m / H_{nm} = \sum_{\underline{l}} \sum_{\underline{l}'} \int e^{i\alpha(\underline{l}-\underline{l}')\cdot\hbar} \phi_n^*(\underline{r}-\underline{aL}') [E_0 + V(\underline{r}) - U(\underline{r}-\underline{aL})] \phi_m(\underline{r}-\underline{aL}) d\tau \quad 3.10$$

Now
$$\frac{1}{\alpha_n \alpha_m} \sum_{\underline{l}} \sum_{\underline{l}'} \int e^{i\alpha(\underline{l}-\underline{l}')\cdot\hbar} \phi_n^*(\underline{r}-\underline{aL}') E_0 \phi_m(\underline{r}-\underline{aL}) d\tau = \frac{E_0}{\alpha_n \alpha_m} \int \psi_{nh}^* \psi_{nh} d\tau = E_0 \delta_{nm}$$

with the assumption of orthogonality already made, for the remaining terms in 3.10 change the origin to $\underline{aL}$. Then $V(\underline{r}+\underline{aL}) - V(\underline{r})$ since V has the lattice periodicity; also the terms in the summation over $\underline{l}$ are all identical. Let there be N atoms in the crystal and write $\underline{l}$ for $(\underline{l}'-\underline{l})$; then:-

$$H_{nm} = E_0 \delta_{nm} + \frac{N \sum_{\underline{l}} e^{-i\alpha \underline{l} \cdot \hbar} \int \phi_n^*(\underline{r}-\underline{aL}) [V(\underline{r}) - U(\underline{r})] \phi_m(\underline{r}) d\tau}{\alpha_n \alpha_m}$$

Using the same change of origin and nomenclature:-

$$\alpha_n^* = N \sum_{\underline{l}} e^{-i \underline{a} \cdot \underline{l} \cdot \underline{k}} \int \phi_n^*(\underline{r} - \underline{a} \underline{l}) \phi_n(\underline{r}) d\tau$$

Assuming the contributions from all other atoms ($\underline{l} \neq \underline{0}$) to be negligible in this expression compared with that from the atom at the origin ($\underline{l} = \underline{0}$), i.e. assuming orthogonality between wave functions on different atoms, then:-

$$\alpha_n^* \approx N \int \phi_n^*(\underline{r}) \phi_n(\underline{r}) d\tau = N$$

since the ϕ_n are normalized to unity. Substituting for $\alpha_n \alpha_m$ in H_{nm} :-

$$H_{nm} = E_0 \delta_{nm} + \sum_{\underline{l}} e^{-i \underline{a} \cdot \underline{l} \cdot \underline{k}} \int \phi_n^*(\underline{r} - \underline{a} \underline{l}) (V - U) \phi_m(\underline{r}) d\tau \quad 3.11$$

where summation is over all atoms in the crystal. consider,

however, the particular case of the central atom, i.e. for which

$\underline{l} = \underline{0}$. It will be seen later that the approximation is made that

$V - U$ within a sphere centred on this atom and of diameter equal

to the distance from it to a nearest neighbour, thereby making

$\int \phi_n^*(\underline{r}) (V - U) \phi_n(\underline{r}) d\tau$ over this sphere zero. Also $\int \phi_n^*(\underline{r}) \phi_n(\underline{r}) d\tau = \delta_{nn}$

and it will therefore be assumed that:-

$$\int \phi_n^*(\underline{r}) (V - U) \phi_n(\underline{r}) d\tau = C \delta_{nn}$$

an assumption to be discussed later in this chapter. C will be

referred to as the self-energy of the central atom. Then 3.11

$$\text{becomes:- } H_{nm} = (E_0 + C) \delta_{nm} + \sum_{\underline{l} \neq \underline{0}} e^{-i \underline{a} \cdot \underline{l} \cdot \underline{k}} \int \phi_n^*(\underline{r} - \underline{a} \underline{l}) (V - U) \phi_m(\underline{r}) d\tau \quad 3.12$$

Now consider the assumptions made in the above treatment.

(For further details the standard books may be consulted; Matyas (1948) also gives a full derivation of the essential equations).

(1) The fundamental assumption of tight binding is that the atoms in the crystal are far enough apart for interaction between them to be small. It is this interaction that causes the discrete energy levels of the isolated atom to broaden into

bands of allowed energy for the crystal and the assumption can only be justified on the grounds of consistency if the bandwidths obtained are comparatively small. The value of 2.7 eV obtained for the bandwidth in the present calculation satisfies this criterion on comparison with bandwidths obtained for electrons farther from the atomic nucleus and therefore affected to a greater extent by neighbouring atoms in the crystal. It would be more satisfactory to compare the bandwidth with the separation of the energy levels of the free atom, e.g. 3d-4s, but it proves a very difficult problem to select a suitable separation from spectroscopic data for comparison purposes. There is little doubt that for the crystal the band arising from the 4s atomic wave function will overlap the 3d band considerably so that the assumption here would be justified to a much greater extent if the 3d bandwidth proved small when a 4s wave function was included. There is a fundamental difficulty in this, however, that s electrons can hardly be described by tight-binding wave functions (although Lowdin (1951) has done so recently in the case of Na with some success), apart from the increased complexity of calculation involved.

(11) The assumption that 3.2.1.e.:-

$$\psi_{\mathbf{k}} = \sum_{\mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{r}} \phi(\mathbf{r} - \mathbf{r}_0) = e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{r}} e^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0)} \phi(\mathbf{r} - \mathbf{r}_0)$$

is a Bloch function. It can readily be shown that $\sum_{\mathbf{r}} e^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0)} \phi(\mathbf{r} - \mathbf{r}_0)$ has the periodicity of the crystal lattice, if surface effects are ignored, i.e. if the crystal is regarded as being of infinite size. This is obviously legitimate for the problem under consideration

and hence this assumption, and in fact the use of Bloch functions at all, is justified.

(iii) The form assumed for the functions $\bar{\Psi}_n$, with assumption (ii) the exact functions must be Bloch functions, which the $\bar{\Psi}_n$ are. Assuming that the $\bar{\Psi}_n$ are to be formed from one-electron wave functions, a point which will not be considered here, the approximation would be improved by taking more atomic wave functions, e.g. s, p, f, etc., into consideration as mentioned above. This has been done in the cellular method of solution (loc. cit.) but, owing to other approximations in that method, the results do not appear to be any better, if as good (see Chapter VIII).

(iv) The non-orthogonality of the ψ_{nk} with respect to n is neglected, i.e. the approximation is made that:-

$$\sum_{\underline{l} \neq \underline{l}'} e^{i a(\underline{l} - \underline{l}') \cdot \underline{k}} \int \phi_n^*(\underline{r} - a\underline{l}') \phi_m(\underline{r} - a\underline{l}) d\tau = 0 \quad (n \neq m)$$

This approximation is linked with another mentioned above, viz. that $\chi_n^2 \approx 1$ and it is convenient to consider them together, as far as the derivation of equations 3.9 and 3.12 is concerned the neglect of non-orthogonality may be expressed in the alternative form:-

$$\int \psi_{nk}^* \psi_{nk} d\tau \ll \int \psi_{nk}^* \psi_{nk} d\tau \quad (n \neq m)$$

or $\sum_{\underline{l} \neq \underline{l}'} e^{i a(\underline{l} - \underline{l}') \cdot \underline{k}} \int \phi_n^*(\underline{r} - a\underline{l}') \phi_m(\underline{r} - a\underline{l}) d\tau \ll \sum_{\underline{l} \neq \underline{l}'} e^{i a(\underline{l} - \underline{l}') \cdot \underline{k}} \int \phi_n^*(\underline{r} - a\underline{l}') \phi_n(\underline{r} - a\underline{l}) d\tau$

or $\sum_{\underline{l} \neq \underline{l}'} e^{i a(\underline{l} - \underline{l}') \cdot \underline{k}} \int \phi_n^*(\underline{r} - a\underline{l}') \phi_n(\underline{r} - a\underline{l}) d\tau \ll N + \sum_{\underline{l} \neq \underline{l}'} e^{i a(\underline{l} - \underline{l}') \cdot \underline{k}} \int \phi_n^*(\underline{r} - a\underline{l}') \phi_n(\underline{r} - a\underline{l}) d\tau \quad 3.13$

The integrals involved will obviously be much greater for nearest neighbours than for other pairs of atoms; considering nearest neighbours only for $n=1, m=2$, for example, a calculation gives for the left- and right-hand sides of 3.13 respectively the values $-0.028 \sin \int \sin \int$ and $N[1 + 0.08 \cos \{ \cos \gamma - 0.02 (\cos \gamma \cos \int + \cos \{ \cos \int \})]$ so that both approximations appear to be reasonable. It is

stressed that, at least in the present problem, the actual orthogonality of the $\psi_{n\mathbf{k}}$ is immaterial provided the inequality 3.13 is obeyed. This appears to answer a frequent criticism, especially by American workers, based on the fact that, although the contribution to $\int \psi_{n\mathbf{k}}^* \psi_{m\mathbf{k}} d\tau$ from a pair of nearest neighbours may be small, there will be a very large number of pairs in a crystal. In fact Wannier (1937) constructed a different type of atomic function for just the reason that they are orthogonal. Slater (1951) has shown, however, that for a calculation of the H_2 molecule they are not appreciably superior to the type of function used here and it is doubtful whether they would be in the present problem.

(v) Self-energy assumption, i.e. that:-

$$\int \phi_n^*(\mathbf{r})(V-U)\phi_m(\mathbf{r})d\tau = C\delta_{nm} \quad 3.14$$

Now $V-U$ is an even function of $x, y, z, x-y$ or $x+y$ because of the symmetry of the lattice and hence, from considerations of the parity of $\phi_n^* \phi_m$ with respect to one or other of these variables, it is easily shown that the L.H.S. of 3.14 is zero if $n \neq m$. Also $V-U$ must be symmetrical in x, y , and z so that the L.H.S. will have the same value for $n=m=1, 2$ and 3 . An approximate calculation shows that the absolute values of this integral for $n=m=4$ and 5 are slightly less than that for $n=m=1, 2$ and 3 as would be expected since $\phi_1 \cdot \phi_2$ and ϕ_3 have antinodes in the directions of nearest neighbours while $\phi_4 \cdot \phi_5$ have their antinodes in the directions of next-nearest neighbours. Owing to the assumption, already mentioned, that $V=U$ for $r < \frac{a}{2^{3/2}}$, however, the differences are very small and the assumption expressed in 3.14 is unlikely to

introduce any serious error.

(b) Previous Applications of the Approximation.

The tight-binding approximation was applied to d bands for a b.c.c. lattice by Jones and Mott (1937) and the present work was in fact started as an extension of their calculations to the f.c.c. lattice. They point out that the fivefold degenerate atomic d level splits in a cubic field into one triply-degenerate level Γ_5 (using Bethe's notation) and a doubly-degenerate one Γ_3 . This can be shown by an application of group theory (Bethe 1929). It is therefore argued that in a metal of cubic lattice there will be two d bands, which may or may not overlap, one containing six electrons (when full), the other four. By further qualitative argument they seek to show that in a b.c.c. lattice the Γ_5 band lies above the Γ_3 and that the position is reversed in a f.c.c. lattice. The present investigation has shown, however, that in the latter case at least, and using the particular wave functions and approximations detailed here, and elsewhere, the Γ_3 band lies entirely within the Γ_5 and is of very nearly the same width (the Γ_5 level does lie below the Γ_3 at $k=0$, however, the case considered by Bethe). A similar situation may well arise for the b.c.c. lattice and Mott and Jones' next assumption, that the Γ_5 band can be considered separately by using just three of the atomic d functions, cannot then be justified by a priori qualitative arguments. They are able to express the elements H_{nm} in terms of two coefficients A and B (cf. A, in present work), which they argue qualitatively are approximately equal if the atoms are very far apart. They correct for this later, in only a qualitative

way, however. The corresponding coefficients in the case of the f.c.c. lattice prove to be roughly in the ratio 3:1 in the present quantitative work and qualitative deductions of the type made by Jones and Mott have proved to be very misleading (see p. 48). The remainder of their calculation of a density of states curve is also rather approximate (for details see the original paper) but shows up the relevant features, e.g. a sharp peak in the curve near the top of the band.

Brooks (1940) again considers the Γ band separately but admits that it is a poor approximation. He repeats the work of Jones and Mott as far as setting up the secular equation and evaluating the matrix elements of the Hamiltonian, and also considers the f.c.c. lattice. A qualitative argument that the coefficients A_i used here (see later) satisfy $\frac{A_1 + A_2}{A_3} \gg 1$ has been only partly verified in this work, the calculated ratio being only about 3:1.

Matyas (1948) has applied the tight-binding approximation to the s and p electrons of Al, whereas here they would not be expected to be at all tightly bound so that the approximation would appear to be most unsuitable in this case (see Leigh 1950). This is confirmed by the large values he obtains for the coefficients A_i indicating a large overlap of the wave functions of neighbouring atoms.

Other applications of the approximation have been made but, it is believed, nowhere in anything like the present detail and precision.

Chapter IV.

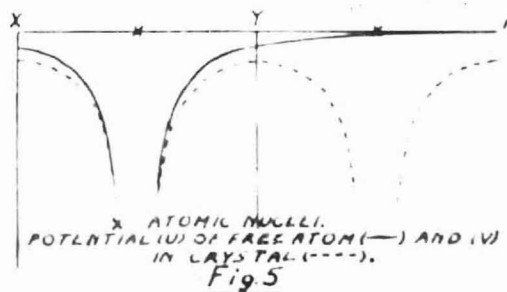
Calculation of the Matrix Elements H_{nm}

(a) Summation over Nearest Neighbours.

The expression obtained for H_{nm} was:-

$$H_{nm} = (\xi_c + C)\delta_{nm} + \sum_{\underline{l} \neq 0} e^{-i a \underline{l} \cdot \underline{k}} \int \phi_n^*(\underline{r} - a \underline{l}) (V - U) \phi_m(\underline{r}) d\tau$$

It will be assumed that the major contribution is from nearest neighbours. If a is the length of the side of unit cell in the f.c.c. lattice, then $\underline{l} = (\pm \frac{1}{2}, \pm \frac{1}{2}, 0), (0, \pm \frac{1}{2}, \pm \frac{1}{2}), (\pm \frac{1}{2}, 0, \pm \frac{1}{2})$ gives the twelve nearest neighbours of a given atom in the lattice, each being a distance $a/\sqrt{2}$ away. The next-nearest neighbours, given by $\underline{l} = (\pm 1, 0, 0)$ etc., are only a distance a away from the central atom, however, so that they may well make an important contribution also. This point is discussed later.



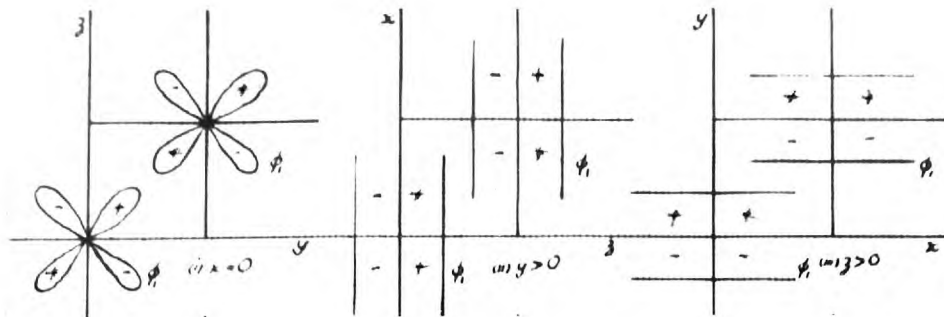
The form of the potential V in the crystal lattice has already been discussed in Chapter II (Fig. 1). The potential U in the free atom will vary in the manner shown above in Fig. 5, and therefore $V - U$ will be negative everywhere. Let:-

$$\xi = \frac{1}{2} a k_x ; \quad \eta = \frac{1}{2} a k_y ; \quad \zeta = \frac{1}{2} a k_z$$

and consider each H_{nm} in turn. In the following diagrams the nodal planes and signs of the wave functions are shown and some idea of their relative magnitudes in different directions. Consider

the variable parts $H_{Am} = (\epsilon_0 + U) \phi_{Am}$

II.



(1) Neither function $\phi_1(\underline{r})$ nor $\phi_1(\underline{r}-a\underline{\ell})$, where $\underline{\ell} = (0, \pm \frac{1}{2}, \pm \frac{1}{2})$, changes sign on crossing the plane $x=0$ and hence these four atoms contribute:- $-[e^{-i(\eta+\zeta)} + e^{-i(\eta-\zeta)} + e^{-i(-\eta+\zeta)} + e^{-i(-\eta-\zeta)}] A_1$

where:- $A_1 = -\int \phi_1^*(x, y - \frac{1}{2}a, z - \frac{1}{2}a)(V-U)\phi_1(x, y, z) d\tau$

which is positive, since both wave functions have the same sign in the region of maximum overlap, i.e. halfway between the atoms, and $V-U$ is negative. Hence the contribution is:-

$$-2A_1[\cos(\eta+\zeta) + \cos(\eta-\zeta)] = -4A_1 \cos \eta \cos \zeta$$

where:-

$$A_1 = -\int_{\frac{1}{2}} \phi_1^*(V-U)\phi_1 d\tau$$

the nomenclature being obvious.

(ii) $\phi_1(\underline{r})$ and $\phi_1(\underline{r}-a\underline{\ell})$, where $\underline{\ell} = (\pm \frac{1}{2}, 0, \pm \frac{1}{2})$, both change sign with y and hence these four atoms contribute:-

$$4A_2 \cos \zeta \cos \eta$$

where

$$A_2 = \int_{\frac{1}{2}} \phi_1^*(V-U)\phi_1 d\tau$$

which is again positive for similar reasons. All A_i will be so defined as to be positive or probably so, as will be seen by reference to the diagrams.

(iii) Similarly the four atoms at $\underline{\ell} = (\pm \frac{1}{2}, \pm \frac{1}{2}, 0)$ contribute:-

$$4A_2 \cos \zeta \cos \eta$$

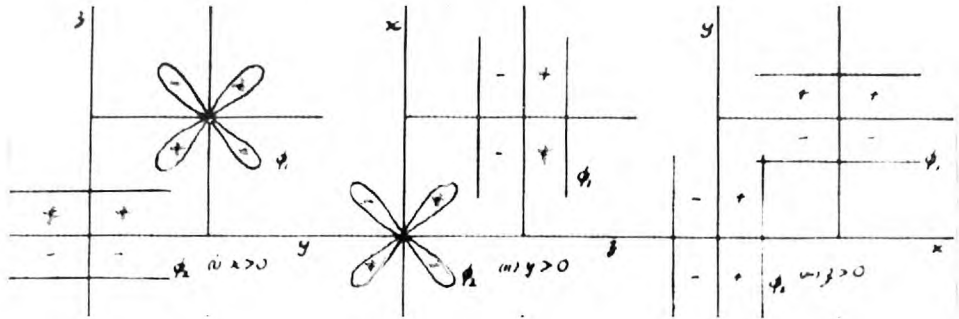
Finally, including now the constant terms:-

$$H_{11} = -4A_1 \cos \eta \cos \xi + 4A_2 (\cos \xi \cos \xi + \cos \xi \cos \eta) + E_0 + C$$

Similarly:- $H_{22} = -4A_1 \cos \xi \cos \xi + 4A_2 (\cos \xi \cos \eta + \cos \eta \cos \xi) + E_0 + C$

and:- $H_{33} = -4A_1 \cos \xi \cos \eta + 4A_2 (\cos \eta \cos \xi + \cos \xi \cos \xi) + E_0 + C$

Fig. 2/9



(i) $\phi_1(\underline{r}-\underline{a}\underline{\ell})$, where $\underline{\ell}=(0, \pm \frac{1}{2}, \pm \frac{1}{2})$, does not change sign with x but $\phi_2(\underline{r})$ does and hence these atoms contribute nothing.

(ii) Similarly the atoms at $\underline{\ell}=(\pm \frac{1}{2}, 0, \pm \frac{1}{2})$ contribute nothing.

(iii) Both $\phi_2(\underline{r})$ and $\phi_1(\underline{r}-\underline{a}\underline{\ell})$, where $\underline{\ell}=(\pm \frac{1}{2}, \pm \frac{1}{2}, 0)$, change sign with z and hence these atoms contribute:-

$$[e^{-i(\xi+\eta)} - e^{-i(-\xi+\eta)} - e^{-i(\xi-\eta)} + e^{-i(-\xi-\eta)}] A_3$$

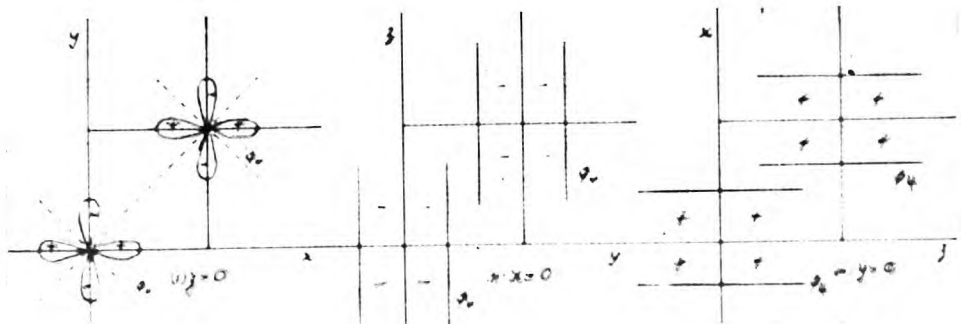
$$= 2A_3 [\cos(\xi+\eta) - \cos(\xi-\eta)] = -4A_3 \sin \xi \sin \eta$$

where:-

$$A_3 = \int_{x,y} \phi_1^* (V-U) \phi_2 d\tau$$

Similarly:- $H_{12} = H_{21} = -4A_3 \sin \xi \sin \eta$ and $H_{31} = H_{13} = -4A_3 \sin \xi \sin \eta$

Fig. 2/10



(i) Neither $\phi_4(\underline{r})$ nor $\phi_4(\underline{r}-a\underline{l})$, where $\underline{l}=(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$, changes sign with z and hence these atoms contribute:-

$$4A_4 \cos \eta \cos \zeta$$

where:-

$$A_4 = \int_{xy} \phi_4^* (V-U) \phi_4 d\tau$$

(ii) Neither $\phi_4(\underline{r})$ nor $\phi_4(\underline{r}-a\underline{l})$, where $\underline{l}=(0, \pm\frac{1}{2}, \pm\frac{1}{2})$, changes sign with x and hence these atoms contribute:-

$$-4A_5 \cos \eta \cos \zeta$$

where:-

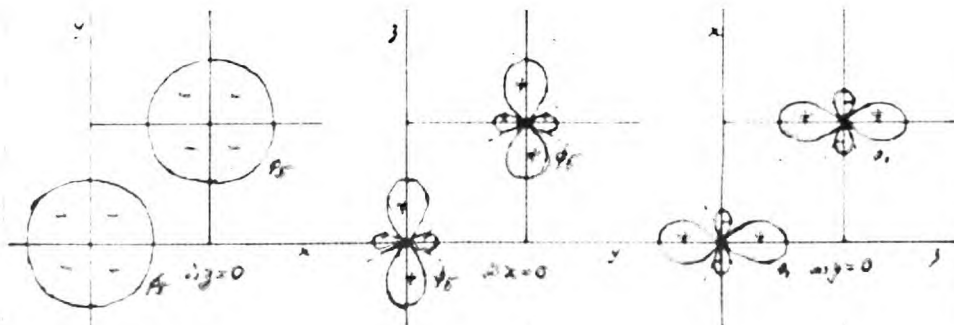
$$A_5 = - \int_{yz} \phi_4^* (V-U) \phi_4 d\tau$$

(iii) similarly the atoms at $\underline{l}=(\pm\frac{1}{2}, 0, \pm\frac{1}{2})$ contribute:-

$$-4A_5 \cos \eta \cos \zeta$$

$$\therefore H_{44} = 4A_4 \cos \eta \cos \zeta - 4A_5 (\cos \eta \cos \zeta + \cos \zeta \cos \eta) + E_0 + C$$

Fig 5.3



(i) Neither $\phi_5(\underline{r})$ nor $\phi_5(\underline{r}-a\underline{l})$, where $\underline{l}=(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$, changes sign with z and hence these atoms contribute:-

$$-4A_7 \cos \eta \cos \zeta$$

where:-

$$A_7 = - \int_{xy} \phi_5^* (V-U) \phi_5 d\tau$$

(ii) Neither $\phi_5(\underline{r})$ nor $\phi_5(\underline{r}-a\underline{l})$, where $\underline{l}=(0, \pm\frac{1}{2}, \pm\frac{1}{2})$, changes sign with x and hence these atoms contribute:-

$$4A_8 \cos \eta \cos \zeta$$

where:-

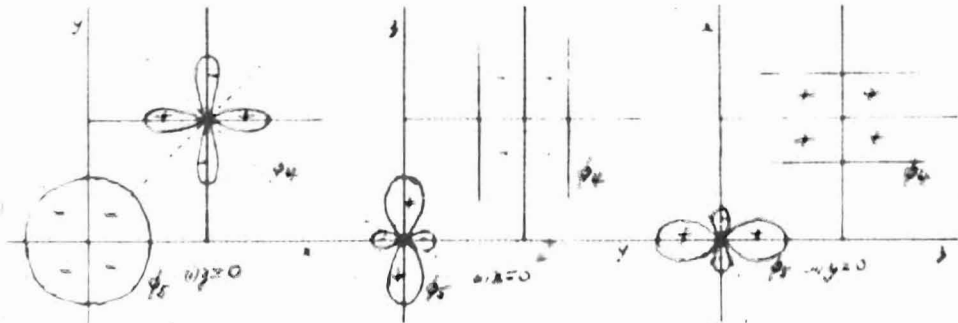
$$A_8 = \int_{yz} \phi_5^* (V-U) \phi_5 d\tau$$

(iii) Similarly the atoms at $\underline{l} = (\pm \frac{1}{2}, 0, \pm \frac{1}{2})$ contribute:-

$$4A_9 \cos \eta \cos \xi$$

$$\therefore H_{55} = -4A_7 \cos \eta \cos \xi + 4A_9 (\cos \eta \cos \xi + \cos \xi \cos \eta) + E_0 + C$$

$H_{55} = H_{55}$



(i) $\phi_5(\underline{r})$ is symmetrical about the plane $x=y$, whereas $\phi_7(\underline{r}-a\underline{l})$, where $\underline{l} = (\frac{1}{2}, \frac{1}{2}, 0)$, is antisymmetrical and hence the atoms at $\underline{l} = (\pm \frac{1}{2}, \pm \frac{1}{2}, 0)$ contribute nothing.

(ii) Neither $\phi_5(\underline{r})$ nor $\phi_7(\underline{r}-a\underline{l})$, where $\underline{l} = (0, \pm \frac{1}{2}, \pm \frac{1}{2})$, changes sign with x and hence these atoms contribute:-

$$4A_9 \cos \eta \cos \xi$$

where:-

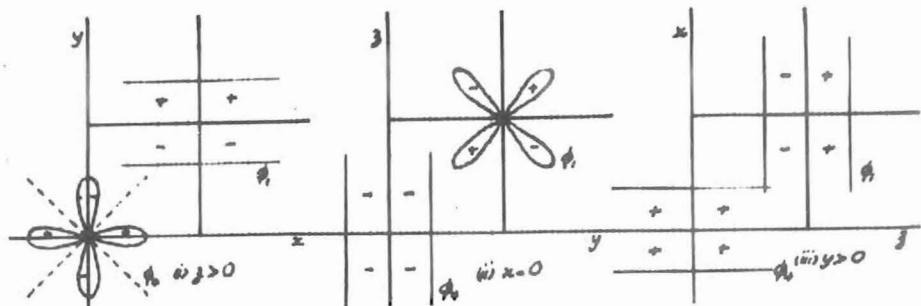
$$A_9 = \int \phi_4^* (V-U) \phi_5 d\tau$$

(iii) Similarly the atoms at $\underline{l} = (\pm \frac{1}{2}, 0, \pm \frac{1}{2})$ contribute:-

$$-4A_9 \cos \eta \cos \xi$$

$$\therefore H_{45} = H_{54} = 4A_9 (\cos \eta \cos \xi - \cos \xi \cos \eta)$$

$H_{45} = H_{54}$



(i) $\phi_4(\underline{r})$ does not change sign with z but $\phi_1(\underline{r}-a\underline{\ell})$, where $\underline{\ell}=(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$, does and hence these atoms contribute nothing.

(ii) Neither $\phi_4(\underline{r})$ nor $\phi_1(\underline{r}-a\underline{\ell})$, where $\underline{\ell}=(0, \pm\frac{1}{2}, \pm\frac{1}{2})$, changes sign with x and hence these atoms contribute:-

$$-4A_6 \sin \eta \sin J$$

where:-

$$A_6 = \int \phi_1^* (V-U) \phi_4 d\tau$$

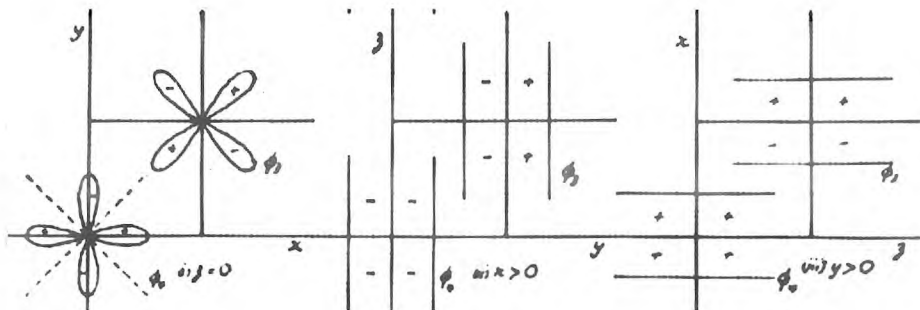
(iii) $\phi_4(\underline{r})$ does not change sign with y but $\phi_1(\underline{r}-a\underline{\ell})$, where $\underline{\ell}=(\pm\frac{1}{2}, 0, \pm\frac{1}{2})$, does and hence these atoms contribute nothing.

$$\therefore H_{44} = H_{41} = -4A_6 \sin \eta \sin J$$

Similarly:-

$$H_{24} = H_{42} = 4A_6 \sin J \sin \xi$$

$$H_{34} = H_{43}$$



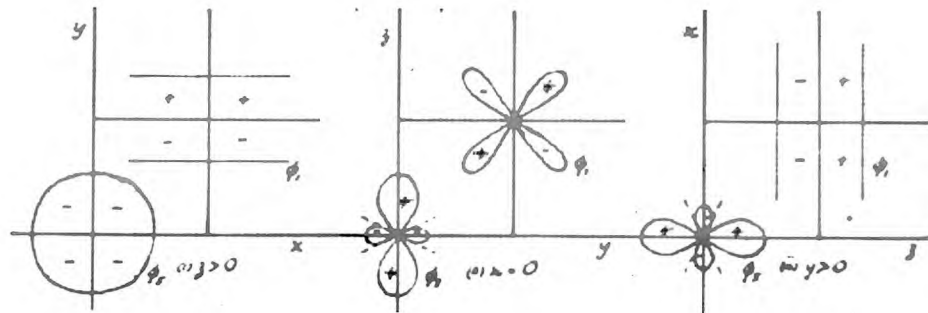
(i) $\phi_4(\underline{r})$ is antisymmetrical about $x=y$, whereas $\phi_1(\underline{r}-a\underline{\ell})$, where $\underline{\ell}=(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$, is symmetrical and hence the atoms at $\underline{\ell}=(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$ contribute nothing.

(ii) $\phi_4(\underline{r})$ does not change sign with x , whereas $\phi_1(\underline{r}-a\underline{\ell})$, where $\underline{\ell}=(0, \pm\frac{1}{2}, \pm\frac{1}{2})$, does and hence these atoms contribute nothing.

(iii) Similarly the atoms at $\underline{\ell}=(0, \pm\frac{1}{2}, \pm\frac{1}{2})$ contribute nothing.

$$\therefore H_{34} = H_{43} = 0$$

H₅=H₅₇



(i) $\phi_5(\underline{r})$ does not change sign with z but $\phi_1(\underline{r}-a\underline{l})$, where $\underline{l}=(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$, does and hence these atoms contribute nothing.

(ii) Neither $\phi_5(\underline{r})$ nor $\phi_1(\underline{r}-a\underline{l})$, where $\underline{l}=(0, \pm\frac{1}{2}, \pm\frac{1}{2})$, changes sign with x and hence these atoms contribute:-

$$4A_{10} \sin \eta \sin \zeta$$

where:-

$$A_{10} = - \int \phi_1^* (V-U) \phi_5 d\tau$$

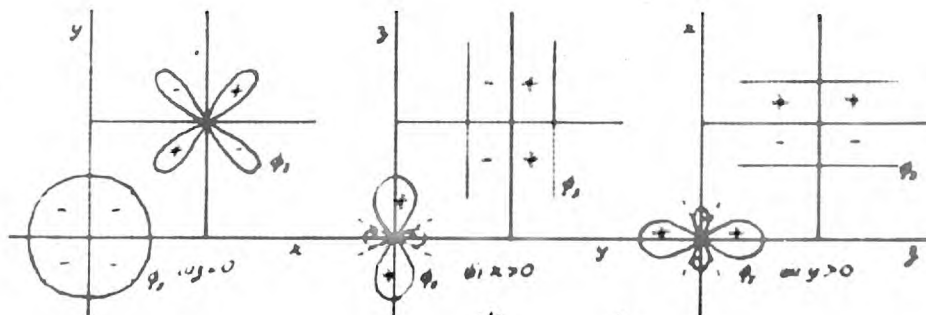
(iii) $\phi_5(\underline{r})$ does not change sign with y but $\phi_1(\underline{r}-a\underline{l})$, where $\underline{l}=(\pm\frac{1}{2}, 0, \pm\frac{1}{2})$, does and hence these atoms contribute nothing.

$$\therefore H_{15} = H_{51} = 4A_{10} \sin \eta \sin \zeta$$

Similarly:-

$$H_{25} = H_{52} = 4A_{10} \sin \zeta \sin \eta$$

H₅=H₅₇



(i) Neither $\phi_5(\underline{r})$ nor $\phi_3(\underline{r}-a\underline{l})$, where $\underline{l}=(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$, changes sign with z and hence these atoms contribute:-

$$-4A_{11} \sin \zeta \sin \eta$$

where:-

$$A_{11} = \int_{x,y} \phi_3^* (V-U) \phi_5 d\tau$$

(11) $\phi_3(\underline{r})$ does not change sign with x but $\phi_3(\underline{r}-a\hat{e})$, where

$\underline{e} = (0, \pm \frac{1}{2}, \pm \frac{1}{2})$, does and hence these atoms contribute nothing.

(111) Similarly the atoms at $\underline{e} = (\pm \frac{1}{2}, 0, \pm \frac{1}{2})$ contribute nothing.

$$\therefore H_{15} = H_{53} = -4A_{11} \sin \xi \sin \eta$$

It will now be shown that of the eleven coefficients A_i so defined only six are independent. For convenience let:-

$$\phi_6 = \sqrt{\frac{15}{16\pi}} \frac{y^2 - z^2}{r^2} f(r)$$

Then:-

$$\phi_5 = \frac{1}{\sqrt{3}} \sqrt{\frac{15}{16\pi}} \left[\frac{2z^2 - x^2 - y^2}{r^2} \right] f(r) = \frac{1}{\sqrt{3}} (-2\phi_6 - \phi_u)$$

Then:-

$$A_7 = - \int_{x,y} \phi_5^* (V-U) \phi_5 d\tau = - \frac{1}{3} \int_{x,y} (2\phi_6 + \phi_u)^* (V-U) (2\phi_6 + \phi_u) d\tau$$

$$= - \frac{1}{3} \left\{ 4 \int_{x,y} \phi_6^* (V-U) \phi_6 d\tau + 4 \int_{x,y} \phi_6^* (V-U) \phi_u d\tau + \int_{x,y} \phi_u^* (V-U) \phi_u d\tau \right\}$$

By cyclic permutation of x, y and z :-

$$\int_{x,y} \phi_6^* (V-U) \phi_6 d\tau = \int_{x,z} \phi_u^* (V-U) \phi_u d\tau = -A_5$$

Also:-

$$\int_{x,y} \phi_6^* (V-U) \phi_u d\tau = - \frac{1}{2} \int_{x,y} (\sqrt{3}\phi_5 + \phi_u)^* (V-U) \phi_u d\tau = 0 - \frac{1}{2} A_u$$

$$\therefore A_7 = - \frac{1}{3} (-4A_5 - 2A_u + A_u) = \frac{1}{3} (4A_5 + A_u)$$

$$A_8 = \int_{y,z} \phi_5^* (V-U) \phi_5 d\tau = \frac{1}{3} \left\{ 4 \int_{y,z} \phi_6^* (V-U) \phi_6 d\tau + 4 \int_{y,z} \phi_6^* (V-U) \phi_u d\tau + \int_{y,z} \phi_u^* (V-U) \phi_u d\tau \right\}$$

But:-

$$\int_{y,z} \phi_6^* (V-U) \phi_6 d\tau = \int_{x,y} \phi_u^* (V-U) \phi_u d\tau = A_u$$

and:-

$$\int_{y,z} \phi_6^* (V-U) \phi_u d\tau = \int_{x,y} \phi_6^* (V-U) \phi_u d\tau = -\frac{1}{2} A_u$$

as can be seen from diagrams of the type already used.

$$\therefore A_8 = \frac{1}{3} (4A_u - 2A_u - A_u) = \frac{1}{3} (2A_u - A_u)$$

$$A_9 = \int_{y,z} \phi_u^* (V-U) \phi_5 d\tau = \frac{2}{\sqrt{3}} \int_{y,z} \phi_u^* (V-U) \phi_6 d\tau = \frac{1}{\sqrt{3}} \int_{y,z} \phi_u^* (V-U) \phi_u d\tau$$

$$= \frac{1}{\sqrt{3}} (A_u + A_u)$$

$$A_{10} = - \int_{y,z} \phi_1^* (V-U) \phi_5 d\tau = \frac{1}{\sqrt{3}} \left[2 \int_{y,z} \phi_1^* (V-U) \phi_6 d\tau + \int_{y,z} \phi_1^* (V-U) \phi_u d\tau \right]$$

$$= \frac{1}{\sqrt{3}} \left[2 \int_{x,y} \phi_3^* (V-U) \phi_u d\tau + \int_{y,z} \phi_1^* (V-U) \phi_u d\tau \right]$$

$$= \frac{1}{\sqrt{3}} (0 + A_6) = \frac{1}{\sqrt{3}} A_6$$

$$A_{11} = \int_{x,y} \phi_5^* (V-U) \phi_5 d\tau = \frac{1}{\sqrt{3}} \left[2 \int_{x,y} \phi_3^* (V-U) \phi_6 d\tau + \int_{x,y} \phi_3^* (V-U) \phi_u d\tau \right]$$

$$= \frac{1}{\sqrt{3}} \left[2 \int_{x,z} \phi_1^* (V-U) \phi_u d\tau + \int_{y,z} \phi_3^* (V-U) \phi_u d\tau \right]$$

$$= \frac{1}{\sqrt{3}} [-2A_6 + 0] = -\frac{2}{\sqrt{3}} A_6$$

Summarizing:-

$$H_{11} = -4A_1 \cos \eta \cos \xi + 4A_2 (\cos \xi \cos \xi + \cos \xi \cos \eta) + E_0 + C$$

$$H_{12} = -4A_1 \cos \xi \cos \xi + 4A_2 (\cos \xi \cos \eta + \cos \eta \cos \xi) + E_0 + C$$

$$H_{13} = -4A_1 \cos \xi \cos \eta + 4A_2 (\cos \eta \cos \xi + \cos \xi \cos \xi) + E_0 + C$$

$$H_{44} = 4A_4 \cos \xi \cos \eta - 4A_5 (\cos \eta \cos \xi + \cos \xi \cos \xi) + E_0 + C$$

$$H_{55} = -\frac{4}{3}(A_4 + 4A_5) \cos \xi \cos \eta + \frac{4}{3}(2A_4 - A_5)(\cos \eta \cos \xi + \cos \xi \cos \xi) + E_0 + C$$

$$H_{12} = H_{21} = -4A_3 \sin \xi \sin \eta; H_{23} = H_{32} = -4A_3 \sin \eta \sin \xi; H_{31} = H_{13} = -4A_3 \sin \xi \sin \xi$$

$$H_{14} = H_{41} = -4A_6 \sin \eta \sin \xi; H_{44} = H_{44} = 4A_6 \sin \xi \sin \xi; H_{14} = H_{41} = 0$$

$$H_{15} = H_{51} = \frac{4}{\sqrt{3}} A_6 \sin \eta \sin \xi; H_{25} = H_{52} = \frac{4}{\sqrt{3}} A_6 \sin \xi \sin \xi; H_{35} = H_{53} = -\frac{8}{\sqrt{3}} A_6 \sin \xi \sin \eta$$

$$H_{45} = H_{54} = \frac{4}{\sqrt{3}} (A_4 + A_5)(\cos \eta \cos \xi - \cos \xi \cos \xi)$$

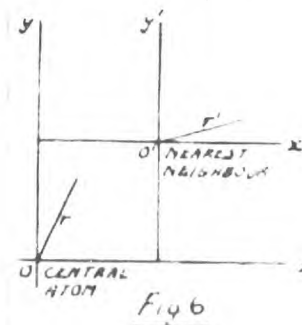
The above give explicit expressions for the variable parts of the matrix elements H_{nm} in the secular equation $|H_{nm} - E \delta_{nm}| = 0$ in terms of the three coordinates of $\underline{k}$ -space (related to ξ, η, ζ by $k_x = \frac{2}{a}\xi; k_y = \frac{2}{a}\eta; k_z = \frac{2}{a}\zeta$) and of the six coefficients A_i , involving the atomic wave functions and potential, which will be considered next.

(b) Radial Parts of the wave functions and Potential.

In order to calculate the numerical values of the coefficients A_i , some assumption must be made regarding the radial wave function and the potential $V-U$. The forms of V and U have been indicated in Fig. 5. V should have the symmetry of the lattice, becoming infinite at each ion, but no such function has as yet been constructed and the usual assumption was made that $V=U$ within the atomic polyhedron of the central atom and $V-U=V$ elsewhere, since U is small outside the polyhedron. For ease of computation an approximation was made to the polyhedron by assuming it to be spherical and of diameter equal to the

distance between nearest neighbours. As an approximation to V outside this sphere it was decided to use an atomic potential centred about the nearest neighbour (n.n.) since this should be fairly accurate in the regions of importance, i.e. where the product of the two wave functions is relatively large. Unfortunately the wave function and potential for Ni, which is the metal to which particular application is to be made, have not been calculated and it was felt that the best figures to use were those for Cu^+ with exchange (Hartree and Hartree 1936), since this ion contains the same number of electrons as the Ni atom. In order to avoid double numerical integration an attempt was made to fit Hartree's figures for $P=rf(r)$ and $E_p=rV$ as closely as possible by explicit algebraic expressions containing exponentials.

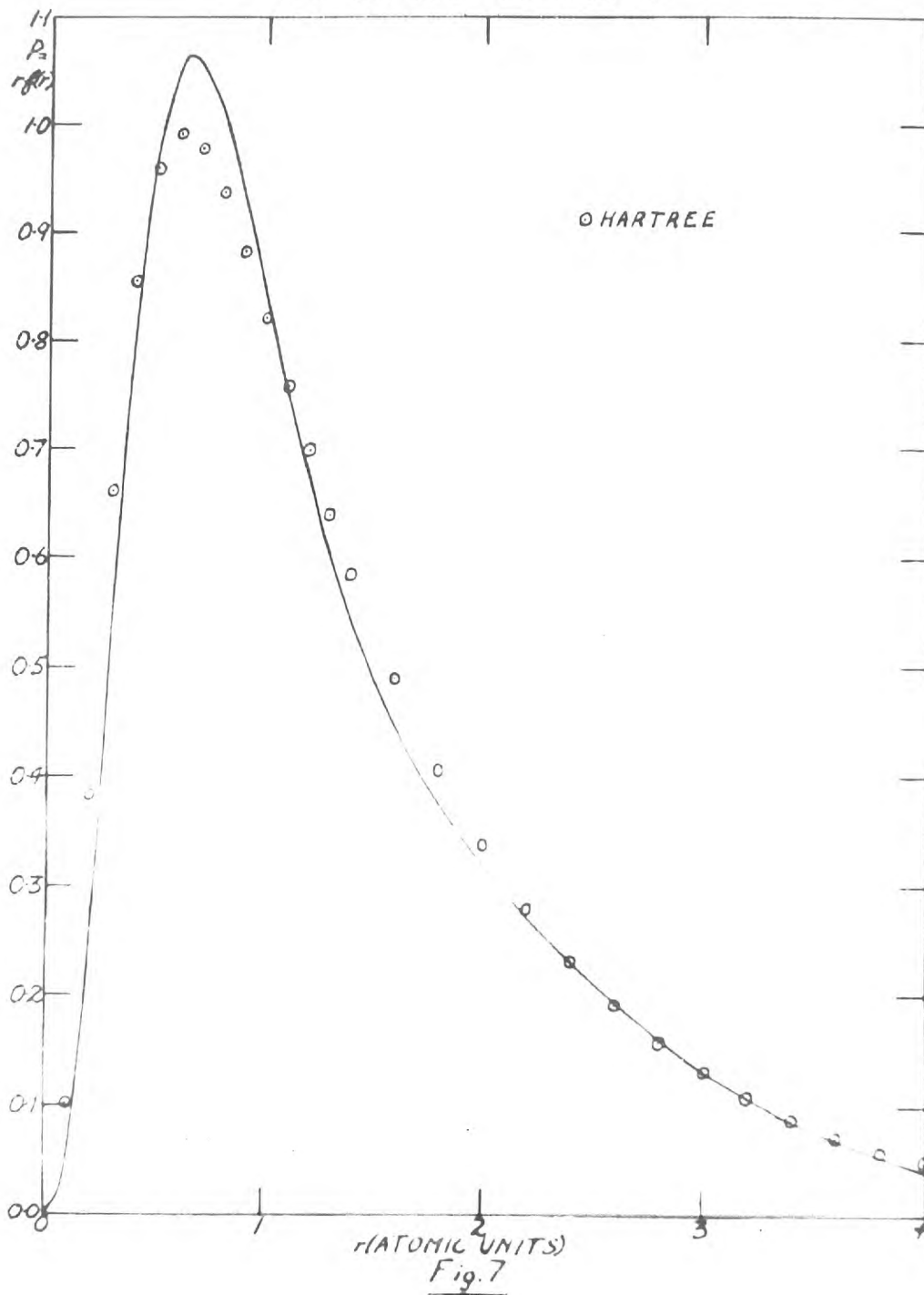
In investigating the accuracy of fit required it was calculated that the contribution to A , from a sphere centred the n.n. O' (see Fig. 6), radius $\sim \frac{2}{5}A$, where $OO' = 2A$, was only about 1% due mainly to the nodal characteristics of



ϕ' (primed symbols refer to O'), so that only a good fit to $f(r')$ and $V(r')$ for $r' > \frac{2}{5}A$ seemed necessary. The same fit should certainly be valid for $f(r)$ since it is assumed that $V-U=0$ for $r < A$ anyway. Under these assumptions the following fairly simple expressions were obtained and are shown in Figs. 7 and 8 compared with Hartree's figures:-

$$f(r') = 85.88r'^4 e^{-5r'} + 1.979r'^2 e^{-2r'}$$

RADIAL WAVE-FUNCTION USED FOR CALCULATING A_{∞}
 $P = r^3(85.88e^{-5r} + 1.979e^{-2r})$



POTENTIAL FUNCTION USED FOR CALCULATING A:

$$-rV = 1 + 28e^{-2r}$$

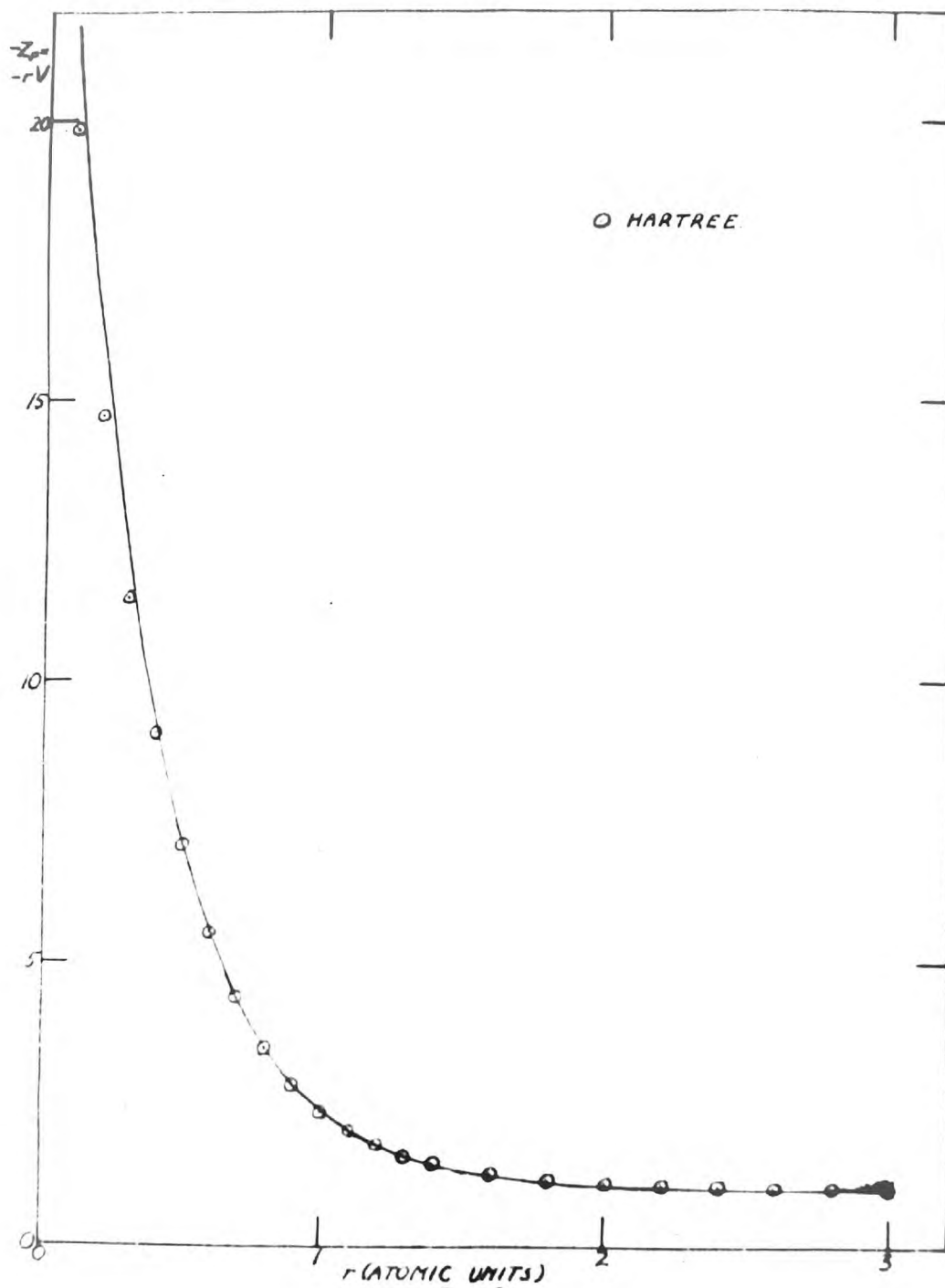


Fig 8

$$V(r') = -\frac{1}{r'} (1 + 28e^{-3r'}) \quad 4.2$$

V being in atomic units. It has been assumed in the previous theory that $f(r)$ is normalized to unity, whereas it can easily be shown that the expression 4.1 is not. Hartree's figures, however, are correctly normalized and 4.1 fits these figures closely over the range, which is regarded as important, which justifies the use of this expression, since the discrepancy over the range $0 < r \leq \frac{2}{3}A$ is virtually being ignored.

Investigations of the range of integration showed that the most accurate of the simple possibilities was integration over all space less the atomic sphere of 0 (written a.s.-at.s.). Within this range $85.88r^2 e^{-5r}$ is comparatively very small and was neglected so that:-

$$f(r) = 1.979r^2 e^{-2r} \quad 4.3$$

was assumed. Finally for the integration over at.s. both $85.88r^2 e^{-5r}$ and $\frac{28e^{-3r}}{r}$ are small and were neglected so that for these integrals it was assumed that:-

$$f(r) = 1.979r^2 e^{-2r}; f(r') = 1.979r'^2 e^{-2r'}; V(r') = -\frac{1}{r'}$$

Note that, although $85.88r^2 e^{-5r}$ is not small within at.s., this term has been neglected in calculating the integral over a.s. and must therefore be neglected in calculating the integral over at.s. Thus 3 r instances:-

$$A_1 = K \iiint_{a.s.} xy (1.979e^{-2r}) x'y' (85.88e^{-5r'} + 1.979e^{-2r'}) \frac{(1 + 28e^{-3r'})}{r'} d\tau$$

$$- K \iiint_{at.s.} xy (1.979e^{-2r}) x'y' (1.979e^{-2r'}) \frac{1}{r'} d\tau$$

(c) Integrations.

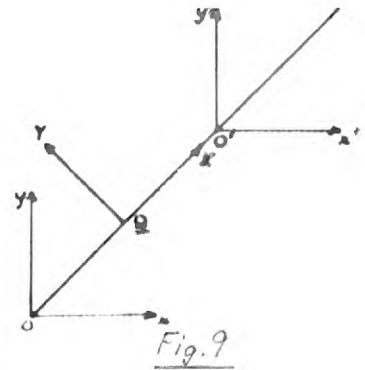
It was decided that the simplest coordinates to use for this purpose were prolate spheroidal with 0,0' as foci. The trans-

formation was made in two steps.

Consider the case shown in Fig. 9;

then it is easily shown that:-

$$\begin{aligned} y &= \frac{1}{\sqrt{2}} (Y-Z+A) & y' &= \frac{1}{\sqrt{2}} (Y-Z-A) \\ z &= \frac{1}{\sqrt{2}} (Y+Z+A) & z' &= \frac{1}{\sqrt{2}} (Y+Z-A) \\ x &= X & x' &= X \end{aligned}$$



The transformation to prolate

spheroidal coordinates is a

standard one (Margenau and Murphy 1943):-

$Y = A\mu$; $Z = A\sqrt{(A^2-1)(1-\mu^2)} \sin \phi$; $X = A\sqrt{(A^2-1)(1-\mu^2)} \cos \phi$
and it can also be shown that:-

$$\begin{aligned} r+r' &= 2A & \text{and} & & |r-r'| &= 2A\mu \\ r &= A(1+\mu) & \text{and} & & r' &= A(1-\mu) \quad (\text{since } \mu \leq 1 \text{ always}). \end{aligned}$$

Also:- $d\tau = dX dY dZ = A^3 (1-\mu^2) d\mu d\phi$

The limits of integration are as follows.

All space:- $1 \leq A \leq \infty$; $-1 \leq \mu \leq 1$; $0 \leq \phi \leq 2\pi$

Atomic sphere, centre O:- $1 \leq A \leq 2$; $-1 \leq \mu \leq 1-A$; $0 \leq \phi \leq 2\pi$

The calculations for A, will be given in full while the first few steps only will be given in the other cases, since the method is similar for all of them.

A.2

$$\begin{aligned} yzy'z' &= \frac{1}{4} (Y+Z+A)(Y+Z-A)(Y-Z+A)(Y-Z-A) \\ &= \frac{1}{4} [(Y+Z)^2 - A^2][(Y-Z)^2 - A^2] = \frac{1}{4} [(Y^2+Z^2)^2 - 2(Y^2+Z^2)A^2 + A^4] \\ Y^2+Z^2 &= A^2 [A^2\mu^2 + (A^2-1)(1-\mu^2)\sin^2 \phi] \\ Y^2-Z^2 &= A^2 [A^2\mu^2 - (A^2-1)(1-\mu^2)\sin^2 \phi] \end{aligned}$$

Then:- $A_1^{(0)} = \int_{\text{a.s.}} yze^{-x_0 r} y'z'e^{-x_0 r'} \frac{1}{r} d\tau$

$$\begin{aligned} &= \int_0^{2\pi} \int_{-1}^1 \int_{-A}^{\infty} \frac{A^4}{4} \left\{ [A^2\mu^2 - (A^2-1)(1-\mu^2)\sin^2 \phi]^2 - 2[A^2\mu^2 + (A^2-1)(1-\mu^2)\sin^2 \phi] + 1 \right\} \\ &\quad \times e^{-x_0 - 2A\mu} \frac{1}{A(1-\mu)} A^3 (1-\mu^2) d\mu d\phi \end{aligned}$$

$$\therefore A_1^{(0)} = \frac{A^6}{4} \int_0^{2\pi} \int_{-1}^1 \int_0^{\infty} (1+\mu) \left\{ (A^4 \mu^4 - 2A^2 \mu^2 + 1) + 2(A^4 \mu^4 - A^2 \mu^2 - A^2 \mu^4 + 2A^2 \mu^2 - A^2 \mu^2 + 1) \sin^2 \phi \right. \\ \left. + (A^4 \mu^4 - 2A^2 \mu^2 + A^2 - 2A^2 \mu^4 + 4A^2 \mu^2 - 2A^2 \mu^2 + 1) \sin^4 \phi \right\} e^{-\alpha \mu} d\mu d\phi$$

where:-

$$\alpha = 2A x_0$$

Now:- $\int_0^{2\pi} d\phi = 2\pi$; $\int_0^{2\pi} \sin^2 \phi d\phi = \pi$; $\int_0^{2\pi} \sin^4 \phi d\phi = \frac{3\pi}{4}$

$$\therefore A_1^{(0)} = \frac{\pi A^6}{4} \int_0^{\infty} (1+\mu) \left\{ A^4 \left(\frac{19}{4} \mu^4 - \frac{7}{2} \mu^2 + \frac{3}{4} \right) + A^2 \left(-\frac{7}{2} \mu^4 + 3\mu^2 - \frac{7}{2} \right) + \left(\frac{3}{4} \mu^4 - 2\mu^2 + \frac{19}{4} \right) \right\} e^{-\alpha \mu} d\mu \quad 4.4$$

$$= \frac{\pi A^6}{4} \cdot 2 \int_0^{\infty} \left\{ A^4 \left(\frac{19}{20} - \frac{7}{6} + \frac{3}{4} \right) + A^2 \left(-\frac{7}{10} + 1 - \frac{7}{2} \right) + A \left(\frac{3}{20} - \frac{7}{6} + \frac{19}{4} \right) \right\} e^{-\alpha \mu} d\mu$$

$$= \frac{\pi A^6}{2} \left\{ \frac{8}{15} \left(\frac{1}{\alpha} + \frac{5}{\alpha^2} + \frac{20}{\alpha^3} + \frac{60}{\alpha^4} + \frac{120}{\alpha^5} + \frac{120}{\alpha^6} \right) - \frac{16}{5} \left(\frac{1}{\alpha} + \frac{7}{\alpha^2} + \frac{6}{\alpha^3} + \frac{6}{\alpha^4} \right) + \frac{52}{15} \left(\frac{1}{\alpha} + \frac{1}{\alpha^2} \right) \right\} e^{-\alpha}$$

$$= \frac{8\pi A^6}{15} \left(\frac{1}{\alpha} - \frac{3}{\alpha^2} - \frac{8}{\alpha^3} + \frac{12}{\alpha^4} + \frac{60}{\alpha^5} + \frac{60}{\alpha^6} \right) e^{-\alpha}$$

$$A_1^{(1)} = \int_0^{2\pi} \int_{-1}^1 \int_0^{\infty} y z e^{-\alpha_0 r} y' z' e^{-\alpha_0 r'} \frac{e^{-\beta_0 r}}{r'} d\tau$$

$$= \int_0^{2\pi} \int_{-1}^1 \int_0^{\infty} \frac{A^6}{4} \left\{ [A^4 \mu^4 - (A^2 - 1)(1 - \mu^2) \sin^2 \phi]^2 - 2[A^4 \mu^4 - (A^2 - 1)(1 - \mu^2) \sin^2 \phi] + 1 \right\} \\ \times e^{-\alpha_0 - 2A\mu} \frac{e^{-\beta_0 A(1-\mu)}}{A(1-\mu)} A^2 (1 - \mu^2) d\mu d\phi$$

$$= \frac{A^6}{4} \int_0^{2\pi} \int_{-1}^1 \int_0^{\infty} (1+\mu) \left\{ (A^4 \mu^4 - 2A^2 \mu^2 + 1) + 2[A^4 \mu^4 - \mu^2] + A^2 (-\mu^4 + 2\mu^2 - 1) + (-\mu^2 + 1) \right\} \sin^2 \phi e^{-\beta \mu} e^{\gamma \mu} \\ \times [A^4 (\mu^4 - 2\mu^2 + 1) + A^2 (-2\mu^2 + 4\mu^2 - 2) + (\mu^4 - 2\mu^2 + 1)] \sin^4 \phi d\mu d\phi$$

where $\gamma = A\alpha_0$ and $\beta = 2A\alpha_0 + A\beta_0$

Using 4.4 above:-

$$A_1^{(1)} = \frac{\pi A^6}{4} \cdot 2 \int_0^{\infty} \left\{ A^4 \left[\frac{19}{4} \left(\frac{1}{\gamma} + \frac{12}{\gamma^2} + \frac{24}{\gamma^3} \right) \sinh \gamma - \frac{19}{4} \left(\frac{4}{\gamma^2} + \frac{24}{\gamma^3} \right) \cosh \gamma - \frac{7}{2} \left(\frac{1}{\gamma} + \frac{2}{\gamma^2} \right) \sinh \gamma \right. \right. \\ \left. \left. + \frac{7}{2} \cdot \frac{2}{\gamma} \cosh \gamma + \frac{3}{4} \cdot \frac{1}{\gamma} \sinh \gamma \right] \right. \\ \left. + A^2 \left[\frac{19}{4} \left(\frac{1}{\gamma} + \frac{20}{\gamma^2} + \frac{120}{\gamma^3} \right) \cosh \gamma - \frac{19}{4} \left(\frac{5}{\gamma^2} + \frac{60}{\gamma^3} + \frac{120}{\gamma^4} \right) \sinh \gamma - \frac{7}{2} \left(\frac{1}{\gamma} + \frac{6}{\gamma^2} \right) \cosh \gamma \right. \right. \\ \left. \left. + \frac{7}{2} \left(\frac{3}{\gamma^2} + \frac{6}{\gamma^3} \right) \sinh \gamma + \frac{3}{4} \cdot \frac{1}{\gamma} \cosh \gamma - \frac{3}{4} \cdot \frac{1}{\gamma^2} \sinh \gamma \right] \right. \\ \left. + A^2 \left[-\frac{7}{2} \left(\frac{1}{\gamma} + \frac{12}{\gamma^2} + \frac{24}{\gamma^3} \right) \sinh \gamma + \frac{7}{2} \left(\frac{4}{\gamma^2} + \frac{24}{\gamma^3} \right) \cosh \gamma + 3 \left(\frac{1}{\gamma} + \frac{2}{\gamma^2} \right) \sinh \gamma \right. \right. \\ \left. \left. - 3 \cdot \frac{2}{\gamma} \cosh \gamma - \frac{7}{2} \cdot \frac{1}{\gamma} \sinh \gamma \right] \right. \\ \left. + A^2 \left[-\frac{7}{2} \left(\frac{1}{\gamma} + \frac{20}{\gamma^2} + \frac{120}{\gamma^3} \right) \cosh \gamma + \frac{7}{2} \left(\frac{5}{\gamma^2} + \frac{60}{\gamma^3} + \frac{120}{\gamma^4} \right) \sinh \gamma + 3 \left(\frac{1}{\gamma} + \frac{6}{\gamma^2} \right) \cosh \gamma \right. \right. \\ \left. \left. - 3 \left(\frac{3}{\gamma^2} + \frac{6}{\gamma^3} \right) \sinh \gamma - \frac{7}{2} \cdot \frac{1}{\gamma} \cosh \gamma + \frac{7}{2} \cdot \frac{1}{\gamma^2} \sinh \gamma \right] \right. \\ \left. + A \left[\frac{3}{4} \left(\frac{1}{\gamma} + \frac{12}{\gamma^2} + \frac{24}{\gamma^3} \right) \sinh \gamma - \frac{3}{4} \left(\frac{4}{\gamma^2} + \frac{24}{\gamma^3} \right) \cosh \gamma - \frac{7}{2} \left(\frac{1}{\gamma} + \frac{2}{\gamma^2} \right) \sinh \gamma \right. \right. \\ \left. \left. + \frac{7}{2} \cdot \frac{2}{\gamma} \cosh \gamma + \frac{19}{4} \cdot \frac{1}{\gamma} \sinh \gamma \right] \right. \\ \left. + \left[\frac{3}{4} \left(\frac{1}{\gamma} + \frac{20}{\gamma^2} + \frac{120}{\gamma^3} \right) \cosh \gamma - \frac{3}{4} \left(\frac{5}{\gamma^2} + \frac{60}{\gamma^3} + \frac{120}{\gamma^4} \right) \sinh \gamma - \frac{7}{2} \left(\frac{1}{\gamma} + \frac{6}{\gamma^2} \right) \cosh \gamma \right. \right. \\ \left. \left. + \frac{7}{2} \left(\frac{3}{\gamma^2} + \frac{6}{\gamma^3} \right) \sinh \gamma + \frac{19}{4} \cdot \frac{1}{\gamma} \cosh \gamma - \frac{19}{4} \cdot \frac{1}{\gamma^2} \sinh \gamma \right] \right\} e^{-\beta \mu} d\mu$$

$$\begin{aligned}
 \therefore A_1^{(6)} &= \frac{\pi A^6}{2} \left\{ \left[\left(\frac{2}{\gamma} + \frac{50}{\gamma^3} + \frac{116}{\gamma^5} \right) \sinh \gamma + \left(\frac{-12}{\gamma^2} - \frac{116}{\gamma^4} \right) \cosh \gamma \right] \left(\frac{1}{\beta} + \frac{5}{\beta^3} + \frac{20}{\beta^5} + \frac{60}{\beta^7} + \frac{120}{\beta^9} + \frac{120}{\beta^{11}} \right) \right. \\
 &\quad + \left[\left(\frac{-16}{\gamma^2} - \frac{264}{\gamma^4} - \frac{570}{\gamma^6} \right) \sinh \gamma + \left(\frac{2}{\gamma} + \frac{74}{\gamma^3} + \frac{570}{\gamma^5} \right) \cosh \gamma \right] \left(\frac{1}{\beta^3} + \frac{4}{\beta^5} + \frac{12}{\beta^7} + \frac{24}{\beta^9} + \frac{24}{\beta^{11}} \right) \\
 &\quad + \left[\left(\frac{-4}{\gamma} - \frac{36}{\gamma^3} - \frac{84}{\gamma^5} \right) \sinh \gamma + \left(\frac{8}{\gamma^2} + \frac{84}{\gamma^4} \right) \cosh \gamma \right] \left(\frac{1}{\beta^5} + \frac{3}{\beta^7} + \frac{6}{\beta^9} + \frac{6}{\beta^{11}} \right) \\
 &\quad + \left[\left(\frac{12}{\gamma^2} + \frac{192}{\gamma^4} + \frac{420}{\gamma^6} \right) \sinh \gamma + \left(\frac{-4}{\gamma} - \frac{52}{\gamma^3} - \frac{420}{\gamma^5} \right) \cosh \gamma \right] \left(\frac{1}{\beta^7} + \frac{2}{\beta^9} + \frac{2}{\beta^{11}} \right) \\
 &\quad + \left[\left(\frac{2}{\gamma} + \frac{2}{\gamma^3} + \frac{18}{\gamma^5} \right) \sinh \gamma + \left(\frac{4}{\gamma^2} - \frac{18}{\gamma^4} \right) \cosh \gamma \right] \left(\frac{1}{\beta^9} + \frac{1}{\beta^{11}} \right) \\
 &\quad \left. + \left[\left(\frac{2}{\gamma^2} - \frac{24}{\gamma^4} - \frac{90}{\gamma^6} \right) \sinh \gamma + \left(\frac{2}{\gamma} - \frac{6}{\gamma^3} + \frac{90}{\gamma^5} \right) \cosh \gamma \right] \frac{1}{\beta^{11}} \right\} e^{-\beta} \\
 &= \frac{\pi A^6}{2} \left\{ \left[\left(\frac{16}{\gamma^2} - \frac{96}{\gamma^4} + \frac{48}{\gamma^6} - \frac{240}{\gamma^8} \right) \sinh \gamma + \left(\frac{16}{\gamma^3} - \frac{48}{\gamma^5} + \frac{240}{\gamma^7} \right) \cosh \gamma \right] \frac{1}{\beta} \right. \\
 &\quad + \left[\left(\frac{-32}{\gamma^4} + \frac{144}{\gamma^6} - \frac{672}{\gamma^8} + \frac{336}{\gamma^{10}} - \frac{1440}{\gamma^{12}} \right) \sinh \gamma + \left(\frac{-32}{\gamma^5} + \frac{192}{\gamma^7} - \frac{336}{\gamma^9} + \frac{1440}{\gamma^{11}} \right) \cosh \gamma \right] \frac{1}{\beta^3} \\
 &\quad + \left[\left(\frac{16}{\gamma^5} - \frac{144}{\gamma^7} + \frac{784}{\gamma^9} - \frac{2784}{\gamma^{11}} + \frac{1776}{\gamma^{13}} - \frac{6000}{\gamma^{15}} \right) \sinh \gamma + \left(\frac{16}{\gamma^6} - \frac{192}{\gamma^8} + \frac{784}{\gamma^{10}} - \frac{1776}{\gamma^{12}} + \frac{6000}{\gamma^{14}} \right) \cosh \gamma \right] \frac{1}{\beta^5} \\
 &\quad + \left[\left(\frac{96}{\gamma^7} - \frac{336}{\gamma^9} + \frac{2784}{\gamma^{11}} - \frac{6336}{\gamma^{13}} + \frac{6336}{\gamma^{15}} - \frac{13680}{\gamma^{17}} \right) \sinh \gamma + \left(\frac{48}{\gamma^8} - \frac{672}{\gamma^{10}} + \frac{1776}{\gamma^{12}} - \frac{6336}{\gamma^{14}} + \frac{13680}{\gamma^{16}} \right) \cosh \gamma \right] \frac{1}{\beta^7} \\
 &\quad + \left[\left(\frac{240}{\gamma^9} - \frac{336}{\gamma^{11}} + \frac{6000}{\gamma^{13}} - \frac{6336}{\gamma^{15}} + \frac{13680}{\gamma^{17}} - \frac{12660}{\gamma^{19}} \right) \sinh \gamma + \left(\frac{48}{\gamma^{10}} - \frac{1440}{\gamma^{12}} + \frac{1776}{\gamma^{14}} - \frac{13680}{\gamma^{16}} + \frac{12660}{\gamma^{18}} \right) \cosh \gamma \right] \frac{1}{\beta^9} \\
 &\quad \left. + \left[\left(\frac{240}{\gamma^{11}} + \frac{6000}{\gamma^{13}} + \frac{13680}{\gamma^{15}} \right) \sinh \gamma + \left(\frac{-1440}{\gamma^{12}} - \frac{13680}{\gamma^{14}} \right) \cosh \gamma \right] \frac{1}{\beta^{11}} \right\} e^{-\beta}
 \end{aligned}$$

$$\begin{aligned}
 A_1^{(6)} &= \int_{-\infty}^{\infty} y \delta e^{-x_0 r} y' \delta' e^{-x_0 r'} \frac{1}{r'} dr \\
 &= \frac{\pi A^6}{4} \int_{-1}^1 \int_{-1}^1 (1+\mu) \left\{ A^4 \left(\frac{19}{4} \mu^4 - \frac{7}{2} \mu^2 + \frac{3}{4} \right) + A^4 \left(-\frac{7}{2} \mu^4 + \frac{3}{2} \mu^2 - \frac{7}{4} \right) + \left(\frac{3}{4} \mu^4 - \frac{7}{2} \mu^2 + \frac{19}{4} \right) \right\} e^{-x\mu} d\mu \\
 &= \frac{\pi A^6}{4} \int_{-1}^1 \left\{ A^5 \left[\frac{19}{20} (2-5A+10A^2-10A^3+5A^4-A^5) - \frac{7}{6} (2-3A+3A^2-A^3) + \frac{3}{2} (2-A) \right] \right. \\
 &\quad + A^4 \left[\frac{19}{20} (-6A+15A^2-20A^3+15A^4-6A^5+A^6) - \frac{7}{6} (-4A+6A^2-4A^3+A^4) + \frac{1}{2} (-2A+A^2) \right] \\
 &\quad + A^3 \left[-\frac{7}{10} (2-5A+10A^2-10A^3+5A^4-A^5) + (2-3A+3A^2-A^3) - \frac{7}{2} (2-A) \right] \\
 &\quad + A^2 \left[-\frac{7}{12} (-6A+15A^2-20A^3+15A^4-6A^5+A^6) + \frac{7}{4} (-4A+6A^2-4A^3+A^4) - \frac{7}{6} (-2A+A^2) \right] \\
 &\quad + A \left[\frac{3}{20} (2-5A+10A^2-10A^3+5A^4-A^5) - \frac{7}{6} (2-3A+3A^2-A^3) + \frac{19}{4} (2-A) \right] \\
 &\quad \left. + \left[\frac{1}{8} (-6A+15A^2-20A^3+15A^4-6A^5+A^6) - \frac{7}{8} (-4A+6A^2-4A^3+A^4) + \frac{19}{8} (-2A+A^2) \right] \right\} \\
 &\quad \times e^{-x\mu} d\mu \\
 &= \frac{\pi A^6}{4} \int_{-1}^1 \left\{ A^5 \left(\frac{16}{15} - 2A + 6A^2 - \frac{25}{3} A^3 + \frac{19}{4} A^4 - \frac{19}{20} A^5 \right) + A^4 \left(-2A + 7A^2 - \frac{17}{3} A^3 + 11A^4 - \frac{19}{4} A^5 + \frac{19}{20} A^6 \right) \right. \\
 &\quad + A^3 \left(-\frac{12}{5} + 4A - 4A^2 + 6A^3 - \frac{7}{2} A^4 + \frac{7}{10} A^5 \right) + A^2 \left(4A - 6A^2 + \frac{25}{3} A^3 - 8A^4 + \frac{7}{2} A^5 - \frac{3}{12} A^6 \right) \\
 &\quad \left. + A \left(\frac{112}{15} - 2A - 2A^2 - \frac{1}{5} A^3 + \frac{1}{4} A^4 - \frac{3}{20} A^5 \right) + \left(-2A - A^2 + A^3 + A^4 - \frac{3}{4} A^5 + \frac{1}{8} A^6 \right) \right\} e^{-x\mu} d\mu
 \end{aligned}$$

$$\begin{aligned}
 A_1^{(1)} = & \frac{\pi A^6}{4} \left\{ \frac{86}{15} \left[\left(\frac{1}{\alpha} + \frac{1}{\alpha^2} \right) e^{-\alpha} - \left(\frac{2}{\alpha} + \frac{1}{\alpha^2} \right) e^{-2\alpha} \right] - 3 \left[\left(\frac{1}{\alpha} + \frac{2}{\alpha^2} + \frac{2}{\alpha^3} \right) e^{-\alpha} - \left(\frac{4}{\alpha} + \frac{4}{\alpha^2} + \frac{4}{\alpha^3} \right) e^{-2\alpha} \right] \right. \\
 & - \frac{12}{5} \left[\left(\frac{1}{\alpha} + \frac{1}{\alpha^2} + \frac{6}{\alpha^3} + \frac{1}{\alpha^4} \right) e^{-\alpha} - \left(\frac{8}{\alpha} + \frac{12}{\alpha^2} + \frac{12}{\alpha^3} + \frac{6}{\alpha^4} \right) e^{-2\alpha} \right] \\
 & - \frac{4}{3} \left[\left(\frac{1}{\alpha} + \frac{4}{\alpha^2} + \frac{12}{\alpha^3} + \frac{24}{\alpha^4} + \frac{24}{\alpha^5} \right) e^{-\alpha} - \left(\frac{16}{\alpha} + \frac{22}{\alpha^2} + \frac{48}{\alpha^3} + \frac{48}{\alpha^4} + \frac{24}{\alpha^5} \right) e^{-2\alpha} \right] \\
 & + \frac{56}{15} \left[\left(\frac{1}{\alpha} + \frac{5}{\alpha^2} + \frac{20}{\alpha^3} + \frac{30}{\alpha^4} + \frac{120}{\alpha^5} + \frac{120}{\alpha^6} \right) e^{-\alpha} - \left(\frac{32}{\alpha} + \frac{60}{\alpha^2} + \frac{160}{\alpha^3} + \frac{240}{\alpha^4} + \frac{240}{\alpha^5} + \frac{120}{\alpha^6} \right) e^{-2\alpha} \right] \\
 & + \frac{119}{40} \left[\left(\frac{1}{\alpha} + \frac{6}{\alpha^2} + \frac{30}{\alpha^3} + \frac{120}{\alpha^4} + \frac{360}{\alpha^5} + \frac{720}{\alpha^6} + \frac{720}{\alpha^7} \right) e^{-\alpha} - \left(\frac{64}{\alpha} + \frac{192}{\alpha^2} + \frac{480}{\alpha^3} + \frac{960}{\alpha^4} + \frac{1440}{\alpha^5} + \frac{1440}{\alpha^6} + \frac{720}{\alpha^7} \right) e^{-2\alpha} \right] \\
 & - \frac{19}{3} \left[\left(\frac{1}{\alpha} + \frac{7}{\alpha^2} + \frac{42}{\alpha^3} + \frac{210}{\alpha^4} + \frac{840}{\alpha^5} + \frac{2520}{\alpha^6} + \frac{5040}{\alpha^7} + \frac{5040}{\alpha^8} \right) e^{-\alpha} \right. \\
 & \quad \left. - \left(\frac{128}{\alpha} + \frac{448}{\alpha^2} + \frac{1744}{\alpha^3} + \frac{3360}{\alpha^4} + \frac{6720}{\alpha^5} + \frac{10080}{\alpha^6} + \frac{10080}{\alpha^7} + \frac{5040}{\alpha^8} \right) e^{-2\alpha} \right] \\
 & + \frac{167}{60} \left[\left(\frac{1}{\alpha} + \frac{8}{\alpha^2} + \frac{56}{\alpha^3} + \frac{336}{\alpha^4} + \frac{1680}{\alpha^5} + \frac{6720}{\alpha^6} + \frac{20160}{\alpha^7} + \frac{40320}{\alpha^8} + \frac{40320}{\alpha^9} \right) e^{-\alpha} \right. \\
 & \quad \left. - \left(\frac{256}{\alpha} + \frac{1024}{\alpha^2} + \frac{3554}{\alpha^3} + \frac{10752}{\alpha^4} + \frac{26880}{\alpha^5} + \frac{57760}{\alpha^6} + \frac{80640}{\alpha^7} + \frac{80640}{\alpha^8} + \frac{40320}{\alpha^9} \right) e^{-2\alpha} \right] \\
 & - \frac{19}{120} \left[\left(\frac{1}{\alpha} + \frac{10}{\alpha^2} + \frac{90}{\alpha^3} + \frac{720}{\alpha^4} + \frac{5040}{\alpha^5} + \frac{30240}{\alpha^6} + \frac{151200}{\alpha^7} + \frac{604800}{\alpha^8} + \frac{1814400}{\alpha^9} + \frac{3628800}{\alpha^{10}} + \frac{5618400}{\alpha^{11}} \right) e^{-\alpha} \right. \\
 & \quad \left. - \left(\frac{1024}{\alpha} + \frac{5120}{\alpha^2} + \frac{23040}{\alpha^3} + \frac{92160}{\alpha^4} + \frac{322560}{\alpha^5} + \frac{987680}{\alpha^6} + \frac{2417200}{\alpha^7} + \frac{4835400}{\alpha^8} + \frac{7257600}{\alpha^9} + \frac{7257600}{\alpha^{10}} + \frac{3628800}{\alpha^{11}} \right) e^{-2\alpha} \right] \\
 & = \frac{\pi A^6}{4} \left\{ \frac{11}{15\alpha} - \frac{16}{5\alpha^2} - \frac{41}{15\alpha^3} + \frac{99}{5\alpha^4} + \frac{45}{\alpha^5} + \frac{540}{\alpha^6} + \frac{2394}{\alpha^7} - \frac{13658}{\alpha^8} - \frac{175056}{\alpha^9} - \frac{574560}{\alpha^{10}} - \frac{574560}{\alpha^{11}} \right\} e^{-\alpha} \\
 & \quad - \left\{ \frac{18}{\alpha^2} - \frac{270}{\alpha^3} - \frac{2278}{\alpha^4} - \frac{11668}{\alpha^5} - \frac{62692}{\alpha^6} - \frac{220290}{\alpha^7} - \frac{572552}{\alpha^8} - \frac{1036892}{\alpha^9} - \frac{1149120}{\alpha^{10}} - \frac{574560}{\alpha^{11}} \right\} e^{-2\alpha} \Big\}
 \end{aligned}$$

From Salts (1940, p.6) for Cu:-

$$A = 1.275 \text{ \AA} = \frac{1.275}{529} = 2.41 \text{ atomic units}$$

Putting $\alpha_0 = 2$; $\nu_0 = 3$ gives $\alpha = 9.64$; $\beta = 16.87$; $\gamma = 7.23$

Putting $\alpha_0 = 2$; $\nu_0 = 6$ gives $\alpha = 9.64$; $\beta = 24.10$; $\gamma = 14.46$

With these values it would at first appear that some of the terms in the above expressions could be neglected but this does not prove to be the case owing to the large coefficients of the higher powers of $\frac{1}{\alpha}$ etc.

Then:- $(A_1^{(1)})_{\alpha_0=2, \nu_0=3} = 1.245 \times 10^{-8} \pi A^6$

$$(A_1^{(1)})_{\alpha_0=2, \nu_0=6} = 7.143 \times 10^{-10} \pi A^6$$

$$(A_1^{(1)})_{\alpha_0=2} = 2.246 \times 10^{-6} \pi A^6$$

$$(A_1^{(2)})_{\alpha_0=2} = 6.798 \times 10^{-7} \pi A^6$$

$$\begin{aligned}
 A_1 = & \frac{15}{4\pi} \pi A^6 \left\{ 1.979^2 (A_1^{(1)})_{\alpha_0=2, \nu_0=3} + 1.979 [85.88 + (28 \times 1.979)] (A_1^{(1)})_{\alpha_0=2, \nu_0=6} \right. \\
 & \left. + (1.979 + 85.88 \times 28) (A_1^{(1)})_{\alpha_0=2} - 1.979^2 (A_1^{(2)})_{\alpha_0=2} \right\}
 \end{aligned}$$

$$\therefore A_1 = 48.803 \times 10^{-6} A^6$$

If A is expressed in atomic units of distance, this will be in atomic units of energy.

A. This involves two atoms in the (z, x) plane so that the required transformations are:-

$$x = \frac{1}{\sqrt{2}} (Z + X + A) \quad x' = \frac{1}{\sqrt{2}} (Z + X - A)$$

$$y = Y \quad y' = Y$$

$$z = \frac{1}{\sqrt{2}} (Z - X + A) \quad z' = \frac{1}{\sqrt{2}} (Z - X - A)$$

$$X = A \sqrt{(1-\mu^2)(1-\mu'^2)} \sin \phi, \quad Y = A \sqrt{(1-\mu^2)(1-\mu'^2)} \cos \phi, \quad Z = A \mu$$

$$y z y' z' = \frac{1}{2} [(Z-X)^2 - A^2] Y^2$$

$$\therefore \int_0^{2\pi} y z y' z' d\phi = \frac{A^4}{2} \int_0^{2\pi} (1-\mu^2)(1-\mu'^2) \cos^2 \phi \left\{ A^2 \mu^2 - 2A\mu \sqrt{(1-\mu^2)(1-\mu'^2)} \sin \phi + (1-\mu^2)(1-\mu'^2) \sin^2 \phi - 1 \right\} d\phi$$

Sub:- $\int_0^{2\pi} \sin \phi \cos^2 \phi d\phi = 0$ and $\int_0^{2\pi} \sin^2 \phi \cos^2 \phi d\phi = \frac{\pi}{4}$

$$\begin{aligned} \int_0^{2\pi} y z y' z' d\phi &= \frac{\pi A^4}{2} \left[(1-\mu^2)(1-\mu'^2) + \frac{1}{4} (1-\mu^2)^2 (1-\mu'^2)^2 \right] \\ &= \frac{\pi A^4}{2} \left[\mu^4 \left(-\frac{1}{4} \mu'^4 + \frac{1}{2} \mu'^2 + \frac{1}{4} \right) + 1-\mu^2 \left(\frac{1}{2} \mu'^4 + \mu'^2 - \frac{1}{2} \right) + \left(-\frac{1}{4} \mu'^4 - \frac{1}{2} \mu'^2 + \frac{1}{4} \right) \right] \end{aligned}$$

Proceeding as before:- $A_2 = 14.468 \times 10^{-6} A^6$

A. This involves two atoms in the (x, y) plane and, hence, using a similar transformation:-

$$\begin{aligned} z x y' z' &= \frac{1}{2} (X-Y+A)(X+Y-A) Z^2 = \frac{1}{2} (X^2 - Y^2 + 2AY - A^2) Z^2 \\ &= \frac{A^4}{2} \left[\mu^4 \mu'^2 - (1-\mu^2)(1-\mu'^2) \sin^2 \phi + 2\sqrt{(1-\mu^2)(1-\mu'^2)} \sin \phi - 1 \right] (1-\mu^2)(1-\mu'^2) \cos^2 \phi \end{aligned}$$

$$\begin{aligned} \therefore \int_0^{2\pi} z x y' z' d\phi &= \frac{\pi A^4}{2} \left[(1-\mu^2)(1-\mu'^2) - \frac{1}{4} (1-\mu^2)^2 (1-\mu'^2)^2 \right] \\ &= \frac{\pi A^4}{2} \left[\mu^4 \left(-\frac{5}{4} \mu'^4 + \frac{3}{2} \mu'^2 - \frac{1}{4} \right) + 1-\mu^2 \left(\frac{3}{2} \mu'^4 - \mu'^2 - \frac{1}{2} \right) + \left(-\frac{1}{4} \mu'^4 - \frac{1}{2} \mu'^2 + \frac{1}{4} \right) \right] \end{aligned}$$

Proceeding as before:- $A_3 = 19.647 \times 10^{-6} A^6$

A. This also involves two atoms in the (x, y) plane and hence, proceeding as above:-

$$\begin{aligned} (x^2 - y^2)(x'^2 - y'^2) &= \frac{1}{4} [X^2 + Y^2 - A^2 - 2XY + 2AX - 2AY - X^2 - Y^2 - A^2 - 2XY - 2AX - 2AY] \\ &\quad \times [X^2 + Y^2 - A^2 - 2XY - 2AX + 2AY - X^2 - Y^2 - A^2 - 2XY + 2AX + 2AY] \\ &= 4Y^2(X^2 - A^2) \\ &= 4A^4 (1-\mu^2)(1-\mu'^2) X (1-\mu'^2 - 1) \sin^2 \phi \end{aligned}$$

$$\int_0^{2\pi} (x^2 - y^2)(x'^2 - y'^2) d\phi = 4\pi A^4 [A^4(-\mu^4 - \mu^2) + A^4(\mu^4 - 1) + (-\mu^4 + 1)]$$

Proceeding as before:- $A_y = 34.115 \times 10^{-6} A^6$

A₂ This involves two atoms in the (y,z) plane and hence, proceeding as for A₁:-

$$\begin{aligned} (x^2 - y^2)(x'^2 - y'^2) &= [X^2 - \frac{1}{4}(Y-Z+A)^2][X^2 - \frac{1}{4}(Y-Z-A)^2] \\ &= \frac{1}{4}[2X^2 - Y^2 - Z^2 - A^2 + 2YZ - 2AY + 2AZ][2X^2 - Y^2 - Z^2 - A^2 + 2YZ + 2AY - 2AZ] \\ &= \frac{1}{4}\{[2X^2 - Y^2 - Z^2 - A^2 + 2YZ]^2 - [2AY - 2AZ]^2\} \end{aligned}$$

Now:- $[2X^2 - Y^2 - Z^2 - A^2 + 2YZ]^2 = A^4[2(A^2 + \mu^2 - 1)(\mu^2 - 1)\cos^2\phi - A^4\mu^2 - (A^4 + \mu^2 - 1)(\mu^2 - 1)\sin^2\phi + 2A\mu\sqrt{(A^2 - 1)(1 - \mu^2)}\sin\phi - 1]^2$

$$\begin{aligned} &= A^4\{4[A^4(\mu^4 - 2\mu^2 + 1) + A^4(-2\mu^4 + 4\mu^2 - 2) + (\mu^4 - 2\mu^2 + 1)]\cos^2\phi + A^4\mu^4 + 2A^2\mu^2 + 1 \\ &\quad + [A^4(\mu^4 - 2\mu^2 + 1) + A^4(-2\mu^4 + 4\mu^2 - 2) + (\mu^4 - 2\mu^2 + 1)]\sin^2\phi \\ &\quad + 4[A^4(-\mu^4 + \mu^2) + A^4(\mu^4 - \mu^2)]\sin\phi - 4A\mu(A^2\mu^2 + 1)\sqrt{(A^2 - 1)(1 - \mu^2)}\sin\phi \\ &\quad - 4[A^4(-\mu^4 + \mu^2) + A^4(\mu^4 - 2\mu^2 + 1) + (\mu^4 - 1)]\cos^2\phi \\ &\quad + 2[A^4(-\mu^4 + \mu^2) + A^4(\mu^4 - 2\mu^2 + 1) + (\mu^4 - 1)]\sin^2\phi \\ &\quad - 4[A^4(\mu^4 - 2\mu^2 + 1) + A^4(-2\mu^4 + 4\mu^2 - 2) + (\mu^4 - 2\mu^2 + 1)]\sin\phi\cos^2\phi \\ &\quad - 4A\mu[(A^2 - 1)(1 - \mu^2)]^{3/2}\sin\phi + 8A\mu[(A^2 - 1)(1 - \mu^2)]^{1/2}\sin\phi\cos^2\phi\} \end{aligned}$$

and:-

$$\begin{aligned} 4A^4(Y-Z)^2 &= 4A^4[A\mu - \sqrt{(A^2 - 1)(1 - \mu^2)}\sin\phi]^2 \\ &= 4A^4\{A^2\mu^2 - 2A\mu\sqrt{(A^2 - 1)(1 - \mu^2)}\sin\phi + (A^2\mu^2 + A^2 + \mu^2 - 1)\sin^2\phi\} \end{aligned}$$

Integrating over ϕ from 0 to 2π and ignoring a factor of $\frac{A^4}{4}$, the

contributions to $\int_0^{2\pi} (x^2 - y^2)(x'^2 - y'^2) d\phi$ are:-

Terms independent of ϕ :- $2\pi(A^4\mu^4 + 2A^2\mu^2 + 1 - 4A^2\mu^2) = 2\pi(A^4\mu^4 - 2A^2\mu^2 + 1)$

Terms in $\sin^2\phi$ and $\cos^2\phi$:- $\pi\{4[A^4(-\mu^4 + \mu^2) + A^4(\mu^4 - \mu^2)] - 4[A^4(-\mu^4 + \mu^2) + A^4(\mu^4 - 2\mu^2 + 1) + (\mu^4 - 1)] + 2[A^4(-\mu^4 + \mu^2) + A^4(\mu^4 - 2\mu^2 + 1) + (\mu^4 - 1)] - 4[A^4(-\mu^4 + \mu^2) + (\mu^4 - 1)]\}$

$$= 2\pi\{A^4(-\mu^4 + \mu^2) + A^4(\mu^4 - 2\mu^2 - 3) + (-3\mu^4 + 3)\}$$

Terms in $\sin^2\phi\cos^2\phi$:-

Terms in $\sin^4\phi$ and $\cos^4\phi$:- $-\frac{\pi}{4}\{4[A^4(\mu^4 - 2\mu^2 + 1) + A^4(-2\mu^4 + 4\mu^2 - 2) + (\mu^4 - 2\mu^2 + 1)]\}$

$$\frac{3\pi}{4}\{5[A^4(\mu^4 - 2\mu^2 + 1) + A^4(-2\mu^4 + 4\mu^2 - 2) + (\mu^4 - 2\mu^2 + 1)]\}$$

$$\therefore \int_0^{2\pi} (x^2 - y^2)(x'^2 - y'^2) d\phi = \frac{\pi A^4}{4} \left[A^4 \left(\frac{11}{4}\mu^4 - \frac{7}{2}\mu^2 + \frac{11}{4} \right) + A^4 \left(-\frac{7}{2}\mu^4 + 11\mu^2 - \frac{23}{2} \right) + \left(\frac{11}{4}\mu^4 - \frac{23}{2}\mu^2 + \frac{43}{4} \right) \right]$$

Proceeding as before:- $A_7 = 6.261 \times 10^{-6} A^6$

A₈. This involves two atoms in the (y,z) plane and hence, proceeding as above:-

$$\begin{aligned} (x^2 - y^2)y'z' &= \frac{1}{4}[(X-A)^2 - Z^2][X^2 - \frac{1}{4}(Y-Z+A)^2] \\ &= \frac{A^4}{4} \int_0^{2\pi} [(d\mu-1)^2 - (d^2-1)(1-\mu^2)\sin^2\phi] [2(d^2-1)(1-\mu^2)\cos^2\phi - (d\mu+1-\sqrt{(d^2-1)(1-\mu^2)})\sin\phi]^2 d\phi \\ \int_0^{2\pi} (x^2 - y^2)y'z' d\phi &= \frac{\pi A^4}{4} \left\{ -2(d\mu-1)^2(d\mu+1)^2 + 2(d\mu-1)^2(d^2-1)(1-\mu^2) - (d\mu-1)^2(d^2-1)(1-\mu^2) \right. \\ &\quad \left. + (d^2-1)(1-\mu^2)(d\mu+1)^2 - \frac{1}{4} \cdot 2(d^2-1)^2(1-\mu^2)^2 + \frac{1}{4}(d^2-1)^2(1-\mu^2)^2 \right\} \\ &= \frac{\pi A^4}{4} \left\{ -2(d^4\mu^4 - 2d^3\mu^3 + 1) + 2[d^4(-\mu^2 + \mu^2) + d^4(\mu^2 - 2\mu^2 + 1) + (\mu^4 - 1)] \right. \\ &\quad \left. + \frac{1}{4}[d^4(\mu^4 - 2\mu^2 + 1) + d^4(-2\mu^2 + 4\mu^2 - 2) + (\mu^4 - 2\mu^2 + 1)] \right\} \\ &= \frac{\pi A^4}{4} \left\{ d^4\left(-\frac{15}{4}\mu^4 + \frac{3}{2}\mu^2 + \frac{1}{4}\right) + d^4\left(\frac{1}{2}\mu^4 + \mu^2 + \frac{1}{2}\right) + \left(\mu^4 + \frac{1}{2}\mu^2 - \frac{15}{4}\right) \right\} \end{aligned}$$

Proceeding as before:- $A_8 = 21.812 \times 10^{-6} A^6$

It proves convenient later in solving the secular equation to express the A_i in terms of:-

$$E_0 = 4(A_1 + A_2)$$

Then:-

$$A_1 = .1928 E_0$$

$$A_2 = .0572 E_0$$

$$A_3 = .0776 E_0$$

$$A_4 = .1348 E_0$$

$$A_5 = .0247 E_0$$

$$A_6 = .0862 E_0$$

where:-

$$E_0 = 4(48.803 + 14.468) \times 10^{-6} A^6$$

where $A = 2.41$ atomic units of length and 1 atomic unit of energy is equal to 27.23 eV.

$$E_0 = 1.349 \text{ eV}$$

These figures are very illuminating in that they illustrate the danger in making qualitative deductions regarding the relative values of "overlap integrals" of the type A_i , e.g. from

diagrams as used here. Thus from these diagrams it might be anticipated that A_4 would prove considerably smaller than A_1 , whereas they are of the same order. The reason for this is readily seen if the integrands of $A_1^{(c)}$ and $A_4^{(c)}$ are calculated at various points in space, when it is found that, while that for $A_1^{(c)}$ is large along the line OO' , it falls off rapidly on departure from this line, whereas the integrand of $A_4^{(c)}$ is fairly large over two much more extensive regions on either side of OO' . This is an important point as incorrect qualitative deductions of the type indicated have been made by previous authors and used in obtaining approximate solutions of the secular equation.

The assumptions and approximations made in this part of the work will now be considered.

(1) Summation over nearest neighbours only in calculating the H_{nn} . As has already been pointed out, there may be an important contribution from next-nearest neighbours, which is being neglected. A pictorial investigation similar to that used for nearest neighbours shows that the extra contributions to the A_i , relative to those from the n.n., appear qualitatively to be as follows.

A_1 -- small and negative	A_4 -- large and negative
A_2 -- moderate and positive	A_5 -- moderate and positive
A_3 -- zero	A_6 -- zero

It is unlikely that the extra contribution to A_7 , for example, will bear the same relation to those of A_4 and A_5 as A_7 does to A_1 and A_2 (see p.37). Also in some cases the atoms at $\underline{L} = (\pm 1, 0, 0)$ will not make the same contribution as those at

$\underline{Q} = (0, \pm 1, 0)$, say, i.e. the atoms cannot be considered in groups of four but only in pairs. Altogether the effect is an extremely complicated one and any attempt to assess the change in the final energies appears impossible without numerical computation.

(11) Assumptions regarding $V-U$, $f(r)$ and $f(r')$.

(a) $V-U=0$ within the atomic polyhedron of the central atom. In fact $V-U < 0$ here; as the sign of $V-U$ has been taken into account in defining the Λ_i , the effect of this approximation is to decrease the true values of the Λ_i . The error should be small, particularly since $\phi_m^* \phi_n$ will be small over most of the region affected.

(b) The use of a sphere instead of the atomic polyhedron reduces this region by about half its volume but mainly in the areas, where $\phi_m^* \phi_n$ is very small. If Slater's method of using a sphere equal in volume to the polyhedron had been used, $V-U$ would have been zero in most of the region of maximum overlap of the wave functions for some Λ_i and not for others, causing worse error than in the method employed here.

(c) The effect of assuming $U=0$ and $V=U'$ outside the sphere is difficult to assess. At a point halfway between the atoms $U=U'$ so the assumption is that $V=2U$ here, which may or may not be accurate. Elsewhere the assumed value of U' for $V-U$ is numerically too small, in places greatly so, but the error should not be large since $\phi_m^* \phi_n$ becomes very small for large r and r' . However, the effect of this assumption is obviously to make the calculated values of all the Λ_i slightly too small.

(d) The approximation of $(1+28e^{-3r'})$ for $r'U'$ is almost exact for

$r' > 1$ and quite close for $r' < 1$, which latter region contributes little to the A_z , as already pointed out. The error introduced is additive for $r' < 1$ and subtractive for $r' > 1$ and as a whole will therefore be very small. The neglect of the $e^{-2r'}$ term in calculating the integral over the atomic sphere of 0 reduces this integral very slightly and hence increases the A_z (cf. Fig. 8 above).

(e) The expression 4.1 lies below Hartree's figures for $r' f(r')$ for $0 < r' < .5$, above them for $.5 < r' < 1.1$ and below them for $r' > 1.1$. Since the last named is the most important range, this has the effect of giving values of the A_z , which are too small. The error is increased slightly by neglect of the e^{-5r} term in $f(r)$ but decreased again by neglect of the e^{-5r} and $e^{-5r'}$ terms in calculating the integrals over the atomic sphere of 0 (cf. Fig. 7 above).

(f) The use of Hartree's figures for cu^+ was unfortunately unavoidable as no similar figures have been published for the Ni atom. Although the cu^+ ion is isoelectronic with the Ni atom, the orbitals in the former will be smaller than for Ni with less overlap, therefore, at the actual lattice spacing. This approximation will therefore lead to an underestimate of the bandwidth, although any quantitative estimate of the effect is precluded by the complicated nature of the A_z .

In conclusion some of the above assumptions cause an underestimate of the A_z while others have the opposite effect and no attempt has been made to assess the total error caused. Probably the neglect of next-nearest neighbours is the worst approximation.

Chapter V.

First Approximation to the Energies.

The problem is now reduced to the solution of a quintic equation at every point of the first B.Z. for the f.c.c. lattice, each coefficient of the quintic being a complicated function of three parameters ξ, η and J , i.e. of k_x, k_y and k_z . Analytical solution being impossible, except along a few particular directions (see Chapter VII), the obvious alternative is to solve this equation numerically at various points in the zone and then attempt to link up the five roots. Even when given values of ξ, η and J are substituted in $|H_{nm} - E c_{nm}| = 0$, however, the exact or even approximate solution of this determinantal equation is still a lengthy process and for reasonable accuracy it is found that about 250 of these equations must be solved. It was therefore decided, as a first approximation, to put $A_6 = 0$, thereby reducing the quintic to two separate equations, a cubic and a quadratic, whose solutions correspond to Γ_5 and Γ_3 respectively. This approximation also underlies the calculations of Jones and Mott (1937) on the b.c.c. lattice and of Brooks (1940) on ferromagnetic anisotropy. It is shown here to be a poor approximation but it serves several useful purposes, (i) to obtain certain results which are independent of A_6 , (ii) to obtain an idea of the overlap of the Γ_5 and Γ_3 bands and a first approximation to the $N(E)$ curve, (iii) to find the important regions of the B.Z. where exact solution of the quintic should be carried out, i.e. the regions of maximum energy, since it is the shape of the $N(E)$ curve near the top of the

total energy band which is important and (iv) to give first approximations to the energy values for use in solving the quintic.

(a) The First B.Z. for the F.c.c. Lattice.

Let $\underline{a}_1, \underline{a}_2, \underline{a}_3$ be the three vectors, which map out unit cell of a lattice and $\underline{b}_1, \underline{b}_2, \underline{b}_3$ another set of vectors such that:-
 $\underline{a}_n \cdot \underline{b}_m = \delta_{nm}$
 Then the points $(n_1 \underline{b}_1 + n_2 \underline{b}_2 + n_3 \underline{b}_3)$, where n_1, n_2, n_3 take all integral values, including zero, form the reciprocal lattice. Then it can be shown (Mott and Jones 1936, p.152 ff.) that the planes of energy discontinuity for the lattice are given by:-

$$\underline{n} \cdot \underline{k} + \pi |\underline{n}|^2 = 0$$

as long as the states $\underline{k} + \underline{n}$ and $\underline{k}$ do not combine under a periodic potential V , i.e. as long as:-

$$V_{\underline{n}} = \frac{1}{\Omega_{\text{unit cell}}} \int V(\underline{r}) e^{2\pi i \underline{n} \cdot \underline{r}/a} d\tau \neq 0$$

If there are s atoms per unit cell at positions within it given by (u, v, w) , the array of terms (u_t, v_t, w_t) is called the basis with respect to $\underline{a}_1, \underline{a}_2$ and $\underline{a}_3$. The Fourier coefficients of V may then be written:-

$$\begin{aligned} V_{\underline{n}} &= \sum_{t=1}^s A_{\underline{n}t} e^{2\pi i (n_1 u_t + n_2 v_t + n_3 w_t)} \\ &= A_{\underline{n}} \sum_{t=1}^s e^{2\pi i (n_1 u_t + n_2 v_t + n_3 w_t)} \\ &= A_{\underline{n}} S_{\underline{n}} \end{aligned}$$

if all the atoms are identical. $S_{\underline{n}}$ is called the structure factor and must not vanish for a plane of energy discontinuity. For the f.c.c. lattice:-

$$\underline{a}_1 = (a, 0, 0); \underline{a}_2 = (0, a, 0); \underline{a}_3 = (0, 0, a)$$

and the reciprocal lattice is hence given by:-

$$\underline{b}_1 = (\frac{1}{a}, 0, 0); \underline{b}_2 = (0, \frac{1}{a}, 0); \underline{b}_3 = (0, 0, \frac{1}{a})$$

There are four atoms in unit cell, since each corner atom (8) is shared by 8 cells and each face-centred one (6) by 2 cells;

hence their basis is $(0,0,0), (0,\frac{1}{2},\frac{1}{2}), (\frac{1}{2},0,\frac{1}{2}), (\frac{1}{2},\frac{1}{2},0)$ and the structure factor is:-

$$\begin{aligned} S_n &= e^0 + e^{\pi i(n_2+n_1)} + e^{\pi i(n_2+n_1)} + e^{\pi i(n_1+n_2)} \\ &= 1 + \cos \pi(n_2+n_1) + \cos \pi(n_2+n_1) + \cos \pi(n_1+n_2) \end{aligned}$$

The first few planes, for which this does not vanish, are given by $en = (1,1,1); (2,0,0); (0,2,2); \dots$ and the first B.Z. is therefore bounded by the planes given by $en = (1,1,1)$ and $(2,0,0)$, i.e.:-

$$\pm k_x \pm k_y \pm k_z = 3\pi/a$$

and $k_x = \pm 2\pi/a$; $k_y = \pm 2\pi/a$; $k_z = \pm 2\pi/a$

i.e. considering the all-positive octant of $\underline{k}$ -space only:-

$$\xi + \eta + \zeta = \frac{3\pi}{2} \quad ; \quad \xi = \pi \quad ; \quad \eta = \pi \quad ; \quad \zeta = \pi$$

as shown in Fig. 10.

Having decided to simplify the fundamental secular equation in the manner indicated at the beginning of this chapter, it is now straightforward in principle to obtain energy values as functions of momentum. It is convenient to refer these energies to a zero level of $\xi_0 + C$, since the equation may be written:

$$|H'_{nm} - (E - \xi_0 - C)\delta_{nm}| = 0$$

where:-

$$H'_{nm} = H_{nm} - (\xi_0 + C)\delta_{nm}$$

(see above).

This is permissible as long as relative energies only are of interest, as is the case in all work here.

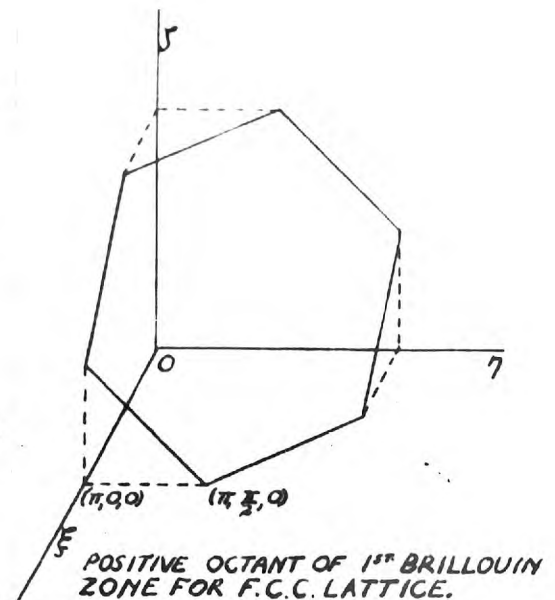


Fig. 10

(b) Solution of the Cubic Equation.

Putting $A_3 = 0$ and dropping the primes on the H_{nm} , the equation reduces to:-

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} \\ H_{12} & H_{22}-E & H_{23} \\ H_{13} & H_{23} & H_{33}-E \end{vmatrix} = 0$$

E being measured from the above zero, so that three roots are those of:-

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} \\ H_{12} & H_{22}-E & H_{23} \\ H_{13} & H_{23} & H_{33}-E \end{vmatrix} = 0$$

$$\text{or:-} \begin{vmatrix} 4A_2(\cos\delta\cos\gamma + \cos\delta\cos\eta) - 4A_1\cos\gamma\cos\delta - E & -4A_2\sin\delta\sin\eta & -4A_2\sin\delta\sin\gamma \\ -4A_2\sin\delta\sin\eta & 4A_2(\cos\delta\cos\eta + \cos\eta\cos\delta) - 4A_1\cos\delta\cos\eta - E & -4A_2\sin\eta\sin\delta \\ -4A_2\sin\delta\sin\gamma & -4A_2\sin\eta\sin\delta & 4A_2(\cos\eta\cos\gamma + \cos\gamma\cos\eta) - 4A_1\cos\gamma\cos\eta - E \end{vmatrix} = 0$$

Change the signs throughout and put:-

$$E_0 = 4(A_1 + A_2); \quad \beta_2 = \frac{A_2}{A_1 + A_2}; \quad \beta_3 = \frac{A_1}{A_1 + A_2}$$

$$\frac{E}{E_0} = \varepsilon + \beta_2(\cos\delta\cos\eta + \cos\eta\cos\delta + \cos\delta\cos\gamma)$$

Then the (1,1) term, for instance, becomes:-

$$\begin{aligned} E + 4(A_1 + A_2)\cos\eta\cos\delta - 4A_2\cos\delta\cos\eta &= 4(A_1 + A_2) \left[\frac{E}{4(A_1 + A_2)} - \frac{A_2}{A_1 + A_2} \cos\delta\cos\eta + \cos\eta\cos\delta \right] \\ &= E_0(\varepsilon + \cos\eta\cos\delta) \end{aligned}$$

similarly the (1,2) term becomes:-

$$4(A_1 + A_2) \frac{A_3}{A_1 + A_2} \sin\delta\sin\eta = E_0 \cdot \beta_3 \sin\delta\sin\eta$$

Dividing throughout by E_0 , the equation becomes:-

$$\begin{vmatrix} \varepsilon + \cos\eta\cos\delta & \beta_3\sin\delta\sin\eta & \beta_2\sin\delta\sin\gamma \\ \beta_3\sin\delta\sin\eta & \varepsilon + \cos\delta\cos\eta & \beta_2\sin\eta\sin\delta \\ \beta_2\sin\delta\sin\gamma & \beta_2\sin\eta\sin\delta & \varepsilon + \cos\gamma\cos\eta \end{vmatrix} = 0$$

$$\text{or:- } \epsilon^3 + \epsilon^2 \sum \cos \xi \cos \eta + \epsilon [\sum \cos^2 \xi \cos \eta \cos \zeta - \beta_1^2 \sum \sin^2 \xi \sin^2 \eta] \\ + [\cos^2 \xi \cos^2 \eta \cos^2 \zeta - \beta_2^2 \sum \sin^2 \xi \sin^2 \eta \cos \xi \cos \eta + 2\beta_3^2 \sin^2 \xi \sin^2 \eta \sin^2 \zeta] = 0$$

where:- $\beta_1 = 2.287$ and $\beta_2 = 3.104$

Since this is symmetrical in ξ, η and ζ , the solutions will be symmetrical about the planes $\xi=\eta$; $\eta=\zeta$ and $\zeta=\xi$. Also, since only even powers of $\sin \xi, \sin \eta$ and $\sin \zeta$ occur, the solutions will be symmetrical about the planes $\xi=0, \eta=0$ and $\zeta=0$. This defines a basic region of the B.Z. equal to $1/48$ of the total volume, as can be deduced from symmetry considerations of the original Schrödinger equation. In practice the above equation was solved in the region bounded by the planes $\xi=0, \eta=0$ and $\xi=\eta$, thereby obtaining a check of the solutions obtained at two equivalent points in most cases and sometimes three, very necessary as there was no other simple check. Within this region it was decided to solve the cubic at each point of a lattice formed by taking intervals of $\pi/12$ for ξ, η and ζ .

(c) Method of Solution.

The equation can be solved analytically in certain planes and along certain directions.

(1) $\zeta=0$ plane. The equation becomes:-

$$\begin{vmatrix} \epsilon + \cos \eta & \beta_1 \sin \xi \sin \eta & 0 \\ \beta_1 \sin \xi \sin \eta & \epsilon + \cos \xi & 0 \\ 0 & 0 & \epsilon + \cos \xi \cos \eta \end{vmatrix} = 0$$

One root is:-

$$\epsilon = -\cos \xi \cos \eta$$

while the others are the roots of:-

$$(\epsilon + \cos \eta)(\epsilon + \cos \xi) - \beta_1^2 \sin^2 \xi \sin^2 \eta = 0$$

or:-
$$\epsilon = -\frac{1}{2} [\cos \xi + \cos \eta \pm \sqrt{(\cos \xi - \cos \eta)^2 + 4\beta_1^2 \sin^2 \xi \sin^2 \eta}]$$

and in all cases:- $\frac{E}{E_0} = \epsilon + \beta_2 (\cos \xi \cos \eta + \cos \xi + \cos \eta)$

(iii) $\xi = \pi$ plane. The roots in this case are:-

$$\epsilon = -\cos \xi \cos \eta$$

and:- $\frac{E}{E_0} = \frac{1}{2} [\cos \xi + \cos \eta \pm \sqrt{(\cos \xi - \cos \eta)^2 + 4\beta_2^2 \sin^2 \xi \sin^2 \eta}]$

where:- $\frac{E}{E_0} = \epsilon + \beta_2 (\cos \xi \cos \eta - \cos \xi - \cos \eta)$

(iii) (100) direction. From (i) the roots are:-

$$\frac{E}{E_0} = -1 + \beta_2 (1 + 2\cos \xi)$$

and:- $\frac{E}{E_0} = -\cos \xi + \beta_2 (1 + 2\cos \xi)$

the latter being a double root. There is hence triple degeneracy at the centre of the zone and double degeneracy along the (100) direction. The value of E/E_0 at the centre of the zone will prove of importance later, i.e.:-

$$\frac{E}{E_0} = -1 + 3\beta_2 = -0.314 \quad \text{or} \quad E = -0.423 \text{ eV}$$

(iv) (110) direction. From (i) the roots are:-

$$\frac{E}{E_0} = -\cos^2 \xi + \beta_2 (\cos^2 \xi + 2\cos \xi)$$

and:- $\frac{E}{E_0} = -\cos \xi \pm \beta_1 \sin^2 \xi + \beta_2 (\cos^2 \xi + 2\cos \xi)$

(v) (111) direction. Putting $\sin \xi = \sin \eta = \sin \zeta = p$; $\cos \xi = \cos \eta = \cos \zeta = q$.

the equation becomes:-

$$\begin{vmatrix} \epsilon + q^2 & \beta_2 p^2 & \beta_1 p^2 \\ \beta_1 p^2 & \epsilon + q^2 & \beta_2 p^2 \\ \beta_2 p^2 & \beta_1 p^2 & \epsilon + q^2 \end{vmatrix} = 0$$

By row and column manipulation this reduces to:-

$$\begin{vmatrix} \epsilon + q^2 - \beta_1 p^2 & 0 & 0 \\ \beta_1 p^2 & \epsilon + q^2 + \beta_2 p^2 & \beta_2 p^2 \\ \beta_1 p^2 & 2\beta_2 p^2 & \epsilon + q^2 \end{vmatrix} = 0$$

One root is:-

$$\begin{aligned} \frac{E}{E_0} &= \epsilon + 3\beta_2 q^2 = \beta_1 p^2 + (3\beta_2 - 1) q^2 \\ &= \beta_1 + (3\beta_2 - 1 - \beta_1) \cos^2 \xi \end{aligned}$$

and of the others one proves to be degenerate with this and the

other is:- $\frac{E}{E_0} = -2\beta_1 + (3\beta_2 + 2\beta_1 - 1) \cos^2 \xi$

Graphs showing the variation of E/E_0 with ξ are shown in figures 11, 12 and 13, the additional curves being the solutions of the quadratic (see later).

There being no simpler method, Cardan's method was used for solving the equation at general points. Consider the general cubic:-

$$x^3 + 3\alpha x^2 + 3\beta x + \gamma = 0$$

Put $x = z - \alpha$:- $z^3 - 3\alpha z^2 + 3\alpha^2 z - \alpha^3 + 3\alpha(z^2 - 2\alpha z + \alpha^2) + 3\beta(z - \alpha) + \gamma = 0$

or:- $z^3 + 3Hz + G = 0$

where:- $H = \beta - \alpha^2$ and $G = \gamma - 3\alpha\beta + 2\alpha^3$

Put $z = u + v$:- $u^3 + 3uv^2 + 3u^2v + v^3 + 3H(u+v) + G = 0$

or:- $u^3 + v^3 + 3(uv + H)(u+v) + G = 0$

Assume:- $uv + H = 0$

Then:- $u^3 + v^3 = u^3 - \frac{H^3}{u^3} = -G$

$$u^3 = \frac{-G}{2} + \sqrt{\frac{G^2}{4} + H^3}$$

$$v^3 = \frac{-G}{2} - \sqrt{\frac{G^2}{4} + H^3}$$

$\sqrt{\frac{G^2}{4} + H^3}$ proves to be negative so put $u^3 = r^3 e^{i\theta}$. Then:-

$$-\frac{G}{2} = r^3 \cos 3\theta ; \sqrt{\frac{G^2}{4} + H^3} = i r^3 \sin 3\theta$$

$$r^3 = -H^3 \text{ or } r = \sqrt[3]{-H}$$

and:- $\theta = \frac{1}{3} \cos^{-1} \left(\frac{-G}{2r^3} \right) = \frac{1}{3} \cos^{-1} \left(\frac{-G}{2(-H)^{3/2}} \right) = \frac{1}{3} \cos^{-1} \left[\frac{3\alpha\beta - 2\alpha^3 - \gamma}{2(\alpha^2 - \beta)^{3/2}} \right]$

$z = u + v = r e^{i\theta} + r e^{-i\theta} = 2r \cos(\theta + \frac{2n\pi}{3})$ where $n=0,1,2$.

$$x = \frac{2\sqrt[3]{-H} \cos(\theta + \frac{2n\pi}{3})}{3} - \alpha$$

Each of the planes $\xi = \frac{\nu\pi}{12}$ ($\nu=1,2,---,11$) was considered in turn; the determinant for that plane was expanded to give the cubic equation in ε , the coefficients being functions of ξ and η . This equation was then solved by Cardan's method for each lattice point in the plane, using a desk calculating machine, and from the roots the three sets of values of E/E_0 were obtained. For

results correct to three D.P. five places of decimal were used during the computation.

(d) Representative Results.

For example in the plane $\int = \pi/6$ the equation reduces to:-

$$\begin{vmatrix} \varepsilon + .86603 \cos \eta & \beta_1 \sin \int \sin \eta & .5 \beta_1 \sin \int \\ \beta_1 \sin \int \sin \eta & \varepsilon + .86603 \cos \int & .5 \beta_1 \sin \eta \\ .5 \beta_1 \sin \int & .5 \beta_1 \sin \eta & \varepsilon + \cos \int \cos \eta \end{vmatrix} = 0$$

Coefficients of ε^2 and ε and the constant term are:-

$$3\alpha = .86603 (\cos \int + \cos \eta) + \cos \int \cos \eta$$

$$3\beta = .86603 (\cos \int + \cos \eta) \cos \int \cos \eta + .75 \cos \int \cos \eta - \beta_1^2 \sin^2 \int \sin^2 \eta - .25 \beta_1^2 (\sin^2 \int + \sin^2 \eta)$$

$$\gamma = .75 \cos^2 \int \cos^2 \eta - \beta_1^2 \sin^2 \int \sin^2 \eta \cos \int \cos \eta - .21651 \beta_1^2 (\sin^2 \int \cos \int + \sin^2 \eta \cos \eta) + .5 \beta_1^2 \sin^2 \int \sin^2 \eta$$

and:-
$$\frac{E}{E_0} = \varepsilon + \beta_1 [\cos \int \cos \eta + .86603 (\cos \int + \cos \eta)]$$

A representative example of this calculation is given at the end of this chapter.

The results were listed in three columns, one corresponding to $\cos \frac{\theta}{3}$, one to $\cos \frac{2\pi+\theta}{3}$ and one to $\cos \frac{4\pi+\theta}{3}$. When the solutions for different $\int$ -planes were compared, however, it was found that, whereas the solutions E_1, E_2, E_3 occurred in columns I, II, III respectively for the point $(\int, \eta, \int)$, they might occur in columns (II, I, III), say, for the point $(\int, \int, \eta)$, whereas by symmetry the two points are equivalent, i.e. any one solution of the problem must take the same value at the two points. It can be shown logically that, assuming there are no discontinuities or near-discontinuities in the E - k curves or energy contours (see later), the three E - k curves for any given direction in k -space can never cross one another, i.e. the highest energy value at any

EXACT SOLUTIONS OF SECULAR EQUATION.
(100) DIRECTION.

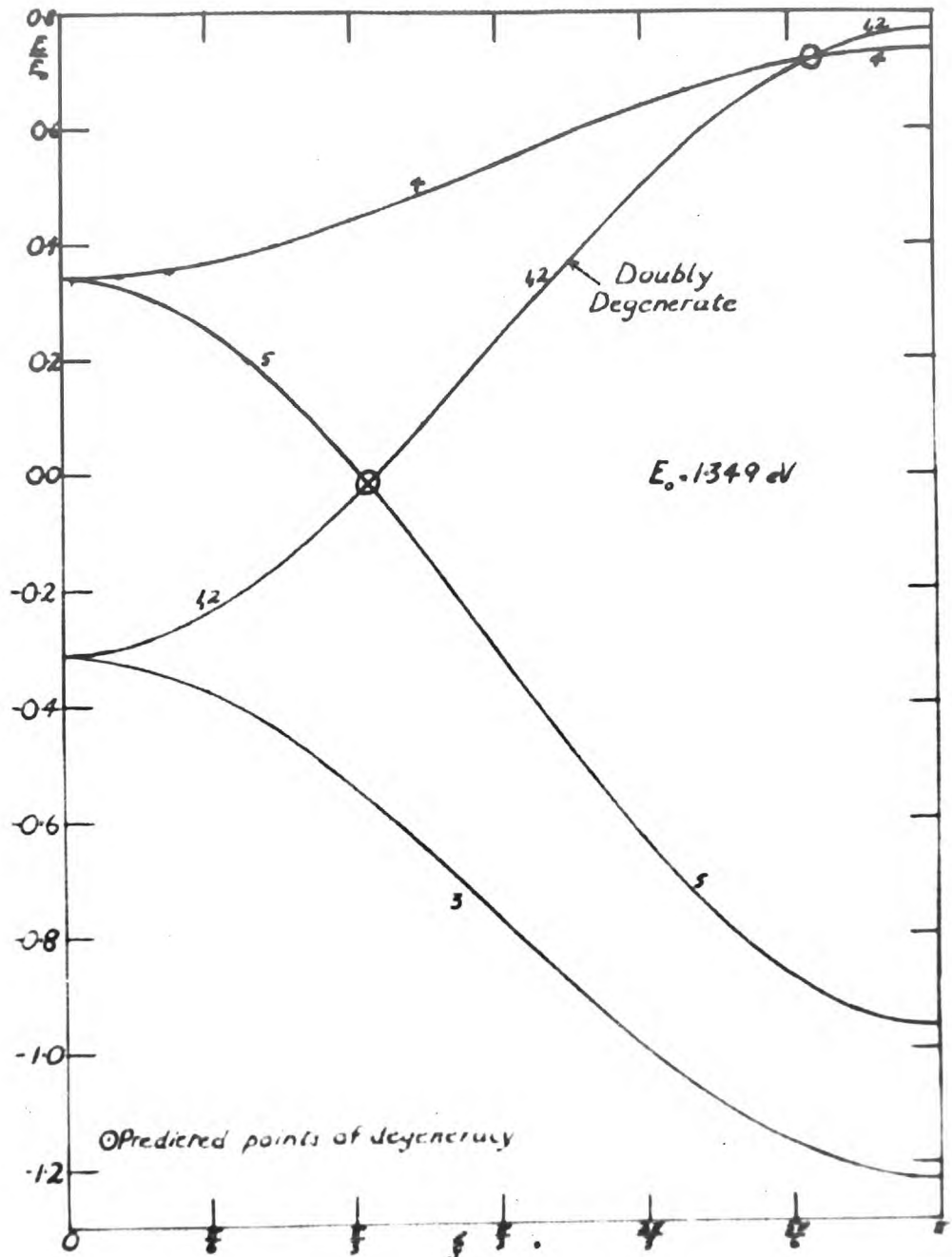


Fig 11

APPROXIMATE SOLUTIONS OF SECULAR EQUATION.

(110) DIRECTION.

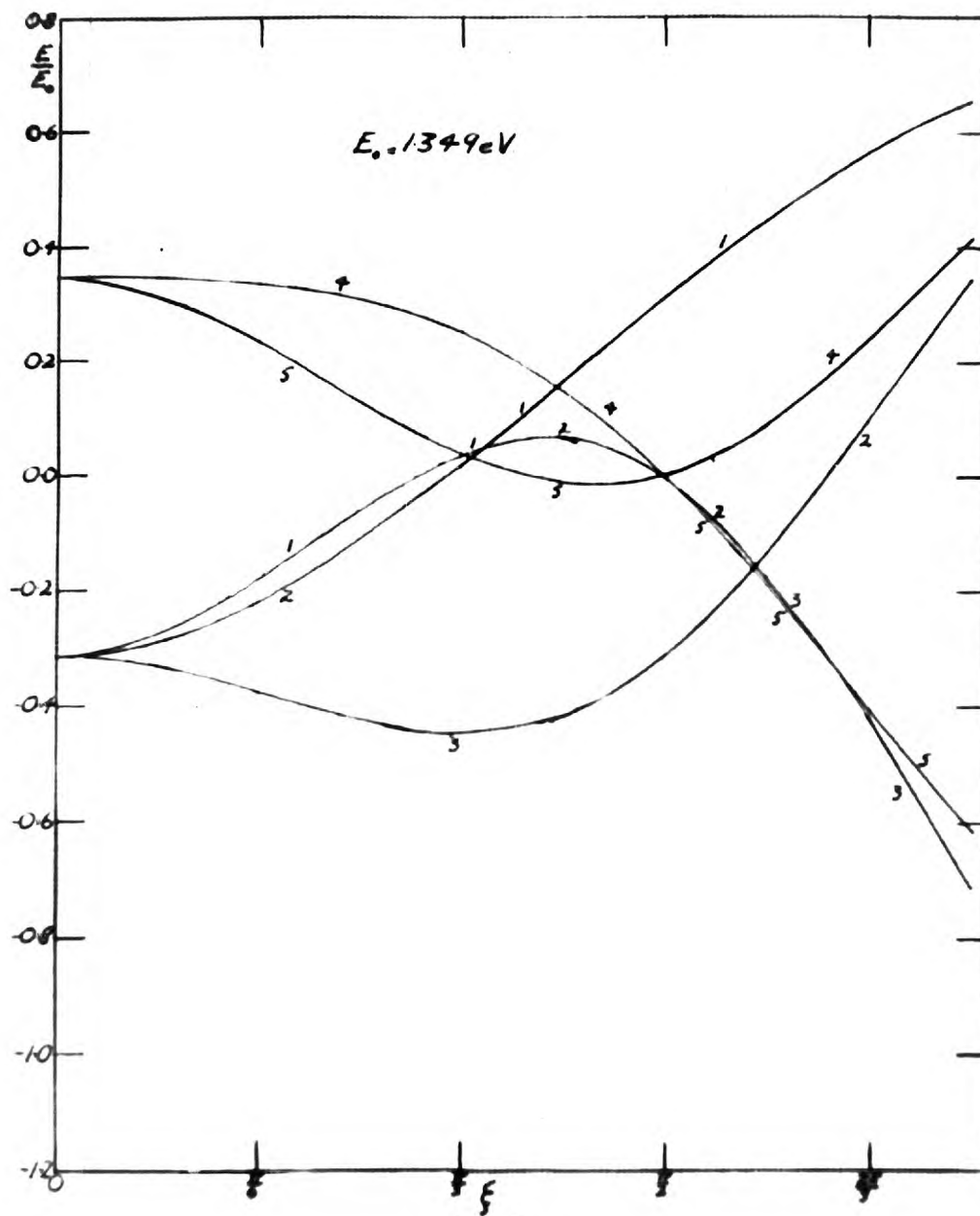


Fig 12

APPROXIMATE SOLUTIONS OF SECULAR EQUATION.

(111) DIRECTION.

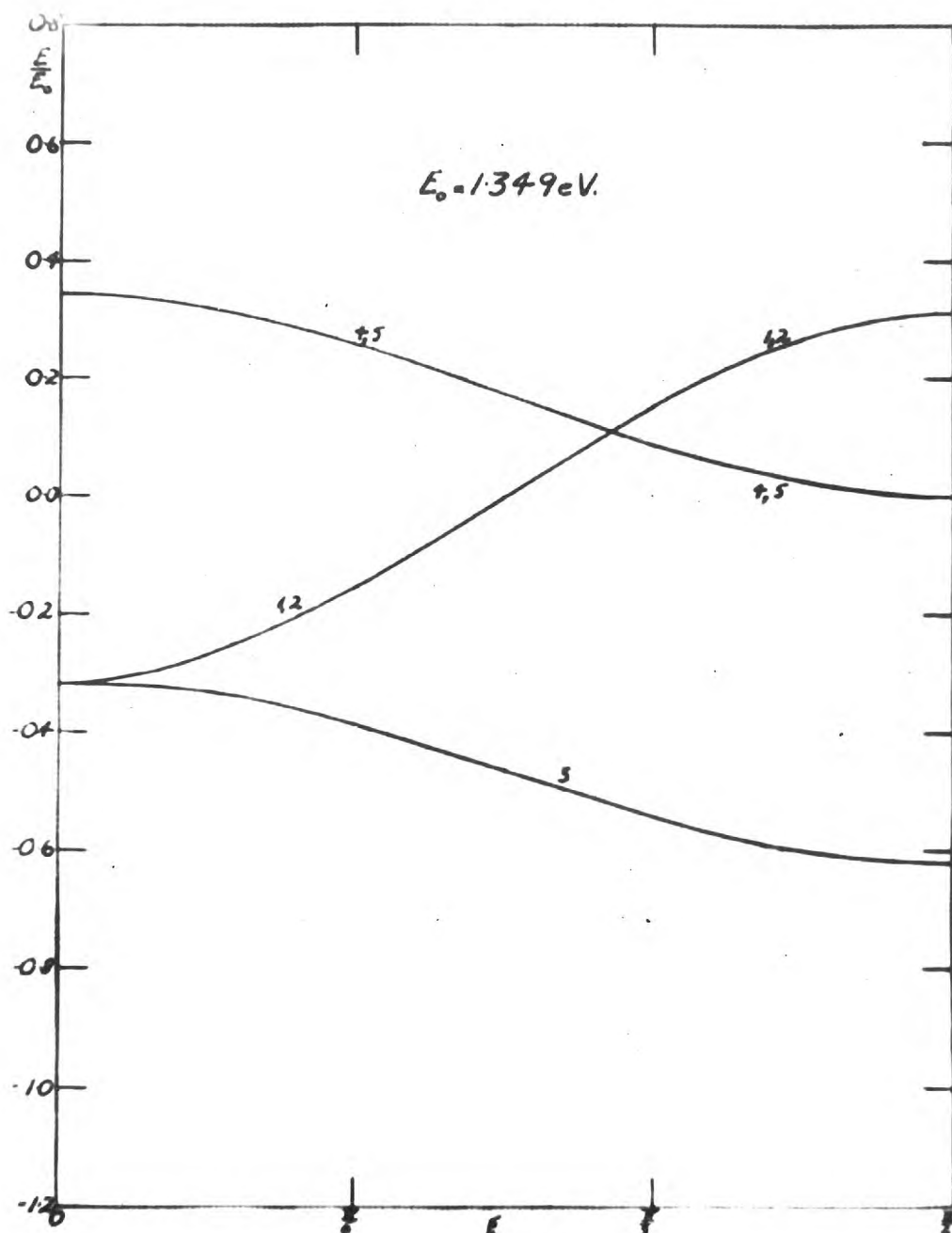


Fig. 13

point in k -space always belongs to the same solution, the next highest to another and the lowest to the third solution. This point is considered again in Chapter VII but the rule given above is supported by two further arguments.

(1) Near a point of degeneracy the E - k curves are as shown below.



E - k curves thro' point of degeneracy.

Fig.14.



E - k curves passing very near to same point.

Fig.15.

(ii) Some of the degeneracies are removed when the quintic is solved exactly and the shape of the resulting E - k curves support the above rule, e.g. compare Figs.13 and 27.

Applying the rule to the E - k curves, the energy contours were found to be smooth curves also. The E - k curves are simply graphs showing the variation of E/E_0 with k_x (or ξ) for each value of η (from 0 upwards in steps of $\pi/12$), there ^{being} three curves on each graph, corresponding to the three solutions of the cubic equation. A set of such graphs was plotted for each plane from $\int=0$ to $\int=\pi$. Typical graphs are shown in Figs.11,12,13,16 and 17. the additional two curves representing solutions of the quadratic. Apart from assisting in deducing the above rule, they were used for interpolation between the calculated values of E/E_0 in plotting the energy contours.

In order to obtain a clear picture of the way, in which E varies with k , it is desirable to know the shape and spacing of the surfaces of constant energy in k -space. These surfaces will

obviously intersect a given plane in k -space in a series of contours. Such contours were plotted at intervals of .05 in k/ξ for each plane from $f=0$ to $f=\pi$. There were three such sets, one for each solution of the cubic, these being distinguished by the suffices 1, 2, 3 in descending order of magnitude. The contours for the plane $f=\pi/6$ are shown in Figs. 10-22, the last two corresponding to the solutions of the quadratic equation.

(c) Solution of the Quadratic Equation.

After removal of the cubic factor from the quintic equation, the quadratic equation remaining is:-

$$\begin{vmatrix} H_{44}-E & H_{45} \\ H_{45} & H_{55}-E \end{vmatrix} = 0$$

or:-

$$E^2 + \alpha E + \beta = 0$$

where:-

$$\alpha = -H_{55} - H_{44}$$

and

$$\beta = H_{44}H_{55} - H_{45}^2$$

Then:-

$$\alpha^2 - 4\beta = (H_{44} - H_{55})^2 + 4H_{45}^2$$

$$\begin{aligned} \text{Now:- } H_{44} - H_{55} &= \frac{4}{3} \left[\{3A_4 + (A_4 + 4A_5)\} \cos f \cos \eta + (-3A_5 - 2A_4 + A_5)(\cos \eta \cos f + \cos f \cos \eta) \right] \\ &= \frac{4}{3} \left[4(A_4 + A_5) \cos f \cos \eta - 2(A_4 + A_5)(\cos \eta \cos f + \cos f \cos \eta) \right] \end{aligned}$$

Put:-

$$B_1 = \frac{4}{3} (A_4 + A_5)$$

$$\text{Then:- } \alpha^2 - 4\beta = 4B_1^2 [2 \cos f \cos \eta - (\cos \eta \cos f + \cos f \cos \eta)]^2 + 12B_1^2 (\cos \eta \cos f - \cos f \cos \eta)^2$$

Put:-

$$\cos f \cos \eta = Z ; \quad \cos \eta \cos f = X ; \quad \cos f \cos \eta = Y$$

$$\begin{aligned} \text{Then:- } \alpha^2 - 4\beta &= 4B_1^2 \{ [2Z - (X+Y)]^2 + 3(X-Y)^2 \} = 16B_1^2 [X^2 + Y^2 + Z^2 - XY - YZ - ZX] \\ &= 16B_1^2 [(X+Y+Z)^2 - 3(XY + YZ + ZX)] \end{aligned}$$

Also:-

$$\begin{aligned} -\alpha &= H_{44} + H_{55} = \frac{4}{3} (A_4 - 2A_5) (\cos f \cos \eta + \cos \eta \cos f + \cos f \cos \eta) \\ &= 2B_2 (X + Y + Z) \end{aligned}$$

where:-

$$B_2 = \frac{4}{3} (A_4 - 2A_5)$$

and the roots of the quadratic are:-

$$E = B_2 (X + Y + Z) \pm 2B_1 \sqrt{(X + Y + Z)^2 - 3(XY + YZ + ZX)}$$

APPROXIMATE SOLUTIONS OF SECULAR EQUATION.

$$\underline{J = \frac{1}{2} : 7 = \frac{5}{12}}$$

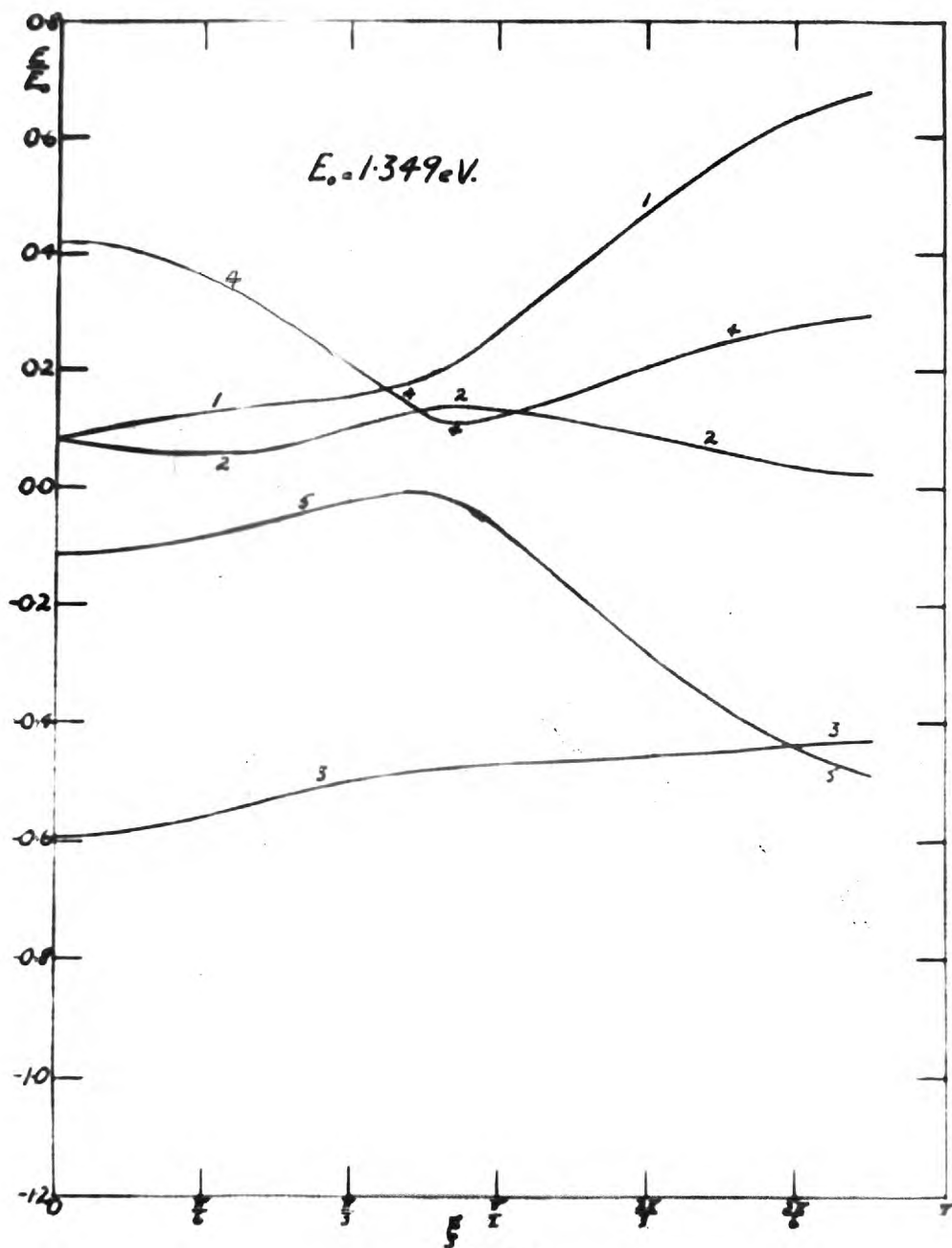


Fig. 16

APPROXIMATE SOLUTIONS OF SECULAR EQUATION.

$J = \frac{7}{2} ; \gamma = \frac{1}{2}$

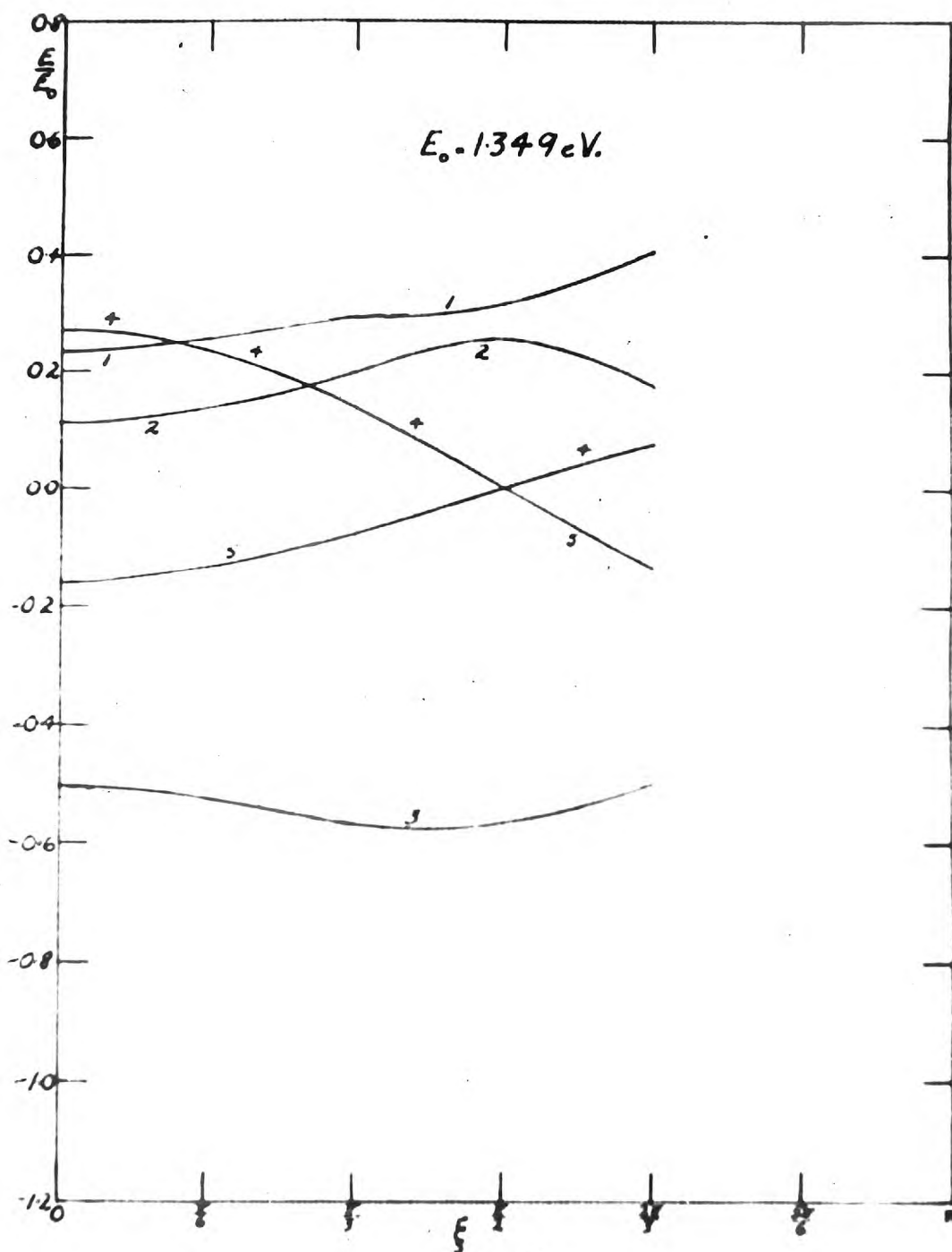


Fig 17

APPROXIMATE
CONTOURS OF CONSTANT ENERGY IN $S-\frac{1}{2}$
PLANE.

$$\frac{E_1}{E_0}$$

$$E_0 = 1349 \text{ eV.}$$

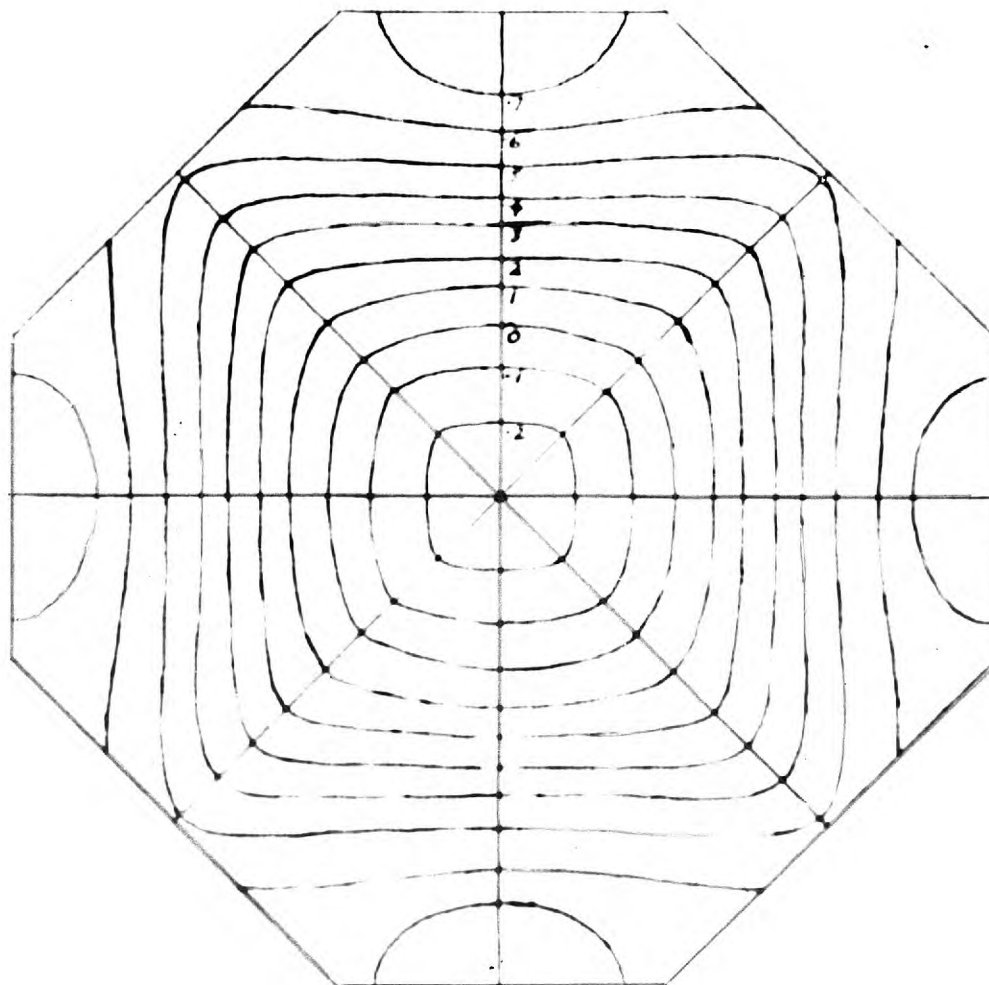


Fig 18

APPROXIMATE
CONTOURS OF CONSTANT ENERGY IN $J-K$
PLANE.

$$\frac{E_1}{E_2}$$

$$E_1 = 1.349 \text{ eV.}$$

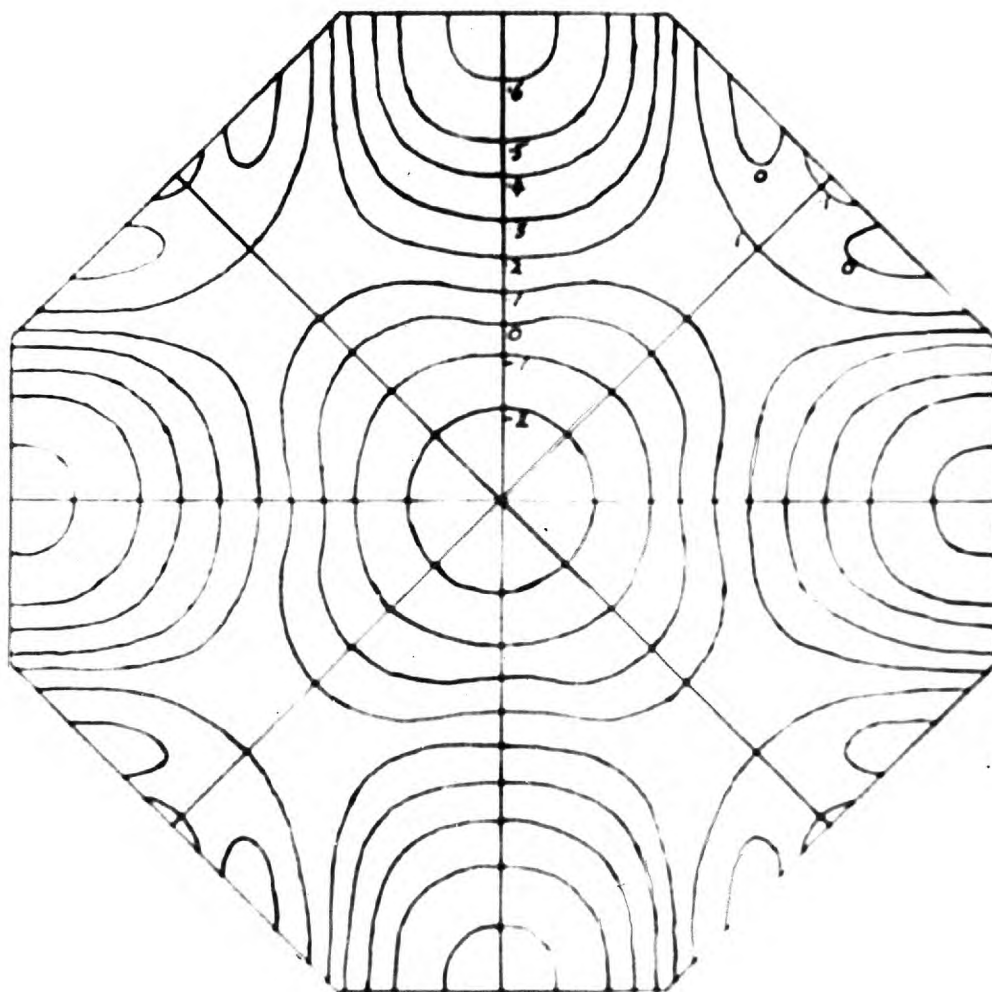


Fig 19

APPROXIMATE
CONTOURS OF CONSTANT ENERGY IN S-E
PLANE.

$$\frac{E_1}{E_2}$$

$$E_2 = 1.349 \text{ eV.}$$

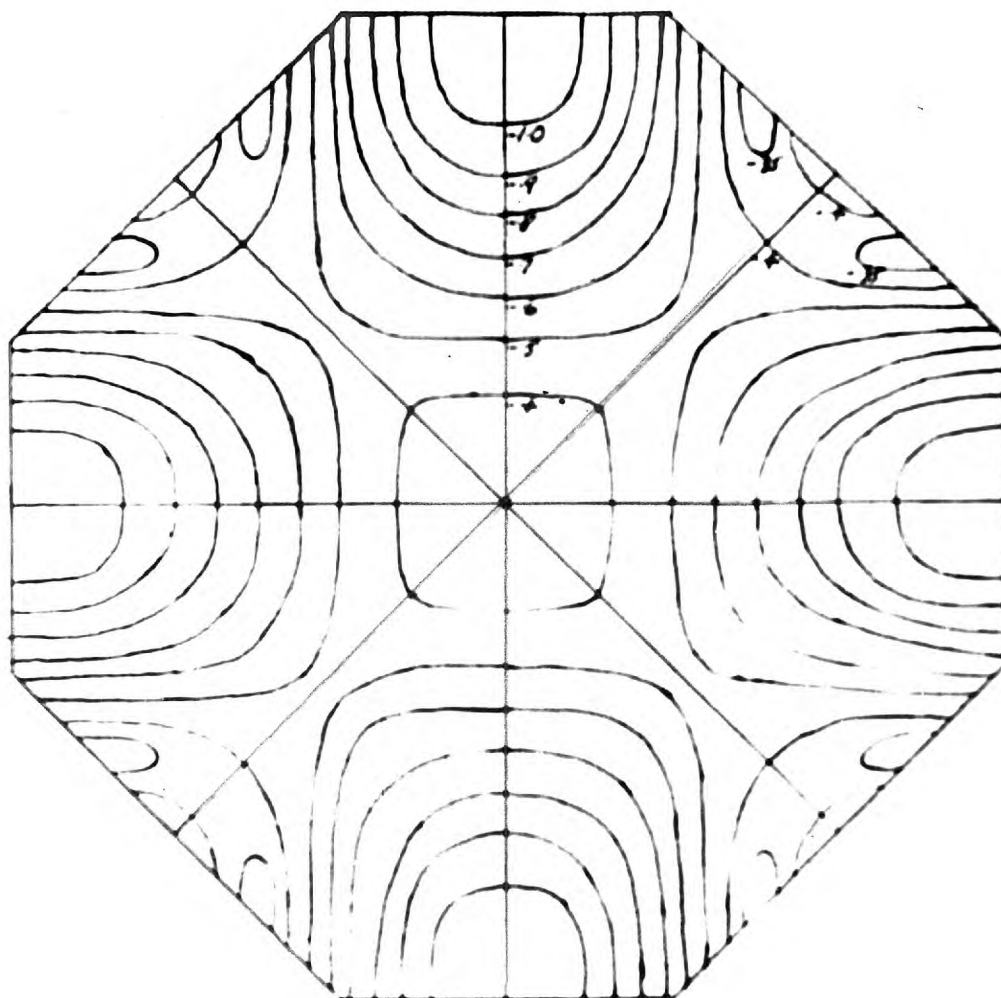


Fig 20

APPROXIMATE
CONTOURS OF CONSTANT ENERGY IN S-f
PLANE.

$$\frac{E_f}{E_0}$$

$$E_0 = 1.349 \text{ eV.}$$

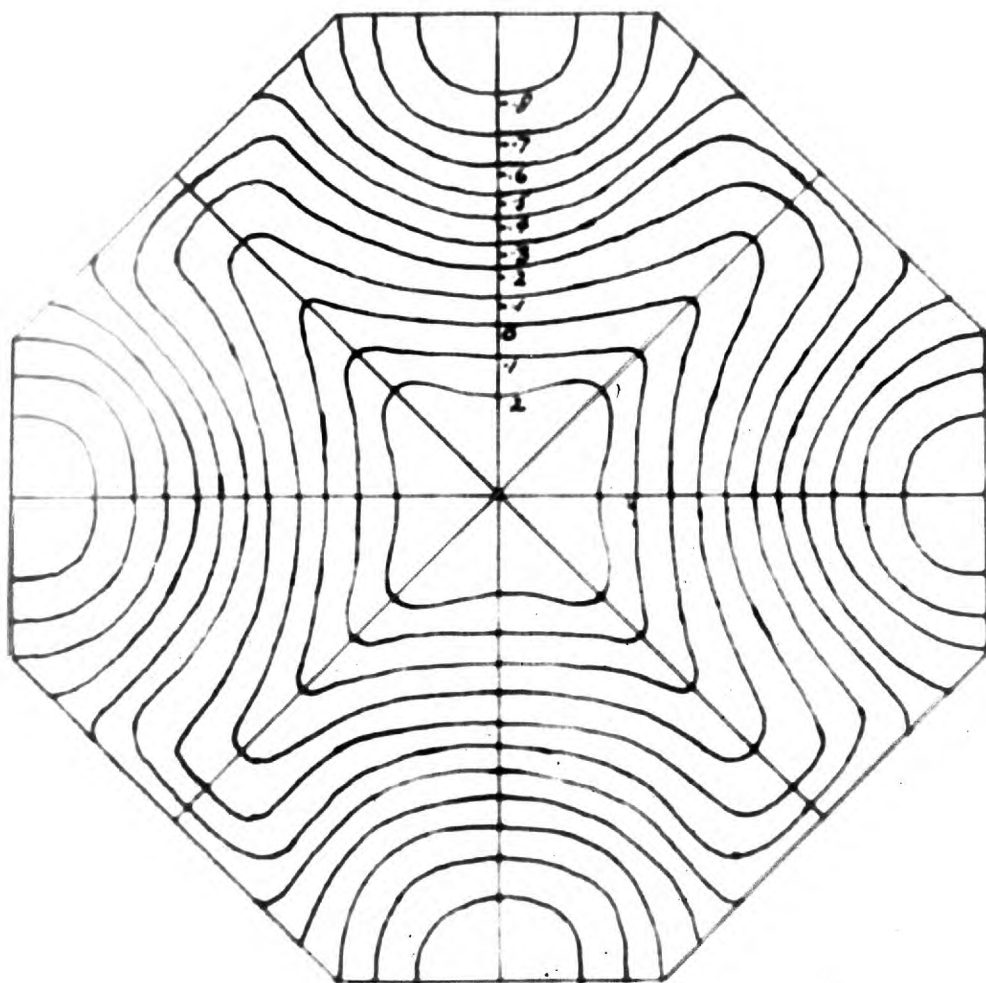


Fig. 22

As before, these are seen to be symmetrical about the planes $\xi=0; \eta=0; \zeta=0; \xi=\eta; \eta=\zeta; \zeta=\xi$, as they should be.

The roots of the quadratic were evaluated at the same points in k -space as for the cubic, giving the same check on the solutions. For easy comparison with those of the cubic they were expressed in units of E_0 . Putting:-

$$\sigma_1 = \frac{2B_1}{E_0} = .4523 \quad \text{and} \quad \sigma_2 = \frac{B_2}{E_0} = .1139$$

$$R = X+Y+Z = \sum \cos \xi \cos \eta; P = 3 \cos \xi \cos \eta \cos \zeta; Q = \sum \cos \xi$$

then:- $3(XY+YZ+ZX) = PQ$

$$\frac{E_4}{E_0} = \sigma_2 R + \sigma_1 \sqrt{R^2 - PQ} \quad \text{and} \quad \frac{E_5}{E_0} = \sigma_2 R - \sigma_1 \sqrt{R^2 - PQ}$$

An example of the calculation involved is given at the end of this chapter. Referring again to Figs. 11, 12 and 13, it is at once evident that the solutions E_4 and E_5 cover almost the same range of E as those of the cubic, i.e. the Γ_1 and Γ_2 bands overlap completely and the approximation $A_6=0$ must therefore be a poor one. This point is discussed later.

$E-k$ curves and energy contours were drawn just as for the cubic.

TYPICAL CALCULATIONS IN SOLVING THE CUBIC EQUATION. $J = \frac{\pi}{6}$

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)
ξ	η	$\cos \xi \cos \eta$	$\cos \xi + \cos \eta$	$\sin^2 \xi$	$\sin^2 \eta$	$\sin^2 \xi \sin^2 \eta$	α	β	γ	$\lambda = \frac{1}{2\sqrt{\alpha^2 - \beta}}$	$G = \gamma - 3\beta\alpha + 2\lambda$	$\cos 3\theta = \frac{-4G}{\lambda^3}$	θ	$z_1 = \lambda \cos \theta$	$z_2 = \lambda \cos(\theta + \frac{2\pi}{3})$	$z_3 = \lambda \cos(\theta + \frac{4\pi}{3})$	$E/E_0 = \frac{z_1 - 3139\alpha}{z_2 - 3139\alpha}$	$E/E_0 = \frac{z_2 - 3139\alpha}{z_3 - 3139\alpha}$	$E/E_0 = \frac{z_3 - 3139\alpha}{z_1 - 3139\alpha}$
0	0	1.00000	2.00000	0	0	0	.91069	.82735	.75000	.089582	.00017972	-1.00000	60 00	.044791	.089582	.044791	-.241	-.375	-.241
15	0	.96593	1.96593	.0016148	0	0	.88950	.78913	.69841	.091220	.00017963	-.94660	53 44	.053960	.090675	.036714	-.225	-.370	-.243
	15	.93302	1.93186		.0016148	.00043269	.86869	.75236	.64986	.095034	.00020944	-.97608	55 49	.053394	.094780	.041386	-.219	-.367	-.231
30	0	.86603	1.86603	.0060265	0	0	.82736	.68101	.55799	.11857	.00036525	-.87645	50 24.5	.075565	-.11691	.041346	-.184	-.377	-.218
	15	.83652	1.83196		.0016148	.0016148	.80769	.64843	.51785	.12543	.00047302	-.95882	54 30	.072837	-.12485	.052015	-.181	-.378	-.202
	30	.75000	1.73206		.0060265	.0060265	.75000	.55648	.40925	.15518	.00092000	-.98478	56 40	.085241	-.15491	.069644	-.150	-.390	-.166

$\alpha = \frac{1}{3}[(3) + .866(4)]$; $\beta = \frac{1}{3}\{[-.75 + .866(4)](3) - (5) - (6) - (7)\}$; $\gamma = (3)[- .75(3) - (7)] - .866(5)\cos \xi - .866(6)\cos \eta + .15528(7)$, where (a) $\equiv$ column (a).

TYPICAL CALCULATIONS IN SOLVING THE QUADRATIC EQUATION. $J = \frac{\pi}{6}$

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
ξ	η	$\cos \xi \cos \eta$	$\cos \xi + \cos \eta$	$R = (3) + .86603(4)$	$P = 2.59809(3)$	$Q = .86603 + (4)$	$\sqrt{R^2 - PQ}$	$E/E_0 = \frac{.11376(5) + .42543(8)}{.11376(5) - .42543(8)}$	$E/E_0 = \frac{.11376(5) - .42543(8)}{.11376(5) + .42543(8)}$
0	0	1.00000	2.00000	2.73207	2.59809	2.86603	.13417	.368	-.254
15	0	.96593	1.96593	2.66850	2.50957	2.83196	.11786	.354	-.254
	15	.93302	1.93186	2.60607	2.42407	2.79789	.096538	.338	-.255
30	0	.86603	1.86603	2.48208	2.25002	2.73206	.11632	.332	-.233
	15	.83652	1.83196	2.42307	2.17335	2.69799	.087131	.312	-.239
	30	.75000	1.73206	2.25000	1.94857	2.59809	0	.260	-.260

Chapter VI.

Derivation of $N(E)$ Curve.

Consider the electrons in unit volume of a metal. Then the Pauli principle states that not more than two of these electrons may be associated with each cell, volume h^3 , of momentum (p) space, i.e. there are two possible corresponding states, one for each direction of spin. Since $p = \hbar k$, there is therefore a volume $\frac{8\pi^3}{2\pi}$ of k -space associated with these two states or $4\pi^2$ per state.

Consider two neighbouring surfaces of constant energy, E and $E + dE$, in k -space and let ds be a surface element of the former. Then the volume element between ds and the neighbouring surface is $ds \cdot \frac{dE}{|\text{grad } E|}$, to which correspond $\frac{1}{4\pi^2} \frac{ds dE}{|\text{grad } E|}$ states. Integrating over the surface of constant energy E , the total number of states in the energy range E to $E + dE$ is hence:-

$$N(E)dE = \frac{1}{4\pi^2} \int \frac{ds}{|\text{grad } E|} dE$$

$$\text{or } N(E) = \frac{1}{4\pi^2} \int \frac{ds}{|\text{grad } E|}$$

Since numerical integration in three variables would obviously prove to be a very lengthy process, it was decided to use graphical methods. Three stages were involved for each solution E_i/E_c as follows.

(i) In each plane $\int = \text{constant}$ the area enclosed (A) by each energy contour was measured.

(ii) For each value of E_i/E_c , a graph was drawn giving the variation of A with $\int$. The area under this graph was then measured, giving thereby the volume K of k -space enclosed by the surface $E_i/E_c = \text{constant}$.

(iii) The difference in volume, ΔK , for consecutive energy

surfaces was calculated and taken as the value of $N(E)$ at the energy value $E + \frac{1}{2}\Delta E$ midway between those of the two surfaces involved, expressed in arbitrary units, i.e.:-

$$N(E) = \frac{1}{4\pi^2} \iint \frac{ds}{|\text{grad } E|} \approx \frac{1}{4\pi^2} \cdot \frac{1}{\Delta E} \iiint ds dk = \frac{1}{4\pi^2} \frac{\Delta K}{\Delta E} \propto \Delta K$$

where $\Delta E (=0.05E_0)$ is the constant energy interval between consecutive surfaces.

These stages will now be considered in detail.

(i) The areas A were measured (a) by counting squares and (b) by planimeter. It was found that the accuracy of (b) was no greater than that obtainable by (a) and was often worse and it was therefore decided to use method (a), checking afterwards by method (b) in order to avoid any large errors due to slips in counting.

(ii) The same procedure for measuring areas was used as in (i). It was found essential to visualize the general shape of each energy surface, particularly in finding the maximum value of $\int$ reached by a surface. Some surfaces consisted of several independent sheets and the volume enclosed by each sheet was calculated separately. For both points it was found advantageous to draw the energy contours and certain $E-k$ curves for the hexagonal face. There proved to be considerable latitude in the possible shape of some of the $A-\int$ curves but this was unavoidable without solving the cubic and quadratic equations over many more planes $\int = \text{constant}$.

(iii) The taking of first differences ΔK as a measure of $N(E)$ is a definite approximation. Theoretically it would be better to

find the slope of the $K-E$ curve but it was felt that any graphical method of doing this would be subject to at least as much error as the method actually employed. A better approximation could be obtained by use of a suitable difference formula but it is found that $\frac{d^2K}{dE^2}$ is small everywhere so that the approximation used should be a good one.

As a check on the accuracy of the whole procedure the area under each $N(E)$ curve can be measured. When reduced to the correct units, this should equal 2, the number of states per atom corresponding to each wave function in the first B.Z. where no differentiation has been made between positive and negative spin, as is the case here. The values so obtained all proved to be within 1% of the correct value. Since approximations fundamental to the tight-binding method and others involved in the actual derivation of the energy contours are likely to introduce at least as large an error as this, the graphical methods employed for obtaining the $N(E)$ curves seem quite adequate for the purpose.

Finally the total $N(E)$ curve, comprising the sum of those corresponding to the three solutions of the cubic and the two of the quadratic equation, was obtained and is shown in Fig. 23. This, of course, is the curve of importance in the discussion of electronic properties (see Chapter I). The ordinate scale has been reduced by one half, thereby giving a total area under the curve corresponding to five states per atom of either spin; the constituent curves, from which it is formed, are also shown. An $N(E)$ curve for the three solutions of the cubic equation only,

FIRST APPROXIMATION TO DENSITY OF STATES CURVE

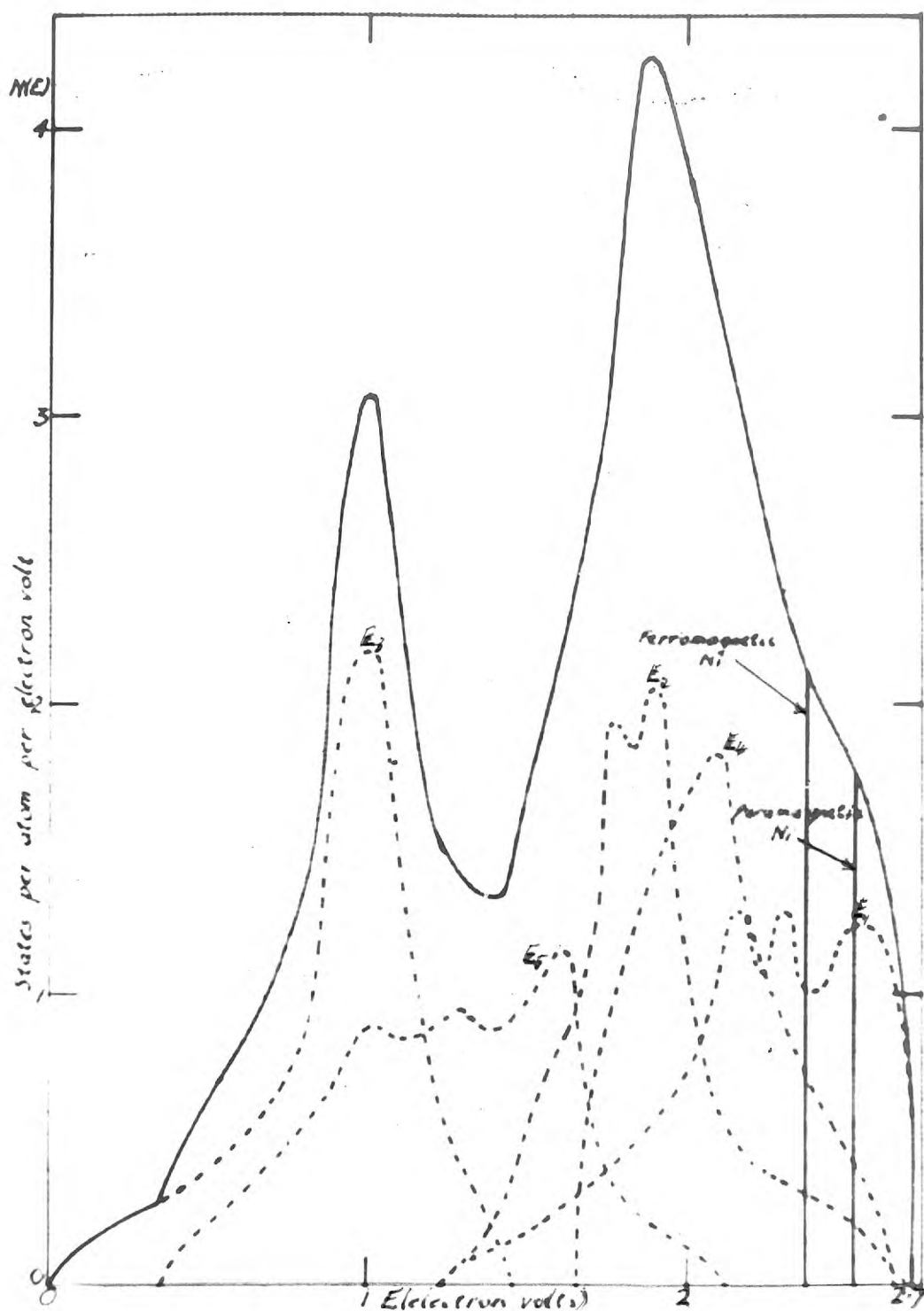


Fig. 23.

DENSITY OF STATES CURVE CORRESPONDING TO CUBIC
SECULAR EQUATION.

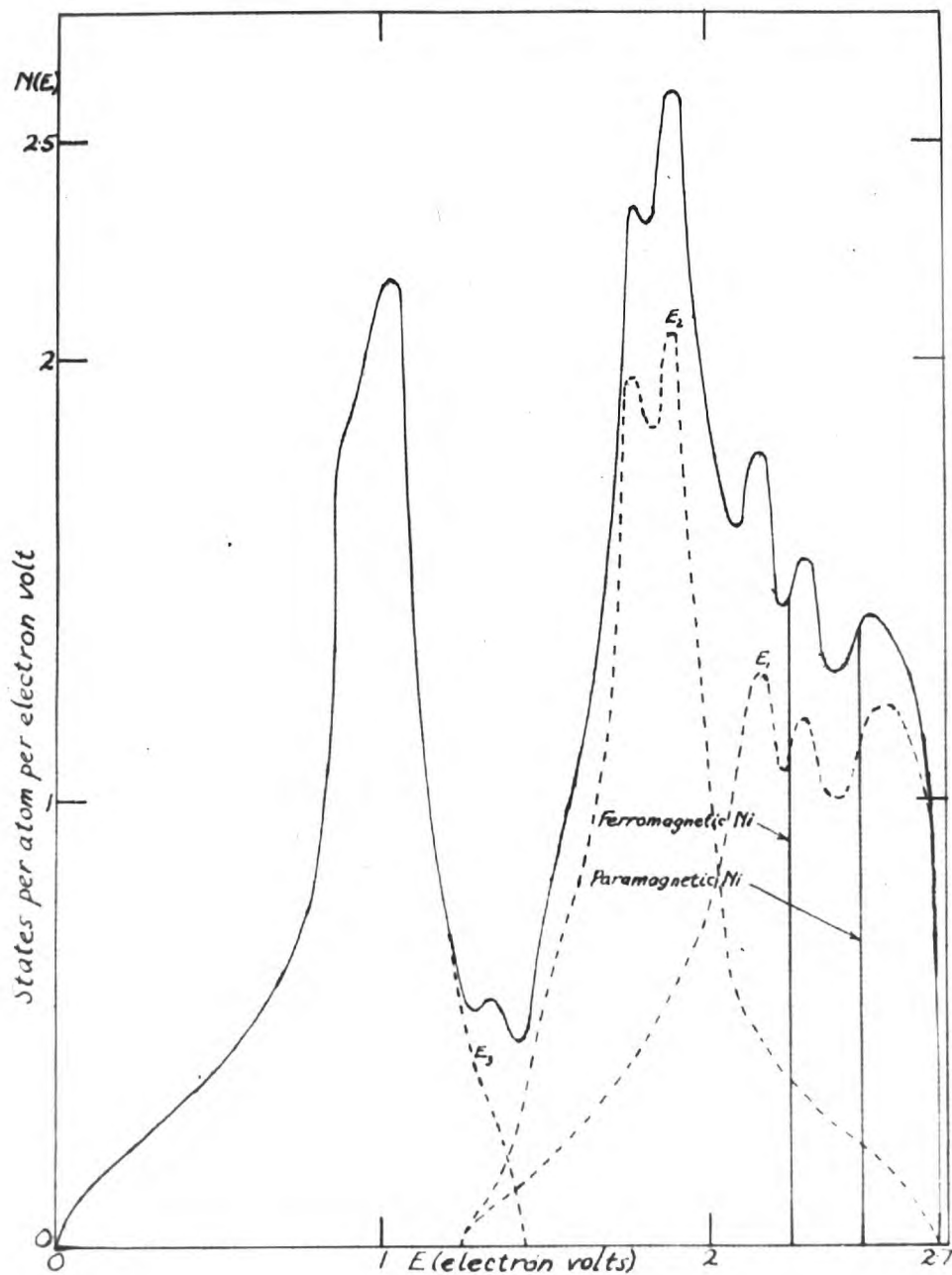


Fig. 23a

which is necessary in Part II of this thesis, was also constructed (see Fig. 23a).

Certain results may be deduced from Fig. 23, which will be given here for comparison with those obtained from the exact solution of the secular equation; their calculation is fully discussed in Chapter VIII.

(a) The energy limits of both Γ_3 and Γ_5 bands all occur at the centres of the square faces of the first B.Z. and are as follows.

$$\text{Bottom of } \Gamma_5 \text{ band} = (-1 - \beta_2)E_c = -4(A_1 + 2A_2) = -1.658 \text{ eV} \quad \text{Bandwidth } 2.696 \text{ eV}$$

$$\text{Top of } \Gamma_5 \text{ band} = (1 - \beta_2)E_c = 4A_1 = 1.040 \text{ eV}$$

$$\text{Bottom of } \Gamma_3 \text{ band} = (-\epsilon_1 - 2\epsilon_2)E_c = -4(5A_4 + 2A_5) = -1.301 \text{ eV} \quad \text{Bandwidth } 2.295 \text{ eV}$$

$$\text{Top of } \Gamma_3 \text{ band} = (-\epsilon_1 + 2\epsilon_2)E_c = 4(A_4 + 2A_5) = 0.994 \text{ eV}$$

Two diagrammatic representations of these results are given in Figs. 24 and 25. It is at once obvious that the bands arising from

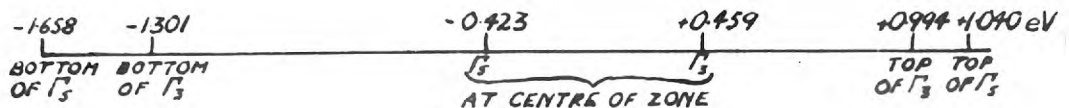


Fig. 24

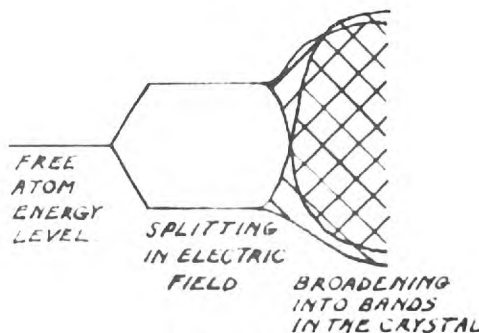


Fig. 25

the Γ_3 and Γ_5 levels overlap completely so that the consideration of each band separately, i.e. neglect of A_6 , is likely to be a

poor approximation. The total width of the 3d band, viz. 2.698eV , is, however, unaffected by this.

(b) At the centre of the zone, $k=0$, the five solutions of the secular equation form one triply- and one doubly-degenerate level with an energy separation of 0.880eV .

(c) The value of the degeneracy temperature calculated from fig. 23 is $2.04 \times 10^3 \text{ }^\circ\text{K}$.

(d) The linear, low temperature, electronic heat coefficient, γ , deduced from fig. 23 is $1.15 \times 10^{-3} \text{ cal.mol}^{-1} \text{ deg}^{-2}$.

Chapter VII.

Exact solution of the Secular Equation.

(a) Method of Solution.

From a study of the $E(E)$ curve obtained by approximate solution of the secular equation, it was decided to solve the equation exactly over the range of energy values $0.5 < E/E_0 < 0.771$ ($2.35 < E < 2.70$ eV in fig. 23), a complete calculation being excessively laborious and unnecessary for many purposes. In effect only those solutions of equation 3.9 were found, which fell within this range. Further reference to the energy contours drawn for the approximate calculation indicated in what regions of the B.Z. such solutions were likely to be found.

Along certain directions in k -space the secular equation can be solved analytically as before.

(1) (100) direction. In this case E_{nm} ($n=1,2,3; m=4,5$) are identically zero so that the solutions already obtained are the exact solutions, viz.:-

$$\begin{aligned} E_{1,2} &= 4A_2 + 4(A_2 - A_1) \cos \xi \\ E_3 &= -4A_1 + 8A_2 \cos \xi \\ E_4 &= 4A_4 - 8A_5 \cos \xi \\ E_5 &= \frac{4}{3} [-A_4 - 4A_5 + (4A_4 - 2A_5) \cos \xi] \end{aligned}$$

(11) (110) direction. Putting $\sin \xi = \sin \eta = p$ and $\cos \xi = \cos \eta = q$, the equation becomes:-

$$\begin{vmatrix} 4q[(q+1)A_2 - A_1] - E & -4A_3p^2 & 4q[2A_2 - qA_1] & 0 & 0 \\ -4A_3p^2 & 4q[(q+1)A_2 - A_1] - E & 0 & 0 & 0 \\ 0 & 0 & 4q(2A_2 - qA_1) - E & 0 & -\frac{8}{\sqrt{3}}A_6p^2 \\ 0 & 0 & 0 & 4q[qA_4 - 2A_5] - E & 0 \\ 0 & 0 & -\frac{8}{\sqrt{3}}A_6p^2 & 0 & \frac{4}{3}q[4A_4 - 2A_5 - q(4A_5 + A_4)] - E \end{vmatrix} = 0$$

Three roots are identical with one of the quadratic and two of

the cubic roots already obtained, viz.:-

$$E_1 = 4A_4 \cos^2 \xi - 8A_5 \cos \xi$$

$$E_{2,3} = 4A_2 \cos^2 \xi + 4(A_2 - A_1) \cos \xi \pm 4A_1 \sin^2 \xi$$

The remaining two are given by the quadratic equation:-

$$E^2 + [(4A_1 + 16A_5/3 + 4A_4/3)q^2 + (8A_5/3 - 16A_4/3 - 8A_2)q]E + \frac{16q^2}{3} [A_1(4A_5 + A_4)q^2 - (8A_2A_5 + 2A_2A_4 + 4A_1A_4 - 2A_1A_5)q + 4A_1(2A_2 - A_5)] - \frac{64A_1^2 \beta^4}{3} = 0$$

The five solutions are shown in Fig. 26.

(111) (111) direction. Putting $\sin \xi = \sin \eta = \sin \zeta = p$ and $\cos \xi = \cos \eta = \cos \zeta = q$

the equation becomes:-

$$\begin{vmatrix} 4(2A_2 - A_1)q^2 - E & -4A_1p^2 & -4A_1p^2 & -4A_1p^2 & \frac{4}{\sqrt{3}}A_1p^2 \\ -4A_1p^2 & 4(2A_2 - A_1)q^2 - E & -4A_1p^2 & 4A_1p^2 & \frac{4}{\sqrt{3}}A_1p^2 \\ -4A_1p^2 & -4A_1p^2 & 4(2A_2 - A_1)q^2 - E & 0 & -\frac{8}{\sqrt{3}}A_1p^2 \\ -4A_1p^2 & 4A_1p^2 & 0 & 4(A_2 - 2A_5)q^2 - E & 0 \\ \frac{4}{\sqrt{3}}A_1p^2 & \frac{4}{\sqrt{3}}A_1p^2 & -\frac{8}{\sqrt{3}}A_1p^2 & 0 & 4(A_5 - 2A_1)q^2 - E \end{vmatrix} = 0$$

By row and column manipulation one root is found to be identical with one of the cubic roots already obtained, viz.:-

$$E_1 = 4[(2A_3 + 2A_2 - A_1) \cos^2 \xi - 2A_3]$$

The other four roots occur in two doubly-degenerate pairs given

by:- $E^2 - 4[(2A_2 - A_1 + A_4 - 2A_5 - A_3) \cos^2 \xi + A_3]E$

$$+ 16 \{ [(A_4 - 2A_5)(2A_2 - A_1 - A_3) - 2A_3^2] \cos^4 \xi + [A_3(A_4 - 2A_5) + 4A_3^2] \cos^2 \xi - 2A_3^2 \} = 0$$

The five solutions are shown in Fig. 27.

(iv) $\xi = \pi; \zeta = 0$ direction. As in (i) the matrix elements H_{nm} ($n=1,2,3;$

$m=4,5$) are identically zero so that the solutions are the same

as those obtained by neglect of A , viz.:-

$$E_{1,2} = \pm 4(A_1 + A_2) \cos \eta - 4A_2$$

$$E_3 = 4A_1$$

$$E_{4,5} = \frac{4}{3} [2A_5 - A_4 \pm 2(A_4 + A_5) \sqrt{(1 + 3 \cos^2 \eta)}]$$

EXACT SOLUTIONS OF SECULAR EQUATION.

(110) DIRECTION.

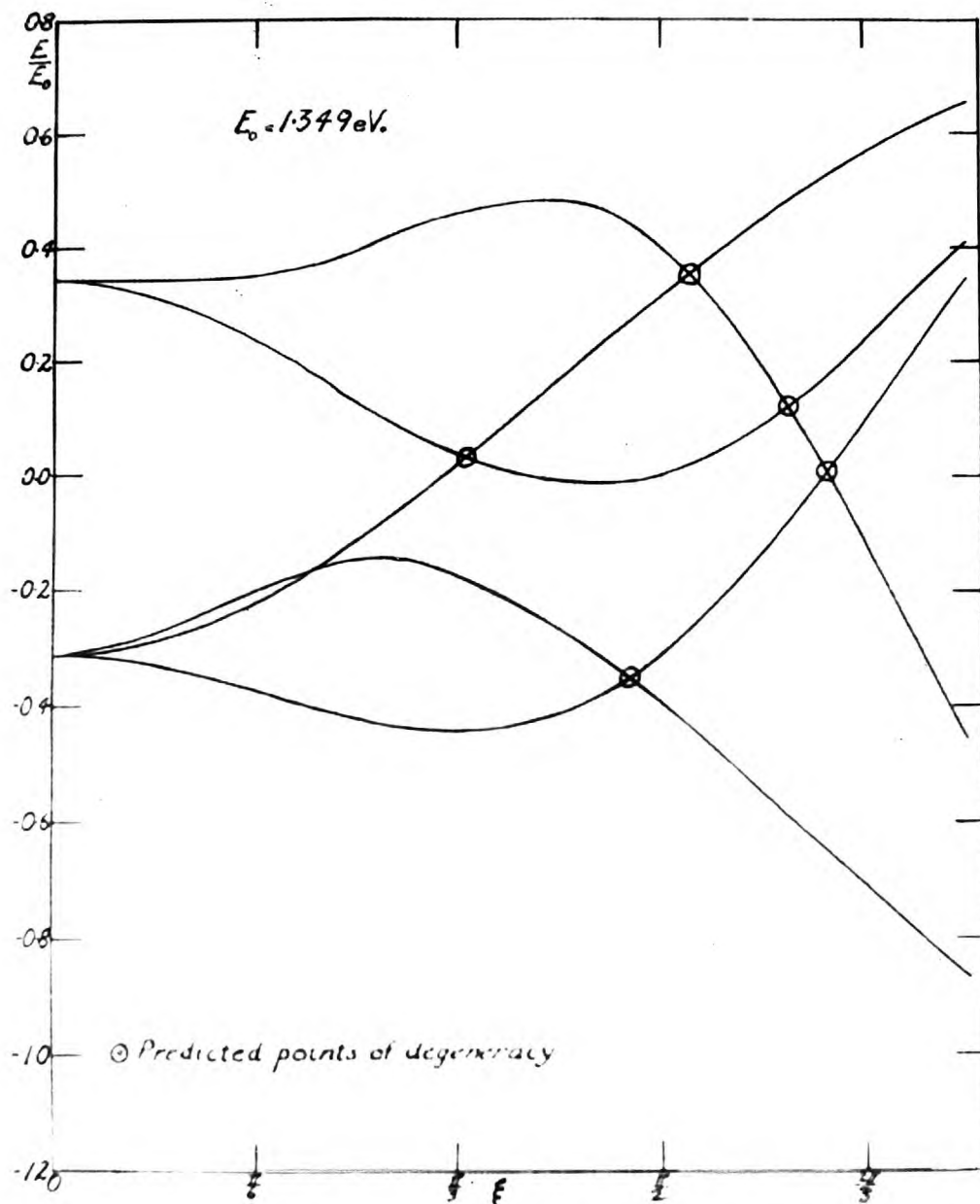


Fig 26

EXACT SOLUTIONS OF SECULAR EQUATION.

$\eta = 3\pi/4; \zeta = \pi/12$

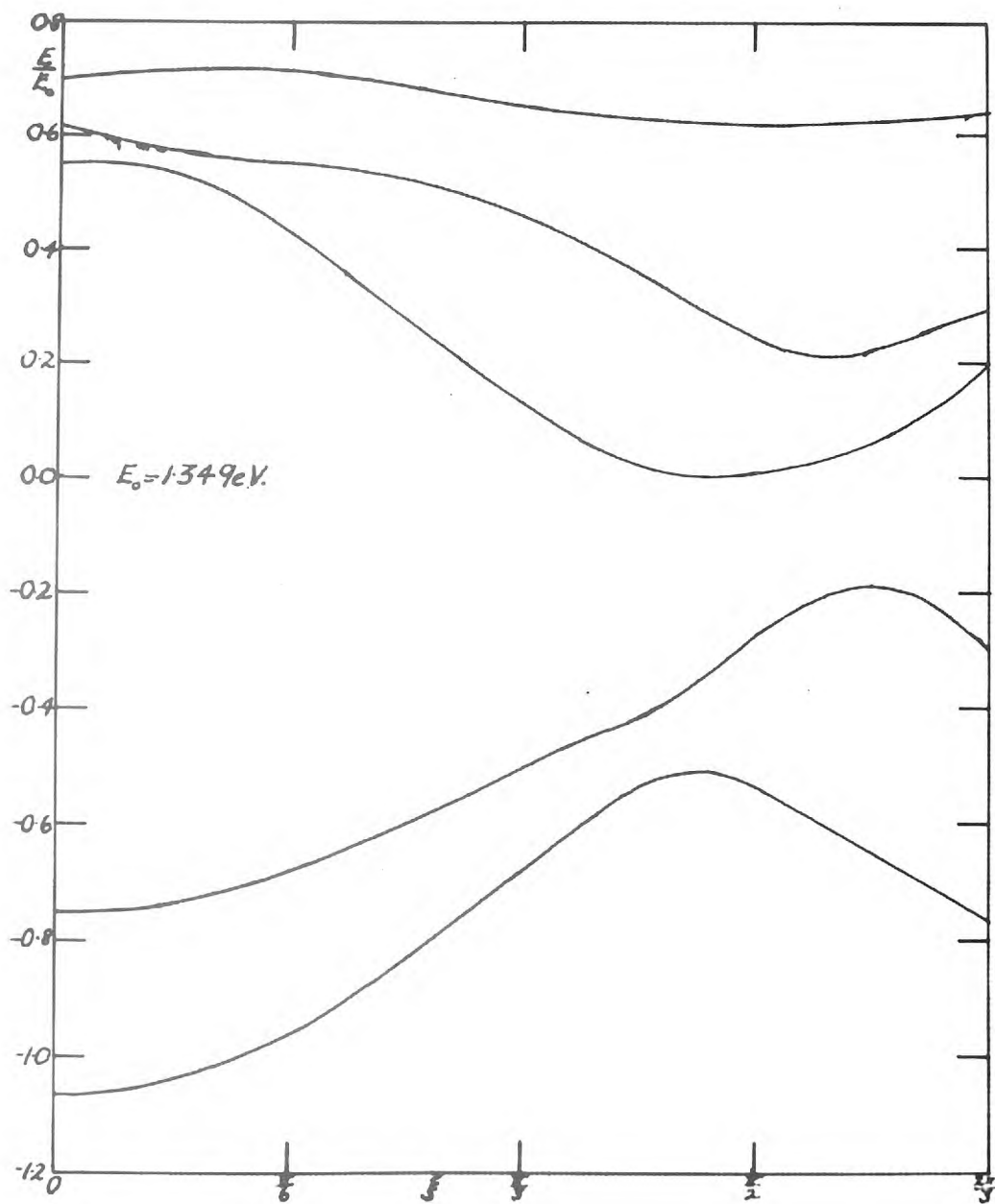


Fig. 28.

For the case of a general wave vector $\underline{k}$ various possible methods of solving the fifth degree secular equation were considered and are discussed briefly below.

(i) Newton's method. This necessitates complete expansion of the secular determinant, making the work laborious. A more serious objection is that it is certainly not convergent at all points of interest.

(ii) Use of the Rayleigh-Schrodinger perturbation formulae. The difficulty here is that often two of the solutions are nearly degenerate. The non-degenerate formula for 2nd order perturbation is then useless, while the degenerate formula can only give a rough approximation to the true solution.

(iii) Matrix method described by Fraser, Duncan and Gellar (1938). This proves to be a simple method for use with a desk calculating machine but does not converge rapidly unless the root required is widely separated from the remaining ones.

(iv) Crawford and Cross (1937) describe another iterative process, which they claim gives solutions accurate to 6 significant figures after 3 or 4 stages. Each stage, however, involves the diagonalizing of the determinant, which can be a very laborious process.

(v) Hicks (1940) describes a method of expanding the determinant $|a_{ij} - \lambda \delta_{ij}|$ in the corresponding polynomial form $\sum a_s \lambda^s$ but it involves numerical computation of the determinant for six equally-spaced values of λ (in the present case). This itself would be laborious, apart from which a fifth-degree equation has still to be solved.

(vi) Collatz (1945) devotes a complete chapter to eigenvalue problems of the type under consideration here but unfortunately it has not been possible to locate a copy of the required edition of this book.

(vii) Probably the quickest method of solution would be by digital computing machine but unfortunately the author did not have access to one. Some time would have to be spent in programming the problem, e.g. it would obviously be desirable to avoid expanding the determinant if possible.

For the various reasons indicated none of the above methods was considered suitable and the following procedure was therefore adopted. For a given wave vector $\underline{k}$ an estimate $\underline{x}$ of the required solution was made from the approximate solutions already obtained. This was substituted in the determinant, which was evaluated; from the value obtained a correction was applied to $\underline{x}$ and the process repeated until a solution correct to three D.P. was obtained. The symmetry of the problem reduced considerably the region of the B.Z. to be investigated, as already mentioned, but it was still necessary to obtain some 270 roots by the above method and check them at symmetrically equivalent points. For each root the determinant had to be evaluated about three times on the average.

For each wave vector $\underline{k}$ the secular equation 3.9 has five roots and a major problem, just as before, is that of collecting these roots into five sets, each set belonging to one B.Z. and having an associated energy band. As a first step the energy degeneracies arising from symmetry considerations, reality of

the Hamiltonian and accidental degeneracy may be investigated as indicated by Bouckaert, Smoluchowski and Wigner (1936) and by Herring (1937).

(b) Application of Group Theory to Problem.

The following points from the above-mentioned papers are relevant to the present work.

(1) No two Bloch wave functions with the same general wave vector $\underline{k}$, i.e. one whose group consists of the identity operator only, will have the same energy due to symmetry considerations or because of the reality of the Hamiltonian. (The group of a wave vector $\underline{k}$ is that subgroup of the group of crystal symmetry operations, ignoring translations, which leave $\underline{k}$ invariant or transform it into $\underline{k} + \underline{b}$, where $\underline{b}$ is a vector of the reciprocal lattice).

(ii) If each wave function for some given $\underline{k}$ is subjected to the group of crystal symmetry operations, a manifold of wave functions is generated, relative to which the group has a certain representation. Two such manifolds are equivalent or non-equivalent according as their associated representations are equivalent or not. For a crystal with an inversion centre isolated points of degeneracy between equivalent manifolds are very unlikely but endless curves of degeneracy may occur in $\underline{k}$ -space, but not lying in symmetry planes. Curves of degeneracy between inequivalent manifolds are only likely in symmetry planes.

(iii) At a point of accidental degeneracy the relevant wave functions will, in general, have different representations, which may be interchanged.

(iv) For a f.c.c. crystal the normal derivative of ϵ vanishes over the square faces of the B.Z. and along every line joining two opposite corners of a hexagonal face. ϵ must have sixfold rotational symmetry over a hexagonal face.

Following the arguments and notation of the papers referred to, the following deductions regarding degeneracy can be made for the present case.

(v) Due to symmetry there should be one triply degenerate level (ϵ_L^1) and one doubly degenerate one (ϵ_L) at $\underline{k} = 0$. A double degeneracy, arising from ϵ_L^1 , should occur along the (100) direction, and two double degeneracies along the (111) direction. The only other symmetry degeneracy (double) should occur at $(2\pi/a, \pi/a, 0)$.

(vi) If the Hamiltonian of a problem is real, it is possible for degeneracy, additional to that due to symmetry, to occur between a wave function and its complex conjugate. For a f.c.c. crystal it is easily shown that no degeneracy of this type can occur.

(vii) Various points of accidental degeneracy and curves of degeneracy between inequivalent manifolds in planes of symmetry must occur, as indicated in Figs. 11 and 26. Their prediction, however, depends on a knowledge of the relative energies of the five wave functions ψ_i (which will, in general, have different symmetry properties) for certain special wave vectors, e.g. $\underline{k} = (0, 0, 0), (2\pi/a, 0, 0)$, etc., so that most of these degeneracies are probably a result of the approximations of the calculation. This view is supported by the disappearance of a number of such degeneracies on passing from the approximate to the exact

solution of the quintic secular equation.

(c) Construction of $N(E)$ Curve.

All the above predicted degeneracies did, in fact, occur amongst the solutions of the quintic; only one other point of accidental degeneracy (in the (110) plane) was discovered. As in the case of the approximate solution, it was found that there was only one possible way to collect the energy values into five sets. Solutions must be interchanged at all points of accidental degeneracy in such a way that for every value of k the highest energy value belongs to B.Z.I, the next highest to B.Z.II and so on. Bouckaert, Smoluchowski and Wigner mention that such interchange is valid (see (111) above) and Manning and Chodorow (1939) in their work on W come to the same conclusion as reached here, but in neither case is any reason given. This procedure results in discontinuities in $\text{grad } E$ but they have no effect on $N(E)$ since on any given surface of constant energy in k -space such discontinuities occur only at isolated points and not over an area.

As before curves showing the variation of E with k were drawn for each value of η and $\int$ from 0 to π at intervals of $\pi/12$ and from these constant energy contours were drawn in the planes $\int = \nu\pi/12$ ($\nu = 0, 1, \dots, 12$) at intervals of $0.025E_c$ for each of the three sets of energy values involved in the energy range considered. Examples of the (E, k) curves and energy contours are shown in Figs. 11, 26-31. From these contours the three corresponding $N(E)$ curves were constructed by the same method of graphical integration as before. It was not possible to check

CONTOURS OF CONSTANT ENERGY IN J-O
PLANE.

EXACT SOLUTION $\frac{E_L}{E_0}$

$E_0 = 1.349 \text{ eV.}$

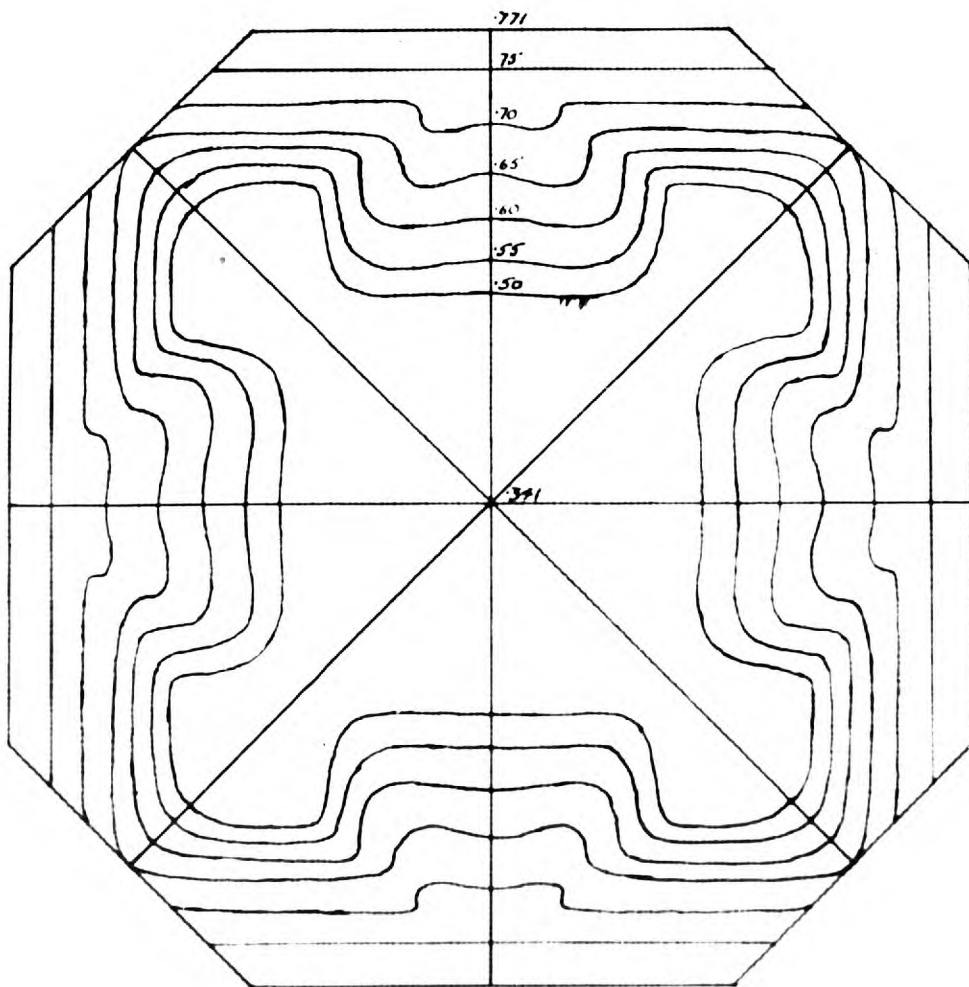


Fig. 29.

CONTOURS OF CONSTANT ENERGY IN $S=\pi/2$
PLANE.

EXACT SOLUTION $\frac{E_x}{E_0}$.

$E_0 = 1.349 \text{ eV.}$

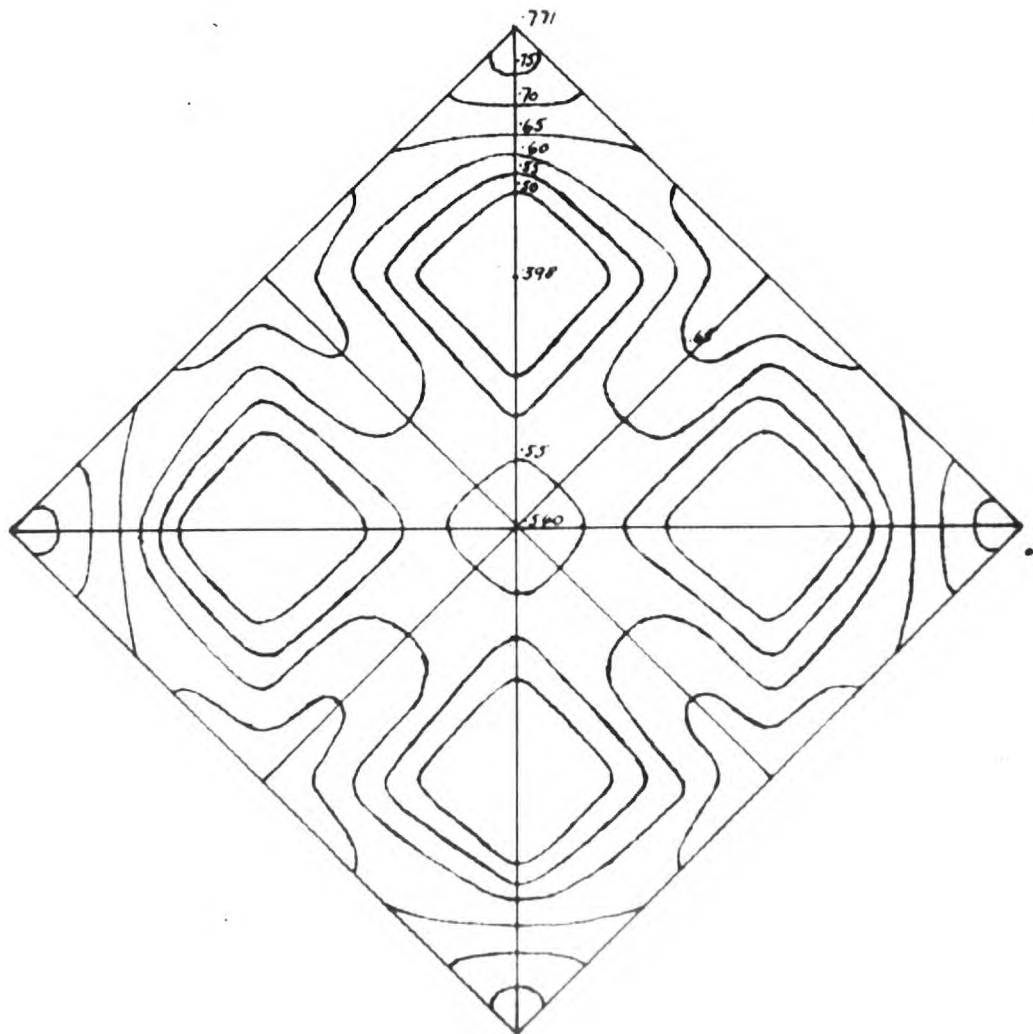


Fig. 30.

CONTOURS OF CONSTANT ENERGY IN $J=\pi$
PLANE AND ON HEXAGONAL FACE.

EXACT SOLUTION $\frac{E_L}{E_0}$.

$E_0 = 1.349 \text{ eV.}$

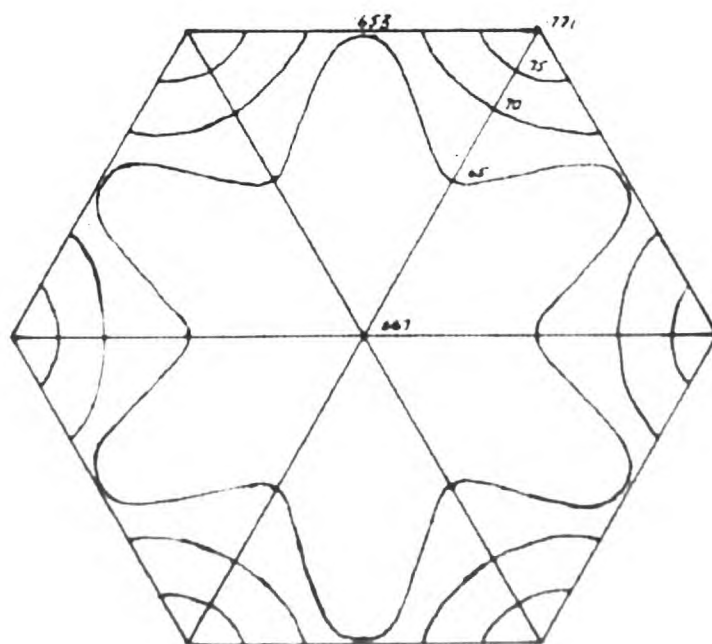
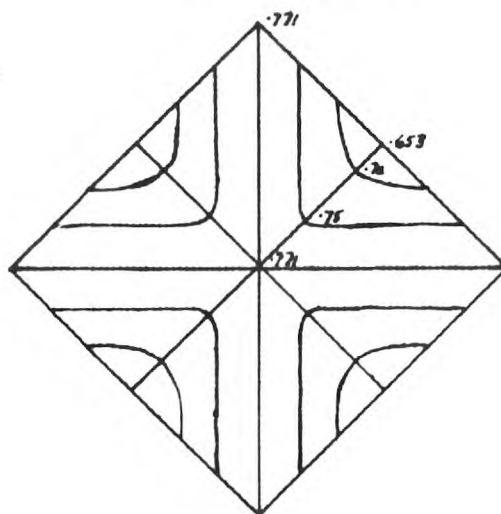


Fig. 31.

DENSITY OF STATES CURVE FROM FULL SECULAR EQUATION.

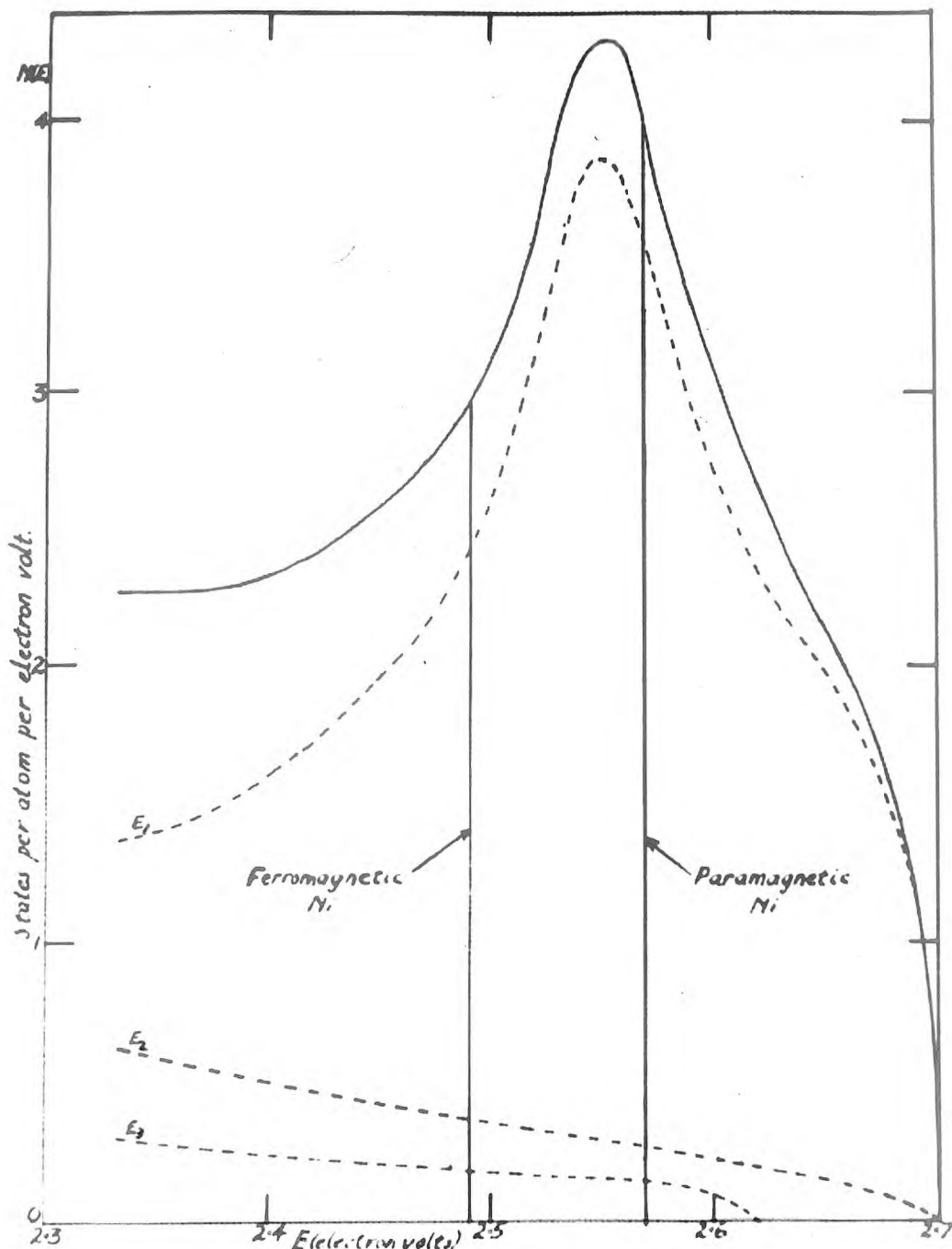


Fig 32.

this stage of the calculation, in this case, by measuring the areas under these curves, since they were incomplete, but any error is unlikely to be greater than in the approximate calculation, viz. $\sim 1\%$. Finally the total $N(E)$ curve over the relevant energy range was obtained by adding the three constituent curves and is shown in Fig. 32.

Chapter VIII.

Results and Discussion.

(a) Results and Comparisons.

(1) The total width of the 3d band is 2.70 eV, as already obtained in the approximate calculation, since the highest and lowest energy values still occur when $\underline{k} = (2\pi/a, 0, 0)$, for which $E_n = 0$ ($n=1, 2, 3; m=4, 5$). On comparison of Fig. 32 with Fig. 23 it is seen that the right-hand peak has moved to a higher energy value nearly at the top of the band. This is readily understood on reference to Figs. 12, 13, 26 and 27. Consider the (111) direction in particular, since here the effect of the previously neglected elements H_{nm} is greatest. Fig. 27 then shows clearly that the result of including these elements is to force the higher solutions of equation 3.9 to still higher energy values and the lower ones to lower values, i.e. to increase the number of states near the limits of the band and decrease the number near the middle. This suggests also, therefore, that the left-hand peak of the $N(E)$ curve should occur nearer the bottom of the band than in Fig. 23. The curve should then resemble that given by Slater (1936) in shape but would have about half the width and a high energy peak about twice the height. The effect of these differences is illustrated in (ii) and (iii) below.

Slater's results were deduced from the work of Krutter (1935) on Cu; for this, however, Hartree's atomic wave functions for Cu, neglecting the intraatomic exchange effect, were ^{used} so that the wave functions overlap more than they should when this effect is taken into consideration. This is one reason for doubting

if the d-band in Ni is as wide as Slater suggests.

Chodorow (1939) obtained a d-band width of 1.7eV for Cu by modifying the cellular method in order to allow partially for the exchange effect, but the method of modification is not specified in the reference quoted, which is an abstract of an M.I.T. thesis.

Greene and Manning (1943) applied the cellular method to f.c.c. Fe and obtained a bandwidth of ~ 5.3 eV. A larger figure than for Cu is to be expected as the lattice spacing is virtually the same and the wave functions extend farther from the nuclei, thereby overlapping more.

Summarizing, it is considered that the bandwidth obtained here is a better approximation to the true one than that given by Slater, although the figure of 2.70eV would be increased a little if the effects of s electrons and next-nearest neighbours were included and better assumptions regarding $V-U$ and $f(r)$ were made. It is considered that the shape of the $N(E)$ curve, as suggested in (1) above, will prove substantially correct.

(11) From Fig. 32 the energy difference ϵ_0 between the top of the band and the right-hand vertical line (paramagnetic), which corresponds to 0.3 vacant states per atom (of each spin), is 0.125eV. Then by definition the degeneracy temperature for Ni is

$$T = \frac{e}{k_B} \times 10^5 \times 0.125 = 1.43 \times 10^3 \text{ } ^\circ\text{K}$$

This value is rather less than that obtained in the approximate calculation owing to the higher, narrower energy peak near the top of the band. It compares with 1600 $^\circ$ K and 2400 $^\circ$ K deduced by Wohlfarth (1949c) from the magnetic and thermal properties of

Ni respectively and about 2000°K deduced as above from Slater's curve. This last is due to the greater width and lower peak obtained by Slater but, although the present value does not compare so favourably with Wohlfarth's figures as does Slater's value or that obtained in Chapter VI, this is to be expected, since Wohlfarth's calculations were based on the assumption of a parabolic band form, to which Slater's $N(E)$ curve and Fig. 33 approximate far more closely than does Fig. 32.

(iii) As explained in Chapter III(i) of Part II of this thesis, no satisfactory estimate of the exchange parameter δ can be made from Fig. 32 without a fairly complicated calculation based on the actual band shape obtained here. However, it is worth noting that, if a parabolic shape is assumed for the head of the band, a value of 0.099eV is obtained for δ in good agreement with the estimate of Wohlfarth (1949c) of 0.106eV for Ni, also based on a parabolic band.

(iv) The electronic property, which provides the simplest check on an $N(E)$ curve as calculated here, is the electronic contribution to the specific heat. From Stoner (1936b) the linear, low temperature electronic heat coefficient γ is given by:-

$$\gamma = 2.835 \times 10^{-4} R N(E)_0$$

where R is the universal gas constant and $N(E)_0$ is the density of states for one direction of spin at the Fermi limit. For a paramagnetic one can assume zero magnetization at 0°K so that the lower energy states are completely filled by pairs of electrons of opposite spins. In the case of ferromagnetic Ni and Co, however, Wohlfarth (1949c) has shown that there must be almost

complete magnetization at very low temperatures. Thus for Ni 5 states per atom of one spin (+) are fully occupied and only 4.4 states per atom of the other spin (-), instead of 4.7 states of each spin. The only electrons, which can take part in the specific heat process (ignoring the overlap of the s band) are those of (-) spin near the top of this unfilled band. The area under the curve of Fig. 32 corresponds to 5 electronic states per atom so that the relevant value of $N(E)_c$ is given by the left-hand vertical line, the area to the right of which corresponds to 0.6 states per atom, i.e. this is the Fermi limit in the unfilled (-) spin band. The resulting value obtained for γ is 1.6×10^{-3} cal. mol.⁻¹.deg.⁻² as compared with an observed value of 1.74×10^{-3} (Keesom and Clark 1935) and values of 1.1×10^{-3} and 1.1×10^{-3} deduced from Fig. 23 and Slater's $N(E)$ curve respectively. The difference compared with these last two figures is again due to the narrower band with a higher peak obtained here. A suitable value for comparison purposes would be somewhat lower than 1.74×10^{-3} , since this figure includes contributions from the s electrons and from d $\rightarrow$ s transitions (Wohlfarth 1948, 1949c), possibly 1.5×10^{-3} . The very close agreement obtained here, however, must be regarded as somewhat fortuitous, owing to the approximations made and the fact that the Fermi limit occurs at a steeply sloping part of the $N(E)$ curve so that any error in its position would introduce a comparatively large error in γ .

It is worth noting that in general electronic specific heats, calculated from d bands derived by the cellular method, are much smaller than those observed, which would seem to

indicate that the method gives too large a bandwidth in general. This is seen from a comparison between ^{calculated} and observed specific heats summarized by Silvidi and Daunt (1950). Thus for W Manning and Chodorow (1939) obtain a value of 4.8×10^{-4} cal. mol. deg.⁻², while the observed value is 51.1×10^{-4} . For b.c.c. Fe Manning (1943) obtains 4.6×10^{-4} as compared with an observed value of 12.0×10^{-4} .

(v) As already mentioned, from group-theoretical considerations a triple and a double degeneracy should occur between the wave functions at the centre of the B.Z., $k=0$. In both calculations here this is confirmed with an energy separation between the two degenerate levels of 0.88 eV. In all applications of the cellular method, however, fivefold degeneracy is obtained for $k=0$, a result due to the method of approximation.

(b) General Discussion.

From the above numerical results it seems that the present calculation, despite several rather drastic approximations and assumptions, has given a better picture of the distribution of 3d electrons among the energy states in metallic Ni than has been obtained before. The occurrence of a high peak near the head of the density of states curve and the location of the Fermi limit near this peak, as forecast from various theoretical interpretations of experimental data, has been confirmed. In fact the general shape of this curve would appear to be established even if its exact width is still somewhat uncertain. Stoner (1938a; 1939; 1943; 1951) has developed the collective electron theory of ferromagnetism for a "parabolic" energy band, for which $N(E) \propto (E_m - E)^{\frac{1}{2}}$, where E_m is the upper energy limit of the band.

Wohlfarth (1951) has carried out similar calculations for a "rectangular" band, for which $N(E)$ is constant, and shows that the observed values of several electronic properties of Ni lie between the values calculated for parabolic and rectangular bands. Use of a band form intermediate between these two might therefore be expected to yield results in good agreement with experiment. The present curve may therefore be of use as a basis for a new calculation of suitable electronic properties for Ni and, of course, this would serve as a much more strenuous test of the accuracy of the curve than has been carried out so far. Apart from the shape of the curve another important point, which might affect such a calculation considerably, is that the ferromagnetic Fermi limit occurs to the left of the peak in the curve, so that the use of a parabolic band would seem most inappropriate, should this in fact occur. Although not related to Stoner and Wohlfarth's calculations, the consideration of ferromagnetic anisotropy and related topics in Part II of this thesis has provided another test of the calculations in this part. The results obtained are reasonably satisfactory although they depend as much on the theory of these topics on the collective electron model, as developed by Brooks (1940), as on this calculation.

Part II. Ferromagnetic Anisotropy and Related Topics on the
Collective Electron Model.

Chapter I.

Previous Theories of Ferromagnetic Anisotropy.

As an application of the calculation of the energy bands for 3d electrons in Ni it was decided to consider the ferromagnetic anisotropy of this metal, since the theory of this effect on the basis of the collective electron model has been considered in only one paper by Brooks (1940) and in this no attempt was made to calculate the coefficients involved, obviously due to the lack of precise information about the energy bands at the disposal of the author. Since it proves a simple task to calculate values of the spectroscopic splitting factor g and the magneto-mechanical factor g' at the same time, these topics are also considered.

(a) Experimental Facts.

The experimental facts regarding ferromagnetic anisotropy have been summarized by various authors, notably Stoner (1948) and Kittel (1949b). Briefly it is not possible to explain the behaviour of ferromagnetics in low and moderate fields in terms of the exchange interaction effect alone, which has proved so powerful in explaining the occurrence of ferromagnetism. Experimental work with single crystals has shown that a crystal is generally magnetized more easily along certain crystal directions than others. The general character of the results obtained are well illustrated by the curves of Honda and Kaya (1926). For iron the cube edges $[100]$ etc. are "easy" and the

body diagonals $[111]$ etc. "hard" directions of magnetization while the reverse is true for nickel; for cobalt the hexagonal axis is the only easy direction. In order to explain the effects portrayed by curves of the type mentioned above it has been found necessary to assume that a crystal is composed of a number of small regions or domains, each of which is magnetized to saturation in one direction. The process of magnetization is by In the unmagnetized state of the crystal there are equal aggregate domain volumes magnetized along each of the easy directions.

they rotate towards the direction of the field. The question as to why there are easy and hard directions of magnetization can first be answered by assuming that the energy of magnetization of a domain depends on the direction $(\alpha_x, \alpha_y, \alpha_z)$ of the magnetization with respect to the crystal axes, expressible as a power series in the α_i . For a cubic crystal symmetry considerations show that the free energy per unit volume must then be of the form:-

$$F = F_0 + K_1 (\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2) + K_2 \alpha_x^4 \alpha_y^4 \alpha_z^4 \quad 1.1$$

and for a hexagonal crystal of the form:-

$$F = F_0 + K' \sin^2 \phi + K'' \sin^4 \phi$$

where the magnetization makes an angle ϕ with the hexagonal axis. Higher order terms could occur but are not found necessary in practice to explain the experimental results. The values of the anisotropy coefficients K may be obtained experimentally, e.g. from magnetization curves such as those of Honda and Kaya. Only values at very low temperatures will be of interest at present

body diagonals $[111]$ etc. "hard" directions of magnetisation while the reverse is true for nickel; for cobalt the hexagonal axis is the only easy direction. In order to explain the effects portrayed by curves of the type mentioned above it has been found necessary to assume that a crystal is composed of a number of small regions or domains, each of which is magnetised to saturation in one direction. The process of magnetisation by an external ^{field} may be considered as taking place in two overlapping stages; first the directions of domain magnetisation change to the easy direction(s) nearest to the field direction and then they rotate towards the direction of the field. The question as to why there are easy and hard directions of magnetisation can first be answered by assuming that the energy of magnetisation of a domain depends on the direction $(\alpha_x, \alpha_y, \alpha_z)$ of the magnetisation with respect to the crystal axes, expressible as a power series in the α_i . For a cubic crystal symmetry considerations show that the free energy per unit volume must then be of the form:-

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since the calculated values obtained later will correspond to such temperatures. The following experimental values at 0°K (except where otherwise stated) have been obtained from Kittel (1949b).

- Ni $K_1 = -8.0 \times 10^5$ ergs/c.c.; $K_2 = 5.0 \times 10^4$ ergs/c.c. (room temperature)
 Fe $K_1 = 5.7 \times 10^5$ ergs/c.c.; $K_2 = 1.5 \times 10^5$ ergs/c.c. (room temperature)
 Co $K' = 7.7 \times 10^6$ ergs/c.c.; $K'' = 3.5 \times 10^6$ ergs/c.c.

The above formal representation of anisotropy effects can then be considered satisfactory, if it is possible to account for the magnitude of the coefficients K by means of atomic theory. This is the purpose of the present work; previous attempts to do so are discussed in the next section. This is only part of the whole problem as the K 's vary considerably with temperature but so far it has not proved possible to provide any simple interpretation of this variation. (Brooks has discussed qualitatively the variation of K_1 in Fe-Ni alloys; such variations are of interest since low values of the anisotropy energy are of considerable importance in developing magnetic materials of high permeability. Finally it can be shown that there will be no linear magnetostriction effects if the anisotropy energy is independent of the state of strain of the crystal (Kittel 1949b). This aspect of the problem will not be considered here, however.

The relation of the present theory of anisotropy to the factors g and g' and experimental work on the latter will be discussed later.

(b) Previous Theories of Ferromagnetic Anisotropy.

The idea of exchange coupling due to Heisenberg, which

accounts so well for the existence and general properties of ferromagnetism, unfortunately provides no explanation of anisotropy since it depends only on the relative orientation of spins on neighbouring atoms and not on their absolute orientating relative to the crystal axes. It is necessary to find some mechanism for coupling the spins to the crystal itself; Van Vleck (1937) has given a critical discussion of the models proposed by various workers to provide this mechanism and a brief resume will be given here.

(1) Magnetic multipole interaction models. The magnetic dipole interaction between spins contains a term depending on the orientation of the spins relative to the line joining them and hence relative to the crystal axes. Inclusion of such terms in the Hamiltonian of the crystal, representing dipole interaction between atomic spins, might therefore be expected to give the desired anisotropy. Actually the atomic spins are not really comparable with point dipoles but with a dipole distribution over a finite region so that higher order multipole interaction between the spins may equally well be included. If all atomic spins are assumed mutually parallel, then dipole-dipole forces alone can give no anisotropy in a cubic crystal (Van Vleck 1937). Mahajan (1929), Akulov (1929) and Gans and Gserlinck (1933) therefore considered a regular quadrupole lattice and obtained results of the right order of magnitude. Becker (1930), however, preferred to consider an elastically strained dipole lattice and also obtained results in agreement with experiment. With a dipole model it is possible to obtain anisotropy for a cubic

lattice, if the atomic moments are not all assumed to be mutually parallel (Bloch and Gentile 1931; Van Vleck 1937) but values obtained for K , on such a model are far too small. Besorth and McKeehan (1937) suggested the use of an unsymmetrical charge distribution of the magnetic electrons about each atom, since these are d electrons, and obtained a quadrupole and hexapole interaction between the atomic moments; using this model McKeehan (1937) obtained values of K_1 and K_2 of the right order of magnitude. Van Vleck (1937) pointed out that the atomic moments should be represented by spin matrices and not simple vectors; due to the commutation relations between these matrices, he also obtained a quadrupole moment. He also shows, however, that there can be no quadrupole coupling between atomic spins < 1 so that a quadrupole model is unlikely to be applicable to H_1 .

(11) Spin-orbit interaction models. Bloch and Gentile (1931) first pointed out that the spin-orbit coupling, acting together with the coupling of the orbit to the crystal by means of the crystal field, might provide the necessary coupling of the spin to the crystal. With such a model they obtain agreement with experiment but Van Vleck (1937) criticizes their treatment, i.e. of a single atom rather than the crystal as a whole. Powell (1930) also Fowler and Powell (1931) obtained the required form (1.1) for the free energy of a cubic crystal by using an anisotropic Weiss field, whose asymmetry is somehow connected with spin-orbit interaction; the association between the two is not investigated. Van Vleck (1937), using a model based on that of Bloch and Gentile but applied strictly to the whole crystal, obtained

values of K , for Fe and Ni in quite good agreement with experiment but results for K_2 and the temperature variation of K , were not so satisfactory. He also demonstrated the relation to multipole models by obtaining apparent dipole-dipole and quadrupole-quadrupole coupling, of much greater magnitude than the purely magnetic interaction, however. Van Peijpe (1938) also carried out a calculation based on Bloch and Gentile's mechanism, again obtaining reasonable agreement with experiment.

Despite the success of some of the above methods, none of them gives a very clear insight into the origin of the various coupling terms and Brooks' (1940) paper represented the first attempt at a calculation, which would indicate clearly how the spin-orbit interaction can lead to anisotropy of the correct order of magnitude. As his paper is a little obscure in parts and will form the basis of the present work of the author, it will be discussed fairly fully.

Chapter II.

Basis of Brooks' Theory of Anisotropy.

Owing to the difficulty of obtaining a rigorous solution of the problem on the many-electron (Heisenberg) model, Brooks' theory is based on the collective electron model of Bloch (1929), Stoner (1938a) and Slater (1936). The collective electron treatment leads to a manageable secular equation, giving rise to ferromagnetic anisotropy in a straightforward manner, and, of course, is the treatment used in Part I of this thesis.

(a) Quenching of Orbital Momentum.

This problem is closely related to that of ferromagnetic anisotropy and so is worth considering here. Measurements of the spectroscopic splitting factor g and gyro-mechanical splitting factor g' for ferromagnetic metals (e.g. Kittel 1951) ^{values of} give both very close to 2, indicating that magnetic effects in these metals are largely due to the spin of the electrons concerned, while their orbital angular momentum is not free to orient and precess in an external field. Thus the crystalline field in a ferromagnetic must be sufficiently strong to maintain a definite orientation of the orbital momenta of the electrons relative to the crystal axes, even in the presence of an external magnetic field. Bethe (1929) has shown that the effect of a cubic field on electrons described by free atom wave functions is only sufficient to split the fivefold degenerate d level of the atom into a doubly degenerate and a triply degenerate level (forming the representations Γ_2 and Γ_5 of the cubic point group; cf. Part I). The former possesses no matrix

elements of the magnetic moment between its substates but the latter does so that, if the Γ_2 substates are not filled in the solid state, there will be orbital contributions to the magnetic moment (as is seen clearly later) with g, g' differing from 2. However, since these substates are still degenerate, the diagonal elements of orbital magnetic moment will be comparatively large, giving $g-2$ and $2-g'$ much larger values than are observed. Alternatively, since m_l is still a good quantum number, the cubic field is insufficient to maintain the orientation of the electronic orbits against the external field. On the collective electron model, however, the crystalline field removes the d-level degeneracy completely for the majority of wave vectors, as seen in Part I, and therefore an external magnetic field has very little effect on the orientation of the orbits. In fact, as will be seen later, the diagonal elements of magnetic moment between the crystal wave functions are zero and it is necessary to introduce the spin-orbit coupling to obtain an orbital effect of the right order. Looked at from another point of view, a tightly bound d electron spends most of its time on one atom but occasionally jumps to a neighbouring one and in so doing changes its values of l and m_l in general. It will make many revolutions in its orbit between jumps and is most likely to jump into another d-type orbit on the neighbour so that l remains a good quantum number. However, the precession of l in an external field is much slower and the electron may make many jumps during one precession, each in general destroying the orientation in the field so that m_l is no longer a good quantum

number and a magnetic field has little effect. Alternatively, if the electron remained on one atom, its energy levels would be determined by the cubic point group, which is the case considered by Bethe. On the collective electron model it moves in a field of symmetry determined by the space group of the whole crystal, i.e. including translations. As stated above, the reality of the corresponding wave functions precludes the existence of diagonal matrix elements of magnetic moment and, since the substates under the space group are non-degenerate for the majority of wave vectors $\underline{k}$, the non-diagonal elements, which are involved due to spin-orbit interaction, join states whose energy differences are large compared with the magnetic perturbation, so that their effect on g and g' is small.

Due to spin-orbit interaction the crystal field, which tends so strongly to orient the electronic orbits relative to the crystal axes, also affects their spins slightly in the same way, so that the energy is not entirely independent of spin orientation and anisotropy results.

(b) Approximate Structure of d Bands.

Brooks next considers the approximate d band structure for f.c.c. and b.c.c. lattices. For this purpose and for the rest of the paper he assumes that the band arising from the Γ_2 level can be ignored and he considers only that arising from the Γ_5 level; this is a similar approximation to that made in the first calculation of Part I. Brooks admits the pooriness of this approximation, as there are matrix elements of magnetic moment between substates of the Γ_3 and Γ_5 levels. It will be shown later that the assumption is unnecessary for an analytic solution of

the problem although the computational difficulties in obtaining numerical values of g, g' and K_i are greatly increased. The formulae given in this section of Brooks' paper are well known; for future reference the approximate form of the diagonalizing transformation in the b.c.c. case is:-

$$\begin{array}{c}
 \phi_1 \qquad \phi_2 \qquad \phi_3 \\
 \begin{array}{l}
 E_1 \\
 E_2 \\
 E_3
 \end{array}
 \left[\begin{array}{ccc}
 -c\varepsilon^{-1} & b\varepsilon^{-1} & a\varepsilon^{-1} \\
 \frac{1}{\sqrt{2}}\tau\varepsilon^{-1} & \frac{1}{\sqrt{2}}\tau^{-1}(a+b\varepsilon^{-1}) & \frac{1}{\sqrt{2}}\tau^{-1}(b+a\varepsilon^{-1}) \\
 -\frac{1}{\sqrt{2}}\tau\varepsilon^{-1} & \frac{1}{\sqrt{2}}\tau^{-1}(a-b\varepsilon^{-1}) & \frac{1}{\sqrt{2}}\tau^{-1}(b-a\varepsilon^{-1})
 \end{array} \right]
 \end{array} \quad 2.1$$

where $\tau^2 = a^2 + b^2$; $\varepsilon^2 = a^2 + b^2 + c^2$; $a = \sin\{\sin\gamma\cos\delta\}$; $b = \sin\{\cos\gamma\sin\delta\}$; $c = \cos\{\sin\gamma\sin\delta\}$. This is in fact the matrix of transformation coefficients $\{a_{rn}\}$ (see next section) where the wave function in the metal is:-

$$\psi_r(\underline{k}; \underline{r}) = \sum_n a_{rn}(\underline{k}) \phi_{n\underline{k}}(\underline{r}) = \frac{1}{\sqrt{N}} \sum_n \sum_{\underline{r}'} a_{rn}(\underline{k}) e^{i\underline{a}\cdot\underline{k}} \phi_n(\underline{r} - \underline{a}')$$

(ψ_r corresponds to $\bar{\Psi}_n$ used in Part I and $\phi_{n\underline{k}}$ to $\psi_{n\underline{k}}$).

In the f.c.c. case Brooks argues that $\{a_{rn}\}$ is nearly diagonal for most $\underline{k}$ since $(A_1 + A_2)/A_3$ is large compared with unity. In fact this ratio has been found to be about 3 and Brooks' argument is not really valid.

(c) Spin-Orbit Interaction.

In order to clarify the method of procedure adopted by Brooks it is as well to consider the Hamiltonian involved in the problem. This may be written in the form:-

$$H = \frac{\hbar^2}{2m} \nabla^2 + U(r) + V(r) - U(r) + \mathcal{E} + 0 - \frac{i\hbar e}{mc} \nabla \cdot \underline{A} + \frac{e^2}{2mc^2} \underline{A}^2 + \frac{e}{mc} \underline{H} \cdot \underline{S} \quad 2.2$$

where U and V have already been defined, 0 represents spin-orbit and $\mathcal{E}$ exchange interaction and $\underline{A}$ is the vector potential of an external magnetic field $\underline{H}$. The terms $\nabla \cdot \underline{A}$, $\mathcal{E}$, 0 and $(\frac{i\hbar e}{mc} \nabla \cdot \underline{A} + \frac{e^2}{2mc^2} \underline{A}^2 + \frac{e}{mc} \underline{H} \cdot \underline{S})$

are considered successively as perturbations of the free atomic energy levels. The first four stages in the calculation will be considered here and the final stage, which is only involved in calculating g and g' , in the next section.

(i) The atomic functions, which form the starting point of the calculation, are in the present work those obtained by a Hartree self-consistent field calculation. In this calculation spin-orbit interaction was neglected by Hartree and Hartree (1936) but the effect of intraatomic exchange was included. The corresponding states are completely degenerate and are characterized by n, ℓ, m_ℓ, s and m_s .

(ii) The first perturbation considered, $V-U$, represents the effect of the crystal field, for which the approximations made have already been detailed. The corresponding states are largely non-degenerate and are characterized by $n, \ell, \underline{k}, s$ and m_s , being still degenerate in m_ℓ .

(iii) The second perturbation $\mathcal{E}$ will represent interatomic exchange only, if it is assumed that (ii) has not affected the intraatomic exchange considered in (i). This is valid as long as the interatomic forces are insufficient to destroy the quantization of the spin of each atom (Van Vleck 1932, Ch. XII); this has been assumed in (ii), for which the calculation was made independent of spin direction. The interatomic forces can only affect the spin of each atom through the spin-orbit coupling and it will be shown later that this effect is generally negligible compared with the interatomic exchange effect. The operator representing the latter should then be $\mathcal{E} = 2 \sum_i \mathcal{E}_i J_i$.

summing over all electrons on other atoms, s being the spin of electron concerned. Heisenberg (1928) has shown that the resulting exchange energy is equivalent to an inner field proportional to the intensity of magnetization, if all the states concerned have the same energy initially. This is not so here but the variation in energy is comparatively small (narrow d band, although it overlaps the s band) and empirically this approximation is quite good. Stoner (1938a) has shown that this is equivalent to assuming an additional energy contribution per electron $\pm \sigma = \pm k\theta' J$ according as the electron's spin is anti-parallel or parallel to the total spin of the crystal. Here J is the fractional magnetization I/I_0 (I_0 = saturation intensity) and $k\theta' = n_d J$, where n_d is the number of free spins per atom corresponding to the saturation magnetization and J is the exchange integral between electronic wave functions normalized per unit cell. θ' is a parameter of dimensions temperature and of the same order of magnitude as the Curie temperature, which gives a measure of the exchange energy of the d electrons in the metal. Since the magnetic energy of an electron in an external field is a minimum when its spin is antiparallel to the field, the energy above will be $\pm \sigma$ according as the spin is parallel or antiparallel to the field, since the majority of spins and hence the total spin of the crystal will be antiparallel to the field.

The corresponding states will be unaffected as far as n, ℓ, s and k are concerned, since spin-orbit interaction has not been introduced but now s will be quantised along the field direction.

(iv) The third perturbation O represents the spin-orbit interaction. Since the effect produced will be shown to be $\sim .08\text{eV}$, it is not really valid to consider it as a perturbation at this stage as far as the exchange effect ($\sim .1\text{eV}$) is concerned, a point considered later, but it is valid as far as the effect of the crystal field is concerned for the great majority of wave vectors $\underline{k}$. For certain wave vectors the perturbation due to $V-U$ will be very small, however, but this is unimportant for the following reason. The integral C defined in the first part of this thesis, although negative, is very small (since $V-U$ is very small within the cell around the central atom) so that the original, free atom energy level corresponds very nearly to $E/E_0 = 0$; it will be seen later that all wave vectors involved in calculating g, g' and K_i correspond to energies well removed from this level, i.e. for which the $V-U$ perturbation is much larger than the spin-orbit one.

The derivation of Brooks' spin-orbit operator will now be considered (see Condon and Shortley 1936, p. 120 et al.). Dirac's relativistic theory of an electron moving in a central electromagnetic field leads, subject to one approximation which has little effect on d states, to a term $\frac{1}{2mc^2} \frac{1}{r} \frac{\partial U}{\partial r} \underline{S} \cdot \underline{L} = f(r) \underline{S} \cdot \underline{L}$ in the Hamiltonian, where $\underline{L}, \underline{S}$ are the orbital and spin angular momentum operators for the electron and U is the potential of the field so that $f(r) \sim \frac{1}{r^3}$. Thomas (1926) and Frenkel (1926) have obtained a similar term from the picture of the electron as a spinning top and giving experimental agreement for spin-orbit splitting. To allow for interaction with other orbits

Condon and Shortley show that an additional term of the form $\sum_j \pi(\mathbf{r}_j \cdot \mathbf{g}) \mathbf{S} \cdot \mathbf{L}_j$, summed over all other electrons, should be included. This term has the effect of reducing the effect of the nuclear field in the first term and is small except for s states so that for d electrons use of a spin-orbit operator $\xi(r) \mathbf{S} \cdot \mathbf{L}$ (where $\xi(r)$ falls off rather more rapidly than $\sim \frac{1}{r^3}$) should be quite accurate enough. In the metal and using wave functions of the type ψ_r , it is necessary to allow for the fact that the electron may be located on any atom at a given instant by forming the operator:-

$$O = \sum_l \xi(r - a_l) \mathbf{S} \cdot \mathbf{L}(r - a_l) \quad 2.3$$

where $\mathbf{L}(r - a_l)$ is the angular momentum operator about the atom at a_l and operates only on that part of a wave function representing motion about that atom. A final point to be considered is the interaction of $\mathbf{S}$ with the orbits of electrons on other atoms. This will be zero for a closed shell of electrons on another atom so that the effect should be small for Ni. Also, owing to the symmetrical arrangement of other atoms about any one considered, the orbital magnetic field at the central atom due to the electrons on all other atoms should be small and the effect on d electrons negligible. Thus the use of 2.3 as the spin-orbit operator seems justified; Brooks argues that $\xi(r)$ would probably fall off exponentially owing to the effect of the other ions cancelling the effect of electrons on these ions. The important point is that, due to the other atoms, the field potential U is no longer spherically symmetrical as was assumed in deriving 2.3 but I do not agree that this will affect $\xi(r)$ for d electrons as drastically as Brooks suggests.

(d) Spin-orbit secular equation.

In order to proceed it is now necessary to obtain the matrix elements of O in the system of representation in which the band-exchange energy is diagonal, i.e. with respect to the wave functions ψ_n with spin quantized along the field direction. Now O is periodic with the period of the lattice and is hence rigorously diagonal in $\underline{k}$ (Kott and Jones 1936, p. 59). Also:-

$$\begin{aligned} \langle n \underline{k} m_s | O | n \underline{k} m_s \rangle &= \frac{1}{N} \sum_{\underline{r}} \sum_{\underline{m}} \sum_{\underline{p}} e^{-i(\underline{r}-\underline{p}) \cdot \underline{k}} \int \phi_n^*(\underline{r}-\underline{a} \underline{p}) \mathcal{F}(\underline{r}-\underline{a} \underline{m}) \underline{S} \cdot \underline{L}(\underline{r}-\underline{a} \underline{p}) \phi_n(\underline{r}-\underline{a} \underline{p}) d\tau \\ &= \frac{1}{N} \sum_{\underline{r}} \sum_{\underline{m}} e^{-i\underline{r} \cdot (\underline{k}-\underline{m})} \int \phi_n^*(\underline{r}-\underline{a} \underline{p}) \mathcal{F}(\underline{r}-\underline{a} \underline{m}) \underline{S} \cdot \underline{L}(\underline{r}-\underline{a} \underline{m}) \phi_n(\underline{r}-\underline{a} \underline{m}) d\tau \\ &= \sum_{\underline{m}} e^{-i\underline{a} \underline{m} \cdot \underline{k}} \int \phi_n^*(\underline{r}-\underline{a} \underline{m} + \underline{q}) \mathcal{F}(\underline{r}-\underline{a} \underline{m}) \underline{S} \cdot \underline{L}(\underline{r}-\underline{a} \underline{m}) \phi_n(\underline{r}-\underline{a} \underline{m}) d\tau \\ &= \sum_{\underline{m}} e^{-i\underline{a} \underline{m} \cdot \underline{k}} \int \phi_n^*(\underline{r}-\underline{a} \underline{m}) \mathcal{F}(\underline{r}) \underline{S} \cdot \underline{L}(\underline{r}) \phi_n(\underline{r}) d\tau, \text{ putting } \underline{s} = \underline{r} - \underline{a} \underline{m} \end{aligned}$$

If $\mathcal{F}(\underline{s})$ falls off sufficiently rapidly the integrals involved will be negligible except that for $\underline{q} = 0$; without the factor $\mathcal{F}(\underline{s})$ they would be non-orthogonality integrals such as were neglected in the band calculation so that it seems justifiable to neglect them here also. Thus the matrix elements of the spin-orbit interaction with respect to the Bloch functions $\phi_{n\underline{k}}$ may be taken to be the same as between the corresponding atomic functions ϕ_n :-

$$\langle n \underline{k} m_s | O | n \underline{k} m_s \rangle = \int \phi_n^*(\underline{r}) \mathcal{F}(\underline{r}) \underline{S} \cdot \underline{L}(\underline{r}) \phi_n(\underline{r}) d\tau = A \langle n m_s | \underline{S} \cdot \underline{L} | n m_s \rangle \quad 2.4$$

where A is the spin-orbit interaction parameter for an individual electron for the case of a free atom, corresponding to α in Condon's notation (Condon 1928). As Brooks says, the perturbation $V-U$ is being assumed sufficient to destroy the Russell-Saunders coupling within the atom so that there is no question of the individual electronic angular momenta combining to form a resultant $\underline{L}$ and $\underline{S}$. He considers this a poor approximation for the tightly bound d electrons.

Assume that the secular equation for the Γ'_5 band has been diagonalized by the set of real transformation coefficients $a_{rn}(\underline{k})$, i.e. for each wave vector $\underline{k}$ the coefficients a_{rn} are known in the expressions for ψ_r . With respect to these wave functions the matrix elements of $\hat{O}$ are found to be:-

$$\begin{aligned} (r\underline{k}m_r | \hat{O} | r'\underline{k}m_{r'}) &= \sum_{n,n'} a_{rn} (n\underline{k}m_n | \hat{O} | n'\underline{k}m_{n'}) a_{r'n'} \\ &= A \sum_{n < n'} (a_{rn} a_{r'n'} - a_{r'n} a_{rn}) \chi(n\underline{k}m_n | \underline{S} \cdot \underline{L} | n'\underline{k}m_{n'}) \end{aligned} \quad 2.5$$

since it will be seen later that $(n'\underline{k}m_{n'} | \underline{S} \cdot \underline{L} | n\underline{k}m_n) = -(n\underline{k}m_n | \underline{S} \cdot \underline{L} | n'\underline{k}m_{n'})$.

These latter matrix elements are obtained in units of $\frac{\hbar^2}{2}$ as follows. Thus the operators

$$L_x = -i(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}); L_y = -i(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}); L_z = -i(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) \text{ and } S_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; S_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; S_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Then:-

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} (\phi_1, \phi_2, \phi_3) = i \begin{pmatrix} \sqrt{3}\phi_2 + \phi_4 & -\phi_3 & \phi_1 \\ \phi_3 & -\sqrt{3}\phi_2 + \phi_4 & -\phi_1 \\ -\phi_2 & \phi_1 & -2\phi_4 \end{pmatrix}$$

$$\text{and:- } (n-\frac{1}{2} | \underline{S} \cdot \underline{L} | n-\frac{1}{2}) = \int \phi_{n-\frac{1}{2}} L_z \phi_{n-\frac{1}{2}} d\tau = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = -(n-\frac{1}{2} | \underline{S} \cdot \underline{L} | n-\frac{1}{2})$$

$$(n-\frac{1}{2} | \underline{S} \cdot \underline{L} | n-\frac{1}{2}) = \int \phi_{n-\frac{1}{2}} (L_x - iL_y) \phi_{n-\frac{1}{2}} d\tau = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & i \\ 1 & -i & 0 \end{pmatrix} \quad 2.6$$

$$(n-\frac{1}{2} | \underline{S} \cdot \underline{L} | n-\frac{1}{2}) = \int \phi_{n-\frac{1}{2}} (L_x + iL_y) \phi_{n-\frac{1}{2}} d\tau = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & i \\ -1 & -i & 0 \end{pmatrix}$$

But the set of transformation coefficients a_{rn} form a unitary orthogonal matrix, e.g. $a_{11} a_{22} - a_{12} a_{21} = 1$, so that it follows from 2.5 that:-

$$\frac{1}{A} (r\underline{k}m_r | \hat{O} | r'\underline{k}m_{r'}) = \begin{pmatrix} iA & B+iC \\ -B+iC & -iA \end{pmatrix} \begin{matrix} m_r = \frac{1}{2} \\ m_r = -\frac{1}{2} \end{matrix} \quad 2.7$$

where:- $A = \begin{pmatrix} 0 & a_{12} & -a_{13} \\ -a_{12} & 0 & a_{11} \\ a_{13} & -a_{11} & 0 \end{pmatrix}$; $B = \begin{pmatrix} 0 & a_{12} & -a_{11} \\ -a_{12} & 0 & a_{11} \\ a_{11} & -a_{11} & 0 \end{pmatrix}$, $C = \begin{pmatrix} 0 & a_{11} & -a_{12} \\ -a_{11} & 0 & a_{11} \\ a_{12} & -a_{11} & 0 \end{pmatrix}$ 2.8

By use of the spin operators given above it has been assumed that the spin is quantized along the z-axis whereas it will be quantized along the direction of domain magnetization, i.e. some arbitrary direction (l, m, n) or (θ, ϕ) relative to the crystal axes. Using primed symbols to denote this quantisation it follows (Condon and Shortley 1936, p.56) that:-

$$\begin{aligned} \psi'_r(\frac{1}{2}) &= \cos \frac{\theta}{2} \psi_r(\frac{1}{2}) + \sin \frac{\theta}{2} e^{i\phi} \psi_r(-\frac{1}{2}) \\ \psi'_r(-\frac{1}{2}) &= \sin \frac{\theta}{2} e^{-i\phi} \psi_r(\frac{1}{2}) - \cos \frac{\theta}{2} \psi_r(-\frac{1}{2}) \end{aligned}$$

Dropping the prime for convenience, the matrix elements of σ with respect to these wave functions are:-

$$\begin{aligned} \frac{1}{A}(\tau \frac{1}{2} / \sigma / \tau' \frac{1}{2}) &= i(A_{\tau\tau'} \cos \theta + B_{\tau\tau'} \sin \theta \sin \phi + C_{\tau\tau'} \sin \theta \cos \phi) = -\frac{1}{A}(\tau \frac{1}{2} / \sigma / \tau' \frac{1}{2}) \\ \frac{1}{A}(\tau \frac{1}{2} / \sigma / \tau' \frac{1}{2}) &= e^{-i\phi} [B_{\tau\tau'} \cos \phi + C_{\tau\tau'} \sin \phi + i(A_{\tau\tau'} \sin \theta - B_{\tau\tau'} \cos \theta \sin \phi - C_{\tau\tau'} \cos \theta \cos \phi)] \\ \frac{1}{A}(\tau \frac{1}{2} / \sigma / \tau' \frac{1}{2}) &= e^{i\phi} [B_{\tau\tau'} \cos \phi - C_{\tau\tau'} \sin \phi + i(A_{\tau\tau'} \sin \theta - B_{\tau\tau'} \cos \theta \sin \phi - C_{\tau\tau'} \cos \theta \cos \phi)] \end{aligned}$$
 2.9

These results may be greatly simplified as follows. Since the matrix $\{a_{rn}\}$ is unitary orthogonal, it may be used to define a new set of rectangular cartesian axes (Brooks' term "skew axes" is misleading):-

$$\underline{i}' = (a_{11}, a_{12}, a_{13}) ; \underline{j}' = (a_{21}, a_{22}, a_{23}) ; \underline{k}' = (a_{31}, a_{32}, a_{33})$$

which will, of course, be different for each wave vector $\underline{k}$. If the direction of quantization of spin is at (θ', ϕ') relative to these axes, then:-

$$\begin{pmatrix} \alpha'_1 \\ \alpha'_2 \\ \alpha'_3 \end{pmatrix} = \begin{pmatrix} \sin \theta' \cos \phi' \\ \sin \theta' \sin \phi' \\ \cos \theta' \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix}$$
 2.10

Brooks has made an error at this stage in his work; implicit in

his formulae (17) is the assumption that under this transformation of axes $\cos\theta\cos\phi$ becomes $\cos\theta'\cos\phi'$, $\cos\theta\sin\phi$ becomes $\cos\theta'\sin\phi'$ and so on, but this will not in general be true. All that can be said is that they will transform into two sets of direction cosines $(\beta'_1, \beta'_2, \beta'_3)$ and $(\gamma'_1, \gamma'_2, \gamma'_3)$, where:-

$$\begin{pmatrix} \beta'_1 \\ \beta'_2 \\ \beta'_3 \end{pmatrix} = \{a_{r'n}\} \begin{pmatrix} \cos\theta \cos\phi \\ \cos\theta \sin\phi \\ -\sin\theta \end{pmatrix} \text{ and } \begin{pmatrix} \gamma'_1 \\ \gamma'_2 \\ \gamma'_3 \end{pmatrix} = \{a_{r'n}\} = \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \quad 2.10$$

being mutually orthogonal and also each orthogonal to $(\alpha'_1, \alpha'_2, \alpha'_3)$

still, of course. Then it is easily shown that 2.9 becomes:-

$$\begin{aligned} (1k \pm 1/0 | 2k \pm 1) &= iA\alpha'_1; (1k \pm 1/0 | 3k \pm 1) = -iA\alpha'_2; (2k \pm 1/0 | 3k \pm 1) = iA\alpha'_3 \\ (1k \pm 1/0 | 2k - 1) &= e^{-i\phi}(-iA\beta'_1 - A\gamma'_1); (1k \pm 1/0 | 3k - 1) = e^{-i\phi}(iA\beta'_2 + A\gamma'_2) \\ (2k \pm 1/0 | 3k - 1) &= e^{-i\phi}(-iA\beta'_3 - A\gamma'_3) \\ (1k - 1/0 | 2k \pm 1) &= e^{i\phi}(-iA\beta'_1 + A\gamma'_1); (1k - 1/0 | 3k \pm 1) = e^{i\phi}(iA\beta'_2 - A\gamma'_2) \\ (2k - 1/0 | 3k \pm 1) &= e^{i\phi}(-iA\beta'_3 + A\gamma'_3) \\ (\tau k \pm 1/0 | \tau' k \pm 1) &= -(\tau k \pm 1/0 | \tau' k \pm 1); (\tau k m_s/0 | \tau' k m_s) = -(\tau' k m_s/0 | \tau k m_s) \end{aligned} \quad 2.11$$

Brooks' formulae (17) contain phase factors $e^{\pm i\phi'}$ whereas they should be $e^{\pm i\phi}$ but in any case they can be dropped, since they have no effect on the physical results obtained. The differences in sign between 2.11 and Brooks' formulae are simply due to the fact that he has defined $(\tau k m_s/0 | \tau' k m_s)$ as $\int \psi_{\tau'}^*(m_s) \psi_{\tau}(m_s) d\tau$ whereas here it is defined as $\int \psi_{\tau}^*(m_s) \psi_{\tau'}(m_s) d\tau$. Thus the secular equation for the energy, including the effect of the crystal field, exchange and spin-orbit interactions, is:-

$E_1 + \delta - E$	$iA\alpha'_1$	$-iA\alpha'_2$	0	$A(-\gamma'_1 - i\beta'_1)$	$A(\gamma'_2 + i\beta'_2)$	$= 0$
$-iA\alpha'_3$	$E_2 + \delta - E$	$iA\alpha'_1$	$A(\gamma'_3 + i\beta'_3)$	0	$A(-\gamma'_1 - i\beta'_1)$	
$iA\alpha'_2$	$-iA\alpha'_1$	$E_3 + \delta - E$	$A(-\gamma'_2 - i\beta'_2)$	$A(\gamma'_1 + i\beta'_1)$	0	
0	$A(\gamma'_2 - i\beta'_2)$	$A(-\gamma'_1 + i\beta'_1)$	$E_1 - \delta - E$	$-iA\alpha'_3$	$iA\alpha'_2$	
$A(-\gamma'_3 + i\beta'_3)$	0	$A(\gamma'_1 - i\beta'_1)$	$-iA\alpha'_2$	$E_2 - \delta - E$	$-iA\alpha'_1$	
$A(\gamma'_3 - i\beta'_3)$	$A(-\gamma'_1 + i\beta'_1)$	0	$-iA\alpha'_1$	$iA\alpha'_1$	$E_3 - \delta - E$	

2.12

E_1, E_2, E_3 are the energies obtained from the band calculation, i.e. including the effect of the crystal field but not exchange or spin-orbit interaction; they are, of course, functions of the wave vector $\underline{k}$, as is $\{u_n\}$ and hence all elements in 2.12. In the system of representation chosen, i.e. with respect to the band wave functions ψ_r , the energy matrix giving the determinant on the L.H.S. of 2.12 is diagonal in everything except the spin-orbit interaction. Since for most wave vectors $\underline{k}$ the off-diagonal elements are small compared with the differences between diagonal elements, the solutions of the secular problem may be expanded in powers of the spin-orbit parameter λ by successive orders of perturbation theory. For certain values of $\underline{k}$, however, two or more of the energies $E_i \pm \sigma$ are degenerate or nearly so; such cases will be considered later.

Chapter III.

Derivation of g and g' factors.

(a) General Discussion.

As has already been stated, the crystal field, by the almost complete removal of the degeneracy between the free atom 3d levels, practically prevents the 3d electrons' orbital moments contributing to the energy of a crystal in a magnetic field, i.e. it prevents these moments reorienting themselves in the magnetic field. Their spin moments can, however, so reorient themselves; due to the spin-orbit interaction this reorientation does have the effect of slightly reorienting the electrons' orbital moments, which therefore contribute slightly to the magnetic energy of the crystal. The last three terms in the Hamiltonian 2.2 may be written $\frac{e}{2mc} \underline{H} \cdot (\underline{L} + 2\underline{S}) + \frac{e^2}{2mc^2} A^2$ and the last may be dropped as representing an effect of far too small an order to be observed (see Condon and Shortley 1936, p.150). Assuming that eigenfunctions ψ corresponding to some Hamiltonian H_0 are known and that in a magnetic field $\underline{H}$ the Hamiltonian becomes:-

$$H = H_0 + \frac{e}{2mc} \underline{H} \cdot (\underline{L} + 2\underline{S}) = H_0 + H_H \quad 3.1$$

then, in order to find the magnetic energy involved, it is necessary to construct the matrix $(n|H_H|n')$. Since, however, no effect of $O(H^2)$ has been observed, the changes in energy levels due to the field will be given by the diagonal elements $(n|H_H|n)$. Similarly, if the total angular momentum in the direction of $\underline{H}$ (denoted by suffix H) was originally zero, the changes in angular momentum due to applying $\underline{H}$ are given by the matrix elements $(n|\underline{L}_H + \underline{S}_H|n) = (n|J_H|n)$.

(b) g' effect.

An electron behaves in some respects as a gyroscope having a magnetic moment along the axis of rotation. In a magnetic field this axis will tend to align itself with the field, thereby increasing both the angular momentum and magnetic moment in this direction. Alternatively, if the body containing the electron is made to rotate about some given axis, the angular momentum of the electron will tend to align itself with this axis due to precessional effects and again there will be an increase of both angular momentum and magnetic moment in this direction. In experiments of the Einstein-de Haas type the magnetic field affecting a body is changed and the corresponding changes ΔJ_H and ΔM_H in angular momentum and magnetic moment of the body are measured. In experiments of the Barnett type the specimen is given some angular momentum ΔJ_H and the resulting magnetic moment ΔM_H in the same direction is measured. In either case the magneto-mechanical factor g' (using terminology of Kittel 1949a) is defined as:-

$$g' = \frac{2mc}{e} \frac{\Delta M_H}{\Delta J_H}$$

which reduces to $\frac{(n/L_H + 2S_H/n)}{(n/L_H + S_H/n)}$ in the case above, if the functions

ψ_n etc. refer to the specimen as a whole. g' would be exactly 2 if the orbital momentum was unable to reorient itself in the field H and experimental values very near 2 are in fact found, particularly for ferromagnetic materials. Due to spin-orbit interaction, however, as explained above, the orbital momentum does have some effect, causing g' to be less than 2.

(c) g Effect.

If a small alternating field h is applied to a ferromagnetic specimen subject to a large constant field H perpendicular to h , it is found that, for given H , there is a critical value of the frequency ω of h , for which the energy absorption by the material exhibits a large peak. If H' is the effective field in the material corresponding to H , the spectroscopic splitting factor g is defined by the equation:-

$$\omega = g \frac{e}{2mc} H'$$

The theory of the effect has been treated from a classical point of view by Kittel (1947;1948) and from a quantum-mechanical viewpoint by Van Vleck (1950) and Polder (1948;1949), using the complete microscopic Hamiltonian of the spin system, while Luttinger and Kittel (1948) and Richardson (1949) obtain identical results using a macroscopic Hamiltonian. The effect is due to the quantum of energy $\hbar\omega$ becoming equal to the separation between adjacent eigenvalues of the energy of the specimen in the field H . Van Vleck puts this in another way when he says that resonance absorption experiments determine the factor g in the formula $E = E_0 + S_H g \mu H$ for the Zeeman energy states, where $\mu = \frac{e\hbar}{2mc}$ and S_H is the total spin of the specimen. In the case considered above the expression for g reduces to $\frac{(n/L_H + 2S_H/n)}{S_H}$. If the orbital angular momentum were unaffected by the field this would have the value 2 but, again due to spin-orbit interaction, the orbital momentum causes the value to be greater than 2. Further discussion of the theory of g and g' will be given later. Their actual calculation in the present case presents some peculiar

difficulties.

(d) Application to Collective Electron Model.

On the collective electron picture only information about an "average atom", with 9.4 d electrons and 0.6 holes in the d band in the present case, is available. Thus, in calculating M_H, J_H etc. for the whole crystal, we are reduced to finding their values for an average atom and multiplying by N , the total number of atoms in the crystal. Since N will cancel out in any formula obtained, M_H, J_H etc. may simply be calculated for one "average atom". The procedure for doing so is illustrated by considering $(n|H_H|n)$. The Hamiltonian 2.2 is a one-electron Hamiltonian of type 3.1 so that the wave functions to be used in calculating $(n|H_H|n)$ must be those corresponding to the solutions of the secular equation 2.12. Then $(n|H_H|n)$ can be calculated with respect to these wave functions, each such calculation giving the magnetic energy for the one state corresponding to $\psi_n(\underline{k})$. The values obtained must then be summed over all occupied states of the Fermi distribution to give the total magnetic energy for the "average atom".

Another problem arises from the fact that the vector potential $\underline{A}$ is linear in the coordinates so that it cannot be treated as a small perturbation throughout the crystal. In other words the application of a magnetic field will completely rearrange the energy levels so that the levels and wave functions obtained (without field) from the secular equation 2.12 should not be used in calculating the magnetic energy, for instance, in the simple manner which will be used later. Strictly speaking a

fresh band calculation, including the magnetic field, should be carried out or, even more strictly, the band theory is no longer applicable since the field makes $\underline{k}$ no longer a good quantum number. However, we really only require the energy of the whole crystal, obtained by summing over the Fermi distribution, and Peierls (1933) and London (1937) have shown that under certain conditions the use of the energy levels and wave functions for zero field gives a good approximation to the true energy, i.e. the rearrangement of levels in the field can be ignored. Following their method of gauge transformation the wave functions $\psi_{n\mathbf{k}} = N^{-1/2} \sum_{\mathbf{r}} e^{i\mathbf{a}\cdot\mathbf{r}\cdot\mathbf{k}} \phi_n(\mathbf{r} - \mathbf{a})$ obtained by solving the secular equation 2.12 should be replaced by:-

$$\psi_{n\mathbf{k}} = N^{-1/2} \sum_{\mathbf{r}} e^{i\mathbf{a}\cdot\mathbf{r}\cdot\mathbf{k}} e^{-\frac{ie}{\hbar c} \mathbf{A}\cdot\mathbf{r}} \phi_n(\mathbf{r} - \mathbf{a})$$

where $\mathbf{A}$ is the value of the vector potential at the lattice point $\mathbf{a}$, and a fresh band calculation made, although these functions are no longer Bloch functions, i.e. $\underline{k}$ is no longer a good quantum number. However, Peierls' and London's results justify to a certain extent the calculation of the magnetic energy from the solution of the field-free secular problem, i.e. the phase factor $e^{-\frac{ie}{\hbar c} \mathbf{A}\cdot\mathbf{r}}$ is ignored. In actual fact Peierls points out that the approximation is only valid for not too low temperatures and if the field-free energy surfaces have not too great a curvature anywhere. Neither of these conditions is strictly obeyed in the present case but it is still considered worth while obtaining values of g and g' using this approximation. Thus, assuming wave functions of the form:-

$$\psi_{n\mathbf{k}} = N^{-1/2} \sum_{\mathbf{r}} e^{i\mathbf{a}\cdot\mathbf{r}\cdot\mathbf{k}} e^{-\frac{ie}{\hbar c} \mathbf{A}\cdot\mathbf{r}} \phi_n(\mathbf{r} - \mathbf{a})$$

and a Hamiltonian:- $H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{ie\hbar}{mc} \nabla \cdot \underline{A} + \frac{e^2}{2mc^2} \underline{A}^2 + \frac{e}{mc} \underline{H} \cdot \underline{S} + V$

it is easily shown that:-

$$H\psi_{nk} = N^{-\frac{1}{2}} \sum_{\underline{r}} e^{i\mathbf{k} \cdot \mathbf{r}} e^{-\frac{ie}{\hbar c} \underline{A} \cdot \underline{r}} \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{ie\hbar}{mc} \nabla \cdot (\underline{A} - \underline{A}_e) + \frac{e^2}{2mc^2} (\underline{A} - \underline{A}_e)^2 + \frac{e}{mc} \underline{H} \cdot \underline{S} + V \right] \phi_n(\underline{r} - \underline{a}_e)$$

so that the operator inside the bracket now differs by only a small amount from its value in the absence of a magnetic field.

Assuming Peierls' conditions, the phase factor $e^{-\frac{ie}{\hbar c} \underline{A} \cdot \underline{r}}$ can be

dropped and, ignoring terms depending on $\underline{H}^2$, this reduces to:-

$$H\psi_{nk} = N^{-\frac{1}{2}} \sum_{\underline{r}} e^{i\mathbf{k} \cdot \mathbf{r}} \left[-\frac{\hbar^2}{2m} \nabla^2 + V + \frac{ie\hbar}{2mc} \underline{H} \cdot [(\underline{r} - \underline{a}_e) \wedge \nabla] + \frac{e}{mc} \underline{H} \cdot \underline{S} \right] \phi_n(\underline{r} - \underline{a}_e)$$

The first two terms in the bracket will give the zero-field energy levels, i.e. the solutions of the secular equation 2.12.

The remaining terms give:-

$$\langle n' | H_H | n \rangle = \sum_{\underline{r}} e^{-i\mathbf{k}' \cdot \mathbf{r}} \int \phi_{n'}(\underline{r} - \underline{a}_e) \left\{ \frac{ie\hbar}{2mc} \underline{H} \cdot \underline{r} \wedge \nabla + \frac{e}{mc} \underline{H} \cdot \underline{S} \right\} \phi_n(\underline{r}) d\tau$$

But $(\underline{r} \wedge \nabla) \phi_n(\underline{r}) = \sum_{\alpha} b_{\alpha n} \phi_{\alpha}(\underline{r})$ and hence, with an error of the order of a non-orthogonality integral:-

$$\langle n' | H_H | n \rangle = \int \phi_{n'}(\underline{r}) H_H \phi_n(\underline{r}) d\tau$$

i.e. the perturbation H_H has the same matrix elements between Bloch functions as between the corresponding atomic functions. As has been indicated, it will only be necessary to calculate the diagonal elements of L_H and S_H with respect to these functions, which will be those corresponding to the solution of 2.12.

(c) Derivation of Formulas.

Applying perturbation theory to equation 2.12, the first order approximation to the wave function arising from the band level $E_3 + \sigma$, for instance, is:-

$$\Psi_3^{\sigma} = \psi_3^{\sigma} - \frac{iA\alpha_1'}{\epsilon_1} \psi_1^{\sigma} + \frac{iA\alpha_2'}{\epsilon_2} \psi_2^{\sigma} - \frac{A(\gamma_1' - i\beta_1')}{\epsilon_1 + i\sigma} \psi_1^{\sigma} + \frac{A(\gamma_2' - i\beta_2')}{\epsilon_2 + i\sigma} \psi_2^{\sigma} \quad 3.2$$

where $\epsilon_1 = E_3 - E_1$; $\epsilon_2 = E_3 - E_2$, the ψ_n are the wave functions obtained

from the band calculations and the suffices $\pm$ are an obvious spin notation. Also:-

$$L_H = -i\hbar \left[\alpha_x \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) + \alpha_y \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) + \alpha_z \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right] \quad 3.3$$

where:- $\alpha_x = \sin\theta \cos\phi$; $\alpha_y = \sin\theta \sin\phi$; $\alpha_z = \cos\theta$

$$\text{Then:- } \int \Psi_j^+ L_H \Psi_j^+ d\tau = \int \Psi_j^+ L_H \Psi_j^+ d\tau - \frac{iA\alpha_i'}{\epsilon_i} \left[\int \Psi_j^+ L_H \Psi_i^+ d\tau - \int \Psi_i^+ L_H \Psi_j^+ d\tau \right] + \frac{iA\alpha_i'}{\epsilon_i} \left[\int \Psi_j^+ L_H \Psi_i^+ d\tau - \int \Psi_i^+ L_H \Psi_j^+ d\tau \right] + O(A^2)$$

$$\text{since:- } \int \Psi_n^+ L_H \Psi_n^+ d\tau = 0$$

$$\begin{aligned} \text{Now:- } \int \Psi_j^+ L_H \Psi_i^+ d\tau &= -\int \Psi_i^+ L_H \Psi_j^+ d\tau = \int (a_{j1}\phi_1^+ + a_{j2}\phi_2^+ + a_{j3}\phi_3^+) L_H (a_{i1}\phi_1^+ + a_{i2}\phi_2^+ + a_{i3}\phi_3^+) d\tau \\ &= -i\hbar [(a_{j1}a_{i2} - a_{j2}a_{i1})\alpha_x + (a_{j1}a_{i3} - a_{j3}a_{i1})\alpha_y + (a_{j2}a_{i3} - a_{j3}a_{i2})\alpha_z] \\ &= -i\hbar (-\alpha_x a_{i1} - \alpha_y a_{i2} - \alpha_z a_{i3}) = i\hbar \alpha_i' \end{aligned}$$

where ϕ_n are the original free-atom wave functions. Similarly:-

$$\int \Psi_j^+ L_H \Psi_j^+ d\tau = 0 \text{ and } \int \Psi_j^+ L_H \Psi_i^+ d\tau = -\int \Psi_i^+ L_H \Psi_j^+ d\tau = -i\hbar \alpha_i'$$

$$\text{Hence:- } (j^+ | L_H | j^+) = 2A\hbar \left(\frac{\alpha_i'^2}{\epsilon_i} + \frac{\alpha_i'^2}{\epsilon_i} \right) + O(A^2) \quad 3.4$$

In obtaining results for the "average atom" summation must be carried out over all occupied states in the Fermi distribution. Now the energy surfaces in $\underline{k}$ -space have the full cubic symmetry so that, in general, there are 48 different vectors $\underline{k}$ having the same set of associated energy values E_1, E_2, E_3 . If the state considered above has wave vector $\underline{k} = (k_x, k_y, k_z)$, then the vector $\underline{k}' = (k_y, k_z, k_x)$, for instance, has the same energies and it is easily shown that the wave function with energy E_3 is:-

$$\Psi_j'^+ = a_{j1}\phi_1^+ + a_{j2}\phi_2^+ + a_{j3}\phi_3^+$$

and so on, so that for this state:-

$$(j^+ | L_H | j^+) = 2A\hbar \left[\frac{(a_{j1}\alpha_x + a_{j2}\alpha_y + a_{j3}\alpha_z)^2}{\epsilon_i} + \frac{(a_{j1}\alpha_x + a_{j2}\alpha_y + a_{j3}\alpha_z)^2}{\epsilon_i} \right] + O(A^2)$$

If all 48 "equivalent" wave vectors $\underline{k}$ are considered together, all terms in $\alpha_x\alpha_y, \alpha_y\alpha_z$ and $\alpha_z\alpha_x$ vanish and the coefficients of $\alpha_x^2, \alpha_y^2, \alpha_z^2$ are all equal to 16 so that the average value of the

element $\langle 3^+ | L_H | 3^+ \rangle$ for these 48 states is:-

$$\langle 3^+ | L_H | 3^+ \rangle_{AV} = \frac{2}{3} A \hbar \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \right) + O(A^4) \quad 3.5$$

Similarly the operator $S_H = \frac{\hbar}{2} \begin{pmatrix} \alpha_z & \alpha_x - i\alpha_y \\ \alpha_x + i\alpha_y & -\alpha_z \end{pmatrix}$ but, since the spins have already been quantized along the direction of H , the operator $S_H = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ can be used directly on the functions $\bar{\Psi}_r$. Owing to the orthogonality of the ψ_r , it is at once obvious that:-

$$\langle \tau^+ | S_H | \tau^+ \rangle = \frac{\hbar}{2} + O(A^4); \quad \langle \tau^- | S_H | \tau^- \rangle = -\frac{\hbar}{2} + O(A^4) \quad 3.6$$

The expressions 3.5 and 3.6 must now be summed over all occupied states in the Fermi distribution in order to obtain the orbital and spin angular momenta in the direction of H for the "average atom". Now, if both states $\bar{\Psi}_r^+(k)$ and $\bar{\Psi}_r^-(k)$ are occupied, their contributions to either sum can be shown to be equal and opposite so that for either:-

$$\sum_{\text{occ. states}} = - \sum_{\text{unocc. states}}$$

Now the empty states will be those corresponding to a positive exchange energy and having the highest band energies E_i . Hence, if δ is taken as positive, they will have wave functions $\bar{\Psi}_r^+$ and for most of them ϵ_1 and ϵ_2 will be positive. Thus both the spin and orbital angular momentum of the "average atom" will be negative. The former must be so, since the states of lowest energy are those with their spin antiparallel to the field, i.e. these will be the occupied states, and in fact the total spin of the average atom must be, for Ni magnetically saturated:-

$$S_H = -0.6 \times \frac{\hbar}{2}$$

Thus finally we obtain for g and $2g'$:-

$$\begin{aligned}
 g &= \frac{\sum_{occ} (\tau/L_H + 2S_H/\tau)}{S_H} = \frac{-\sum_{unocc} (\tau/L_H/\tau) + 2\sum_{occ} (\tau/S_H/\tau)}{S_H} \\
 &= \frac{-\frac{2}{3} A \hbar \sum_{unocc} \left(\frac{1}{\epsilon_i} + \frac{1}{\epsilon_i} \right) - 2 \times 0.6 \times \frac{\hbar}{2}}{-0.6 \times \frac{\hbar}{2}} + O(A^2) \\
 &= 2 + \frac{1}{0.6} \cdot \frac{4}{3} A \sum_{unocc} \left(\frac{1}{\epsilon_i} + \frac{1}{\epsilon_i} \right) + O(A^2)
 \end{aligned}
 \tag{3.7}$$

which will be greater than 2, as observed experimentally.

$$\begin{aligned}
 g' &= \frac{\sum_{occ} (\tau/L_H + 2S_H/\tau)}{\sum_{occ} (\tau/L_H + S_H/\tau)} = \frac{-0.6 \hbar - \frac{2}{3} A \hbar \sum_{unocc} \left(\frac{1}{\epsilon_i} + \frac{1}{\epsilon_i} \right)}{-0.3 \hbar - \frac{2}{3} A \hbar \sum_{unocc} \left(\frac{1}{\epsilon_i} + \frac{1}{\epsilon_i} \right)} + O(A^2)
 \end{aligned}
 \tag{3.8}$$

which will be less than 2, as observed.

Some comments on Brooks' paper may be made at this stage.

- (i) Brooks purports to calculate g' but, by comparison with the above, he actually calculates g . However, he obtains $g < 2$, as Van Vleck (1980) points out. Van Vleck considers that this is caused by taking A as positive when summing over the unoccupied states, arguing that the spin-orbit parameter is of opposite sign for a nearly full electron shell as compared with a nearly empty one. However, Brooks stresses that his parameter A is for a single electron, and not the whole atom, so that it is positive for any electron. His error arises simply from a mistake in sign in his formula for ΔE , corresponding to 3.4 above.
- (ii) Brooks talks of averaging ΔE over the Fermi distribution and then dividing by the total angular momentum (which would be appropriate for g' , not g). Actually one must sum over the Fermi distribution and he has, in fact, divided by S_H . He has, however, made an error here, as he obtains a factor $\frac{2}{3}$ whereas it should be $\frac{4}{3}$ (see 3.7) so that his final value for $g-2$ should be doubled.

(2) Method of Calculation of g and g' .

The method of calculation of g and g' was as follows.

(i) Since 3.7 and 3.8 have been obtained by ignoring the two 3d wave functions ϕ_4 and ϕ_5 , it appeared most consistent to consider all the holes in the d band as occurring in a Γ_5 band obtained from the solutions of the cubic equation only (see Part I). An $H(E)$ curve was therefore drawn (Fig. 23a) by adding the three corresponding constituent $H(E)$ curves and a ferromagnetic normal limit E_f corresponding to 0.6 holes in this band constructed as before. The energy surface $E=E_f$ was then drawn in on the relevant energy contour diagrams, thereby showing the unoccupied regions of the B.Z., over which summation was to be carried out.

(ii) To avoid numerical integration in three dimensions it was considered sufficiently accurate to proceed as follows. The unoccupied part of the B.Z. was divided up into cells by planes parallel to the coordinate planes and midway between the points, at which the cubic equation had been solved, i.e. by planes

$$\xi, \eta, \zeta = \frac{(2\nu+1)\pi}{24}, \text{ with slight modifications at the hexagonal face.}$$

With each cell the energies E_1, E_2, E_3 were assumed to have the values at the centre.

(iii) Summation was carried out over the unoccupied part of the basic region (1/48 of the whole B.Z.). If the volume of any cell is ΔK , then $48 \sum_{\text{unocc. basic cells}} \Delta K$ corresponds to 0.6 states. Since formulae 3.5 and 3.6 correspond to one state:-

$$\sum_{\text{unocc. states}} \left(\frac{1}{E_1} + \frac{1}{E_2} \right) = 48 \sum_{\text{unocc. basic cells}} \left(\frac{1}{E_1} + \frac{1}{E_2} \right) \Delta K \times \frac{0.6}{48 \sum \Delta K} = \frac{0.6 \sum \left(\frac{1}{E_1} + \frac{1}{E_2} \right) \Delta K}{\sum \Delta K}$$

where each summation is over the unoccupied cells of the basic

region, ΔK being in arbitrary units.

(g) Degenerate States.

At certain points in the unoccupied part of the B.Z. the solutions of the cubic equation are degenerate so that ϵ_i becomes zero. For such a wave vector, however, the two states corresponding to the energies E_3 and E_1 will either both be occupied or both unoccupied, since they have the same energy. Their relevant contributions to the above sum will be $\frac{\Delta K}{\epsilon_i}$ and $-\frac{\Delta K}{\epsilon_i}$ but, since this argument is unsatisfactory when $\epsilon_i = 0$, it will be shown that their contribution together is the same as if the terms $\frac{1}{\epsilon_i}$ were ignored. Since the wave functions ψ_i^+ and ψ_3^+ are degenerate, they may be replaced by any two linear combinations of themselves; these are so chosen that the submatrix of O involving them is diagonal and similarly for the functions ψ_i^- and ψ_3^- . Thus, using the wave functions

$\psi_1^+ = \frac{1}{\sqrt{2}}(\psi_i^+ - i\psi_3^+)$; $\psi_2^+ = \frac{1}{\sqrt{2}}(\psi_3^+ - i\psi_i^+)$; $\psi_1^- = \frac{1}{\sqrt{2}}(\psi_i^- + i\psi_3^-)$; $\psi_2^- = \frac{1}{\sqrt{2}}(\psi_3^- + i\psi_i^-)$
the matrix of O becomes:-

$A\alpha_i'$	$\frac{A}{\sqrt{2}}(\alpha_i' + i\alpha_j')$	0	0	$\frac{A}{\sqrt{2}}(-\beta_i' - \beta_j' + i\beta_k')$	$A(\gamma_i' + i\beta_i')$
$\frac{A}{\sqrt{2}}(\alpha_i' - i\alpha_j')$	0	$\frac{A}{\sqrt{2}}(-\alpha_j' + i\alpha_i')$	$\frac{A}{\sqrt{2}}(\beta_i' + \beta_j' + i\beta_k')$	0	$\frac{A}{\sqrt{2}}(-\beta_i' - \beta_j' - i\beta_k')$
0	$\frac{A}{\sqrt{2}}(-\alpha_j' - i\alpha_i')$	$-A\alpha_i'$	$A(-\gamma_i' - i\beta_i')$	$\frac{A}{\sqrt{2}}(\beta_i' + \beta_j' + i\beta_k')$	0
0	$\frac{A}{\sqrt{2}}(\beta_i' + \beta_j' - i\beta_k')$	$A(-\gamma_i' + i\beta_i')$	$A\alpha_i'$	$\frac{A}{\sqrt{2}}(\alpha_i' - i\alpha_j')$	0
$\frac{A}{\sqrt{2}}(-\beta_i' - \beta_j' + i\beta_k')$	0	$\frac{A}{\sqrt{2}}(\beta_i' + \beta_j' - i\beta_k')$	$\frac{A}{\sqrt{2}}(\alpha_i' + i\alpha_j')$	0	$\frac{A}{\sqrt{2}}(-\alpha_j' - i\alpha_i')$
$A(\gamma_i' - i\beta_i')$	$\frac{A}{\sqrt{2}}(-\beta_i' - \beta_j' + i\beta_k')$	0	0	$\frac{A}{\sqrt{2}}(-\alpha_j' + i\alpha_i')$	$-A\alpha_i'$

Proceeding now just as before, the new wave functions to be used

are:- $\Psi_1^+ = \frac{1}{\sqrt{2}}(\psi_1^+ - i\psi_2^+) - \frac{A}{\sqrt{2}} \frac{(\alpha_i' - i\alpha_j')}{\epsilon_i} \psi_2^+ - \frac{A}{2\delta} \frac{(\gamma_i' - i\beta_i')}{\epsilon_i} \frac{1}{\sqrt{2}}(\psi_1^- + i\psi_2^-) + \frac{A}{\sqrt{2}} \frac{(\beta_i' + \beta_j' - i\beta_k')}{\epsilon_i + i\delta} \psi_2^-$ 3.10

and similarly for Ψ_1^- . Then:- $-\frac{A}{4\alpha_i'} \left[2\alpha_i' \alpha_j' + i(\alpha_j'^2 - \alpha_i'^2) \right] \left(\frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + i\delta} \right) \frac{1}{\sqrt{2}}(\psi_1^+ - i\psi_2^+)$

$$(3^+ | L_H | 3^+) = K \alpha_i' + \frac{AK(\alpha_i'^2 - \alpha_j'^2)}{\epsilon_i} + O(A^2)$$

3.11

and :-
$$(1' | L_H | 1'') = -k \alpha_i' + \frac{A k (\alpha_i'^2 + \alpha_i''^2)}{\epsilon_z} + O(A^2)$$

Averaging over the 48 equivalent wave vectors:-

$$(3' | L_H | 3'')_{AV} + (1' | L_H | 1'') = \frac{4k}{3} \frac{A k}{\epsilon_z} + O(A^2) \quad 3.12$$

which is exactly the same as $(3' | L_H | 3'')_{AV} + (1' | L_H | 1'')_{AV}$ if the terms in $\frac{1}{\epsilon_i}$ are ignored. This is sufficient justification for using the expressions obtained by non-degenerate perturbation theory at points of near-degeneracy in the B.Z., the very large contributions from $\frac{1}{\epsilon_i}$ in such a case nearly cancelling out.

(h) Results to $O(A)$.

Using the numerical results of Part I and the method of calculation detailed above, the results obtained for H1 are:-

$$\begin{aligned} g &= 2 + 3.43 \times 10^{-4} A \\ g' &= \frac{2 + 3.43 \times 10^{-4} A}{1 + 3.43 \times 10^{-4} A} \end{aligned} \quad 3.13$$

where A is measured in cm^{-1} .

Goudmit (1928) in a consideration of the effect of spin-orbit interaction on atomic spectra has outlined a method of obtaining estimates of the parameter A for particular electrons of a given atom from spectroscopic data. Brooks states that Goudmit has made estimates of 630 cm^{-1} and 390 cm^{-1} for H1 and Fe respectively, presumably for a 3d electron in both cases, but so far it has not been possible to trace these figures in Goudmit's published work. However, substitution of the former value in 3.13 gives:-

$$\underline{g = 2.21_6} \quad ; \quad \underline{g' = 1.82_3} \quad 3.14$$

The experimental values (see Kittel 1949a) are 2.19-2.42 and 1.93 respectively so that agreement is quite good in the case of g but the calculated value of g' is considerably too small.

It was therefore considered worth while extending the calculation to terms of $O(A^2)$ in order to see the effect of these second order terms.

(1) Calculation and Results to $O(A^2)$.

Second order terms may be said to arise in three ways.

- (i) The function 3.2 is only an eigenfunction of 2.12 to $O(A)$.
- (ii) Owing to spin-orbit interaction the eigenfunctions of 2.12 no longer have their spins quantized exactly along the field direction so that $(n^+ / S_H / n^+) = \hbar/2$ only to $O(A)$.
- (iii) The function 3.2 is only normalized to $O(A)$.

Applying second-order perturbation theory to 2.12 one obtains as a correction to 3.2 for the function Ψ_3^+ :-

$$A^2 \left\{ \left(\frac{-\alpha_1' \alpha_1'}{\epsilon_1 \epsilon_2} + \frac{\alpha_1' \alpha_1' + i \alpha_2'}{\epsilon_1 (\epsilon_2 + 2\delta)} \right) \psi_1^+ + \left(\frac{-\alpha_2' \alpha_1'}{\epsilon_2 \epsilon_1} + \frac{\alpha_2' \alpha_1' + i \alpha_2'}{\epsilon_2 (\epsilon_1 + 2\delta)} \right) \psi_2^+ - \frac{1}{\epsilon_1^2} \left(\frac{\alpha_1'^2}{\epsilon_1} + \frac{\alpha_1'^2}{\epsilon_2} + \frac{1 - \alpha_1'^2}{(\epsilon_1 + 2\delta)^2} + \frac{1 - \alpha_1'^2}{(\epsilon_2 + 2\delta)^2} \right) \psi_3^+ \right. \\ \left. + \left(\frac{\alpha_1' (\beta_2' + i \gamma_2')}{\epsilon_2 (\epsilon_1 + 2\delta)} - \frac{\alpha_1' (\beta_1' + i \gamma_1')}{(\epsilon_1 + 2\delta) (\epsilon_2 + 2\delta)} \right) \psi_1^- + \left(\frac{\alpha_2' (\beta_2' + i \gamma_2')}{\epsilon_1 (\epsilon_2 + 2\delta)} - \frac{\alpha_2' (\beta_1' + i \gamma_1')}{(\epsilon_1 + 2\delta) (\epsilon_2 + 2\delta)} \right) \psi_2^- \right. \\ \left. + \left(\frac{-\alpha_1' (\beta_2' + i \gamma_2')}{2\delta \epsilon_1} - \frac{\alpha_1' (\beta_1' + i \gamma_1')}{2\delta \epsilon_2} + \frac{\alpha_1' (\beta_2' + i \gamma_2')}{2\delta (\epsilon_1 + 2\delta)} + \frac{\alpha_1' (\beta_1' + i \gamma_1')}{2\delta (\epsilon_2 + 2\delta)} \right) \psi_3^- \right\}$$

Using this unnormalised wave function:-

$$(3^+ / L_H / 3^+) = 2A\hbar \left(\frac{\alpha_1'^2}{\epsilon_1} + \frac{\alpha_1'^2}{\epsilon_2} \right) + 2A^2\hbar \left(\frac{\alpha_1'^2}{\epsilon_1 (\epsilon_2 + 2\delta)} + \frac{\alpha_1'^2}{\epsilon_2 (\epsilon_1 + 2\delta)} - \frac{\alpha_1'^2}{(\epsilon_1 + 2\delta) (\epsilon_2 + 2\delta)} \right)$$

$$(3^+ / S_H / 3^+) = \frac{\hbar}{2} + A^2\hbar \left(\frac{1 - \alpha_1'^2}{(\epsilon_1 + 2\delta)^2} + \frac{1 - \alpha_1'^2}{(\epsilon_2 + 2\delta)^2} \right)$$

$$\int \bar{\Psi}_3^+ \Psi_3^+ d\tau = 1 + O(A^2)$$

so that, finally, with the normalised wave function:-

$$(3^+ / L_H + 2S_H / 3^+) = \hbar + \frac{2}{3} A\hbar \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \right) - \frac{2}{3} A^2\hbar \left(\frac{2}{(\epsilon_1 + 2\delta)^2} + \frac{2}{(\epsilon_2 + 2\delta)^2} + \frac{1}{(\epsilon_1 + 2\delta) (\epsilon_2 + 2\delta)} - \frac{1}{\epsilon_1 (\epsilon_2 + 2\delta)} - \frac{1}{\epsilon_2 (\epsilon_1 + 2\delta)} \right) \quad 3.16$$

$$(3^+ / L_H + S_H / 3^+) = \frac{\hbar}{2} + \frac{2}{3} A\hbar \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \right) - \frac{2}{3} A^2\hbar \left(\frac{1}{(\epsilon_1 + 2\delta)^2} + \frac{1}{(\epsilon_2 + 2\delta)^2} + \frac{1}{(\epsilon_1 + 2\delta) (\epsilon_2 + 2\delta)} - \frac{1}{\epsilon_1 (\epsilon_2 + 2\delta)} - \frac{1}{\epsilon_2 (\epsilon_1 + 2\delta)} \right)$$

Before proceeding with the calculation it is obviously

necessary to make some estimate of the exchange energy δ . Since the results in Part I are to be used for ϵ_1, ϵ_2 (and the a_m for K_1), it would be most consistent to estimate δ also from these

results. Regarding Fig. 32 as the most accurate $n(E)$ curve obtained in Part I, it would at first seem best to use this curve for the estimate. In order to do so one should in principle carry out a calculation, of the type made by Stoner (1938a) for a parabolic band and Wohlfarth (1951) for a rectangular band, for the actual band of Fig. 32. Such a calculation would obviously be quite complex and was not considered worth while at present. If it is assumed that the head of the band is parabolic and that $f = 1$, then from Fig. 32 $E_{op} = .125\text{eV}$ and, following Wohlfarth (1949c):-

$$\delta = k \Theta f = \frac{E_{op}}{E_{op}/k\Theta} f = \frac{.125}{2^{1/3}} \cdot 1 = .099\text{eV}$$

in good agreement with Wohlfarth's estimate of .106eV for Ni, also based on a parabolic band. However, the calculations of g , g' and K , are based on Fig. 23a with the assumption that all 0.6 holes per atom occur in this "cubic band". From this curve $E_{op} = .232\text{eV}$ and $E_{of} = .449\text{eV}$ so that the use of $\delta \sim .1\text{eV}$ would be quite incompatible with the assumption that $f = 1$ since some unoccupied states $E_i + \delta$ would then be of lower energy than some occupied states $E_j - \delta$. The use of Fig. 23a for the present calculations has already been discussed; it appears the most suitable for the approximate treatment here and therefore for consistency should be used in obtaining the estimate of δ . If a curve is drawn of q against E for this band, where q is the number of states between E and the top of the band, it is found to be very nearly a straight line, as indicated by $E_{of} \approx 2E_{op}$ above. It would be exactly so for a rectangular band and it seemed therefore most appropriate to use the formula $\frac{E_{op}}{k\Theta} = \left[1 - \exp\left(-\frac{E_{op}}{k\Theta}\right) \right]$.

deduced by Wohlfarth (1951) for such a band, in estimating δ .

Putting $E_{cp} = 232\text{eV}$ and $\Theta = 631^\circ\text{K}$, one obtains:-

$$\delta = 236\text{eV}$$

and this value has therefore been used in the following calculations of the second order corrections to g and g' and of K_1 .

In proceeding with the actual calculations the following points must be mentioned.

(i) It is easily shown that the relation

$$\sum_{\text{occ. states}} = - \sum_{\text{unocc. states}}$$

still holds to $O(A^2)$.

(ii) Proceeding as before, i.e. using the modified matrix 3.9 of 0, it can be shown that:-

$$(3^+|L_H + 2S_H|3^+) + (1^+|L_H + 2S_H|1^+) = (3^+|L_H + 2S_H|3^+) + (1^+|L_H + 2S_H|1^+)$$

to $O(A^2)$ for the degenerate case $\epsilon_i = 0$, where the infinite terms on the R.H.S. are allowed to cancel each other out, so that one is justified in using the ordinary non-degenerate formulae for cases of near-degeneracy as before. This also holds for the matrix elements of $L_H + S_H$. It must be noted, however, that:-

$$\frac{1}{\epsilon_i(\epsilon_i + 2\delta)} - \frac{1}{\epsilon_i(\epsilon_i - \epsilon_j + 2\delta)} = \frac{-1}{(\epsilon_i + 2\delta)(\epsilon_i - \epsilon_j + 2\delta)} \rightarrow \frac{-1}{(\epsilon_i + 2\delta)^2} \text{ as } \epsilon_j \rightarrow 0$$

so that for the completely degenerate case:-

$$(3^+|L_H + 2S_H|3^+)_{AV} + (1^+|L_H + 2S_H|1^+)_{AV} = 2\hbar + \frac{4}{3} \frac{Ak}{\epsilon_L} - \frac{2}{3} Ak \left\{ \frac{5}{(\epsilon_L + 2\delta)^2} + \frac{4}{4\delta^2} - \frac{2}{2\delta\epsilon_L} + \frac{2}{2\delta(\epsilon_L + 2\delta)} \right\}$$

$$(3^+|L_H + S_H|3^+)_{AV} + (1^+|L_H + S_H|1^+)_{AV} = \hbar + \frac{4}{3} \frac{Ak}{\epsilon_L} - \frac{2}{3} Ak \left\{ \frac{3}{(\epsilon_L + 2\delta)^2} + \frac{2}{4\delta^2} - \frac{2}{2\delta\epsilon_L} + \frac{2}{2\delta(\epsilon_L + 2\delta)} \right\}$$

(iii) A far more awkward difficulty arises because for certain unoccupied states $\epsilon_i + 2\delta$ becomes very small, i.e. considerably less than A so that non-degenerate perturbation theory is again not applicable. This difficulty is bound to arise for certain

states near the Fermi surface if it is assumed that J is only just unity at $0^\circ K$ (Stoner, Wohlfarth loc.cit.). It is most important as it also arises in using Brooks' formula for the anisotropy coefficient K_1 . Assuming $\epsilon_1 + 2\delta = 0$, degenerate perturbation theory can be applied in a similar way as above but there is now the vital difference that, whereas the state corresponding to $E_3 + \delta$ is unoccupied, that corresponding to $E_1 - \delta$ is occupied so that only the former occurs in the summations. Putting $\chi_1 + i\beta_1 = R e^{i\chi}$ so that $R^2 = \chi_1^2 + \beta_1^2 = 1 - \alpha_1^2$, one obtains:-

$$\Psi_3^{+'} = \frac{1}{\sqrt{2}} (\Psi_3^+ - e^{-i\chi} \Psi_1^+) + Q(A) \quad 3.17$$

and, for instance:-

$$\begin{aligned} (3^+ / L_{11} + 2S_{11} / \beta_1^2) = A^2 K \left\{ 2 \left(\alpha_1^2 + \frac{\alpha_1^2}{2R} \right) \frac{1}{\epsilon_1} + \left(\alpha_1^2 + \frac{2\alpha_1^2 - \alpha_1^2}{2R} \right) \frac{1}{\epsilon_2} - \left(\alpha_1^2 + \frac{2\alpha_1^2 - \alpha_1^2}{2R} \right) \frac{1}{\epsilon_2 + 2\delta} \right\} \\ + A^2 K \left\{ \left(\alpha_1^2 + \alpha_1^2 + \frac{4\alpha_1^2 - \alpha_1^2 \alpha_1^2}{4R} - \frac{\alpha_1^2 \alpha_1^2}{4R^2} + \frac{\alpha_1^2 \alpha_1^2 \alpha_1^2}{2R^3} \right) \frac{1}{\epsilon_1^2} + \text{similar} \right. \\ \left. \text{terms in } \frac{1}{(\epsilon_2 + 2\delta)^2}, \frac{1}{\epsilon_1 \epsilon_2}, \frac{1}{\epsilon_1 (\epsilon_2 + 2\delta)} \text{ and } \frac{1}{\epsilon_2 (\epsilon_2 + 2\delta)} \right\} \quad 3.18 \end{aligned}$$

So far no suitable means of utilising this formula for the unoccupied states, for which $\epsilon_1 + 2\delta$ is small, has been devised owing to the difficulty in averaging terms such as $\frac{\alpha_1^2}{2R}$ over the 48 equivalent states. It is doubtful if it is applicable, anyway, since one notes that the wave function 3.17 has zero spin momentum in the direction of the applied field (which makes 3.18 of $O(A)$), which is hardly consistent with the method of treatment of the problem so far. The point is that the spin-orbit interaction, although small, is sufficient to distort the Fermi surface considerably so that use of the results of the simple band calculation is a poor approximation from this point of view. In the circumstances it was decided to proceed with the calculation, using the non-degenerate formulae 3.16 for the

states where $\epsilon_1 + 2\delta$ is small; this has some justification on two counts. Firstly, although use of 3.16 for these states results in large contributions from the $O(A^2)$ terms, evaluation of the complete formulae 3.16 and 3.18 (ignoring all terms involving R) gives practically identical figures. Secondly, there are not very many such states compared with the total number of unoccupied ones although nevertheless their effect on the $O(A^2)$ correction to g and g' is quite large; this point is discussed later. The results finally obtained for Ni were:-

$$\begin{aligned} g &= 2 + (3.43 \times 10^{-4})A - (2.181 \times 10^{-7})A^2 \\ g' &= \frac{2 + (3.43 \times 10^{-4})A - (2.181 \times 10^{-7})A^2}{1 + (3.43 \times 10^{-4})A - (0.999 \times 10^{-7})A^2} \end{aligned} \quad 3.19$$

where A is measured in cm.⁻¹. Using the value 630 cm.⁻¹ for the spin-orbit parameter A, these formulae give:-

$$\underline{g = 2.129} \quad ; \quad \underline{g' = 1.810} \quad 3.20$$

It can be seen that incorporation of a second order correction has made the agreement with experiment worse. However, it is worth noting that such second order terms are not negligible and should be considered in any more accurate theory of the gyromagnetic and ferromagnetic resonance effects.

(k) Comparison with Brooks' Results and Comments.

Owing to the fact that no such figures, such as those obtained in Part I, were available to Brooks, he was unable to carry out any calculation such as that above and could only make a very rough estimate of the departure of g from 2 as $A/(\text{"mean bandwidth"})$, using values of 500 and 20,000 cm.⁻¹ for A and the mean band width respectively. Allowing for the mistake in sign and numerical factor mentioned already, this gives the

value $g \sim 2.05$, considerably less than the values 3.14 or 3.20. Apart from the fact that Brooks' estimate is a very ^{rough} one, the real reason for the difference is that his "mean bandwidth" is based on Slater's band calculation, which gives a bandwidth twice that obtained in Part I.

Both Kittel (1949a) and Van Vleck (1950) have shown in their theoretical treatments of the gyromagnetic ratio and the spectroscopic splitting factor that $g \sim 2 - g'$, admittedly by the use of very approximate methods, whereas this is not confirmed by experiment. If the first order effect of spin-orbit interaction gives $g = 2 + a$, then on either treatment $g' = \frac{2+a}{1+a} - 2$, provided a is small as it is in practice. Since the theory used above is the same as that of Kittel, modified to fit the collective electron picture, the results were bound to give $g \sim 2 - g'$. The second order effect of spin-orbit interaction is probably considerably larger than Van Vleck expected but, as he predicted, it acts in the wrong direction. Owing to the number of quite crude approximations used in treating the problem here, it seems fruitless to make any further attempt for the present to improve the agreement with experiment. The first order agreement in the case of g is as much as could have been expected. Detailed consideration of the approximations will be deferred until later.

Chapter IV.

Anisotropy Coefficient K_1 for Nickel.

(a) Theory of the Calculation.

If the energy corrections due to spin-orbit interaction are calculated by applying successive orders of perturbation theory to the secular equation 2.12, it is easily shown that no anisotropy is exhibited until the fourth order correction is reached in the non-degenerate case, when summation is carried out over all occupied states. The degenerate case will be considered later. Thus, by the same arguments as used in chapter III, terms involving $\alpha_i^{1,2}$ average out over the 48 equivalent states to $\frac{1}{3}$, while terms involving $\alpha_i^{1,3}, \alpha_i^{2,3}$ or $\alpha_i^{1,2} \alpha_j^{1,2}$ average out to zero and terms involving $\alpha_i^{1,2} \alpha_j^{1,2}$ do not arise until the fourth order correction. Since all diagonal elements of the operator O are zero, the expression for this correction to the level E_n in the matrix $(n|O|n')$ reduces to:-

$$-\sum_{n' \neq n} \sum_{n'' \neq n} \frac{(n|O|n')(n'|O|n)(n|O|n'')(n''|O|n)}{(E_n - E_{n'})^2 (E_n - E_{n''})} + \sum_{n' \neq n} \sum_{n'' \neq n} \frac{(n|O|n')(n'|O|n'')(n''|O|n)(n|O|n'')}{(E_n - E_{n'}) (E_n - E_{n''}) (E_n - E_{n''})} \quad 4.1$$

Considering the correction to the energy level $E_3 + \sigma$, the first term in 4.1 gives:-

$$-A^4 \left\{ \frac{\alpha_1^{1,2}}{\epsilon_1^2} + \frac{\alpha_1^{1,2}}{\epsilon_2^2} + \frac{1 - \alpha_2^{1,2}}{(\epsilon_1 + 2\sigma)^2} + \frac{1 - \alpha_1^{1,2}}{(\epsilon_2 + 2\sigma)^2} \right\} \left\{ \frac{\alpha_2^{1,2}}{\epsilon_1} + \frac{\alpha_1^{1,2}}{\epsilon_2} + \frac{1 - \alpha_2^{1,2}}{\epsilon_1 + 2\sigma} + \frac{1 - \alpha_1^{1,2}}{\epsilon_2 + 2\sigma} \right\}$$

Putting $\alpha_1^{1,2} = \alpha_1^{1,2} (1 - \alpha_2^{1,2} - \alpha_3^{1,2})$ etc. and dropping all terms, which will not exhibit anisotropy when averaged over the 48 equivalent states, this reduces to:-

$$-A^4 \left\{ \alpha_1^{1,2} \alpha_2^{1,2} \left(\frac{1}{\epsilon_1^2} - \frac{1}{\epsilon_2^2} - \frac{1}{(\epsilon_1 + 2\sigma)^2} + \frac{1}{(\epsilon_2 + 2\sigma)^2} \right) \left(-\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} + \frac{1}{\epsilon_1 + 2\sigma} - \frac{1}{\epsilon_2 + 2\sigma} \right) \right. \\ \left. + \alpha_2^{1,2} \alpha_3^{1,2} \left(\frac{1}{\epsilon_1^2} - \frac{1}{(\epsilon_1 + 2\sigma)^2} \right) \left(-\frac{1}{\epsilon_1} + \frac{1}{\epsilon_1 + 2\sigma} \right) + \alpha_3^{1,2} \alpha_1^{1,2} \left(\frac{1}{\epsilon_2^2} - \frac{1}{(\epsilon_2 + 2\sigma)^2} \right) \left(-\frac{1}{\epsilon_2} + \frac{1}{\epsilon_2 + 2\sigma} \right) \right\} \quad 4.2$$

The second term in the expression 4.1 gives:-

$$A^u \left\{ \frac{i\alpha_i'}{\epsilon_i} \left[\frac{(i\alpha_i'X - i\alpha_i'X - i\alpha_i')}{\epsilon_i \epsilon_i} + \frac{(i\alpha_i')(Y_i' + i\beta_i'X - Y_i' + i\beta_i')}{\epsilon_i(\epsilon_i + 2\sigma)} - \frac{(Y_i' + i\beta_i'X - Y_i' + i\beta_i')}{(\epsilon_i + 2\sigma)\epsilon_i} - \frac{(Y_i' + i\beta_i'X - Y_i' + i\beta_i')}{(\epsilon_i + 2\sigma)(\epsilon_i + 2\sigma)} \right] \right. \\ \left. + \frac{(Y_i' + i\beta_i'X - Y_i' + i\beta_i')}{2\sigma\epsilon_i} + \frac{(Y_i' + i\beta_i'X - Y_i' + i\beta_i')}{2\sigma\epsilon_i} + \frac{(Y_i' + i\beta_i'X - Y_i' + i\beta_i')}{2\sigma(\epsilon_i + 2\sigma)} + \frac{(Y_i' + i\beta_i'X - Y_i' + i\beta_i')}{2\sigma(\epsilon_i + 2\sigma)} \right\} \\ = A^u \left\{ \frac{\alpha_i'^2 \alpha_i'^2}{\epsilon_i^2 \epsilon_i} - \frac{\alpha_i'^2 \alpha_i'^2 + i\alpha_i' \alpha_i' \alpha_i'}{\epsilon_i \epsilon_i (\epsilon_i + 2\sigma)} + \frac{\alpha_i'^2 (1 - \alpha_i'^2)}{\epsilon_i^2 (\epsilon_i + 2\sigma)} + \frac{\alpha_i'^2 \alpha_i'^2 + i\alpha_i' \alpha_i' \alpha_i'}{\epsilon_i (\epsilon_i + 2\sigma)(\epsilon_i + 2\sigma)} + \frac{\alpha_i'^2 (1 - \alpha_i'^2)}{\epsilon_i^2 2\sigma} - \frac{\alpha_i'^2 \alpha_i'^2 + i\alpha_i' \alpha_i' \alpha_i'}{\epsilon_i \epsilon_i 2\sigma} \right. \\ \left. - \frac{\alpha_i'^2 (1 - \alpha_i'^2)}{\epsilon_i (\epsilon_i + 2\sigma) 2\sigma} + \frac{\alpha_i'^2 \alpha_i'^2 + i\alpha_i' \alpha_i' \alpha_i'}{\epsilon_i (\epsilon_i + 2\sigma) 2\sigma} \text{ etc.} \right\}$$

Proceeding as above this reduces to:-

$$A^u \left\{ \alpha_i'^2 \alpha_i'^2 \frac{1}{2\sigma} \left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} + \frac{1}{\epsilon_i + 2\sigma} \right]^2 + \alpha_i'^2 \alpha_i'^2 \left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} + \frac{1}{2\sigma} \right] \left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} \right]^2 \right. \\ \left. + \alpha_i'^2 \alpha_i'^2 \left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} + \frac{1}{2\sigma} \right] \left[\frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} \right]^2 \right\} \quad 4.3$$

4.2 and 4.3 hence together give an expression of the form:-

$$A^u [A_{12} \alpha_i'^2 \alpha_i'^2 + A_{13} \alpha_i'^2 \alpha_j'^2 + A_{13} \alpha_i'^2 \alpha_j'^2] \quad 4.4$$

where:- $A_{12} = \left\{ \frac{1}{\epsilon_i^2} - \frac{1}{\epsilon_i^2} - \frac{1}{(\epsilon_i + 2\sigma)^2} + \frac{1}{(\epsilon_i + 2\sigma)^2} \right\} \left\{ \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} + \frac{1}{\epsilon_i + 2\sigma} \right\} + \frac{1}{2\sigma} \left\{ \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} + \frac{1}{\epsilon_i + 2\sigma} \right\}$

$$A_{13} = \left\{ \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} + \frac{1}{2\sigma} + \frac{1}{\epsilon_i} + \frac{1}{\epsilon_i + 2\sigma} \right\} \left\{ \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} \right\}^2; A_{13} = \left\{ \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} + \frac{1}{2\sigma} + \frac{1}{\epsilon_i} + \frac{1}{\epsilon_i + 2\sigma} \right\} \left\{ \frac{1}{\epsilon_i} - \frac{1}{\epsilon_i + 2\sigma} \right\}^2 \quad 4.5$$

In order to obtain an expression for χ , this energy expression 4.4 must be put in terms of $\alpha_x = \sin\theta \cos\phi$, $\alpha_y = \sin\theta \sin\phi$ and $\alpha_z = \cos\theta$, the direction cosines relative to the crystal axes. from 2.10:-

$$\alpha_i'^2 \alpha_j'^2 = \sum_{i,j,k,l} a_{ij} a_{jk} a_{kl} a_{li} \alpha_i' \alpha_j' \alpha_k' \alpha_l' \\ = \sum_j a_{ij}^2 a_{jk}^2 \alpha_j'^4 + \sum_{j \neq k} [a_{ij}^2 a_{jk}^2 + a_{jk}^2 a_{ij}^2 + 4a_{ij} a_{jk} a_{ij} a_{jk}] \alpha_j'^2 \alpha_k'^2 \\ + 2 \sum_{j \neq k} a_{ij} a_{jk} (a_{ij} a_{jk} + a_{jk} a_{ij}) \alpha_j'^3 \alpha_k' \\ + 2 \sum_{j \neq k \neq l} [a_{ij}^2 a_{jk} a_{kl} + a_{jk} a_{kl} a_{ij}^2 + 2a_{ij} a_{jk} a_{ij} a_{kl} + 2a_{ij} a_{kl} a_{ij} a_{jk}] \alpha_j'^2 \alpha_k' \alpha_l'$$

Putting $\alpha_j'^4 = \alpha_j'^2 (1 - \alpha_k'^2 - \alpha_l'^2)$ and averaging over the 48 equivalent states, the terms in $\alpha_j'^4$ may be ignored as exhibiting no anisotropy and so may the terms $\alpha_j'^2 \alpha_k'$ and $\alpha_j'^2 \alpha_k' \alpha_l'$, since their average coefficients are zero. In this averaging $\alpha_x^2 \alpha_y^2$, $\alpha_y^2 \alpha_z^2$ and $\alpha_z^2 \alpha_x^2$

appear with equal coefficients so that the average coefficient of $A_{\mu\nu}(\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_z^2\alpha_x^2)$ becomes:-

$$\frac{1}{3} \left\{ - \sum_j a_{\mu j}^2 a_{\nu j}^2 - \sum_k a_{\mu k}^2 a_{\nu k}^2 + \sum_{j \neq k} a_{\mu j}^2 a_{\nu k}^2 + 4 \sum_{j < k} a_{\mu j} a_{\mu k} a_{\nu j} a_{\nu k} \right\}$$

Putting $a_{\nu k}^2 = 1 - a_{\nu j}^2 - a_{\nu l}^2$ in the third term and $a_{\mu k} a_{\nu k} = -a_{\mu j} a_{\nu j} - a_{\mu l} a_{\nu l}$ in the fourth term and defining $J_{\mu\nu} = \sum_j a_{\mu j}^2 a_{\nu j}^2$, the expression $\{ \}$ reduces to:- $\{ \} = -2J_{\mu\nu} + 2 - 2J_{\mu\nu} - 4J_{\mu\nu} - [\{ \} + 2J_{\mu\nu}]$

$$\therefore \{ \} = 1 - 5J_{\mu\nu}$$

so that finally the expression 4.4, averaged over the 48 equivalent states, becomes:-

$$\frac{1}{3} A^4 \sum_{\mu \neq \nu} A_{\mu\nu} (1 - 5J_{\mu\nu}) (\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_z^2\alpha_x^2) \quad 4.6$$

(b) method of calculation.

The procedure used was very similar to that used in Chapter III for calculating g and g' . The expression 4.6 represents the lowest order correction to the energy level $E_i + \delta$, which exhibits anisotropy, or rather the average correction for the 48 states, all with unperturbed energy $E_i + \delta$ and with equivalent wave vectors. To obtain the correction for the "average atom" of the collective electron model this expression must be summed over all occupied states in the Fermi distribution. If all states were occupied, this summation would involve all six states $E_i \pm \delta$ (for the same wave vector $\underline{k}$) and by the diagonal sum rule the sum of the corrections for these states must be zero. Hence one has again that:-

$$\sum_{\text{occ. states}} = - \sum_{\text{unocc. states}}$$

Dividing the basic region of the B.Z. up into cells as before, then with the same nomenclature the anisotropic energy correction for the "average atom" is:-

$$-48 \sum_{\substack{\text{unocc} \\ \text{basic} \\ \text{cells}}} \left[\frac{A^4}{3} \sum_{\mu < \nu} A_{\mu\nu} (1-5J_{\mu\nu}) \sum_i \alpha_i^4 \alpha_j^4 \right] \Delta K \times \frac{0.6}{48 \Delta K} = \frac{-0.2 A^4 \sum_{\mu < \nu} [A_{\mu\nu} (1-5J_{\mu\nu}) \sum_i \alpha_i^4 \alpha_j^4] \Delta K}{\sum \Delta K}$$

If there are n atoms per c.c., then by definition:-

$$K_i = \frac{-0.2 n A^4}{\sum \Delta K} \sum_{\text{unocc } \mu < \nu} [A_{\mu\nu} (1-5J_{\mu\nu})] \Delta K \text{ ergo/c.c.} \quad 4.7$$

if A and the ϵ_i are expressed in ergs.

(c) Cases of Degeneracy.

In carrying out the above summation the same cases of degeneracy ($\epsilon_i = 0$) and near-degeneracy ($\epsilon_i, 2\sigma < A$) are encountered as in calculating g and g'. In the former case a perturbation calculation, using the modified matrix 3.9 of 0, must be performed; this has been carried out and gives a perfectly satisfactory result, which, however, can be obtained by a much simpler procedure. As for g and g' it is first to be noted that, if $\epsilon_i = 0$, the two states corresponding to the equal energies E_1 and E_2 will either both be occupied or both unoccupied and so may be considered together. Secondly it is found that the only wave vectors in the region of the B.Z. involved in the summation 4.7, for which $\epsilon_i = 0$, occur on the (100) axis and for these wave vectors $J_{12} = J_{23} = J_{13} = 0$. Denoting the two states by the numbers 1 and 3, it is therefore only necessary to consider:-

$$\sum_{1,3} \sum_{\mu < \nu} A_{\mu\nu} \quad 4.8$$

If the non-degenerate formulae 4.5 are substituted in 4.8 and the limit taken as $\epsilon_i \rightarrow 0$, it is found that the limit is finite and is in fact exactly the same expression as that obtained by use of degenerate perturbation theory. Again this justifies the use of 4.5 in cases of near-degeneracy, i.e. when ϵ_i is small, the contributions to the summation 4.7 from the two states 1

and 3 being separately large but of opposite sign. For the degenerate states 4.8 was evaluated in practice by substituting in the expressions 4.5, modified by dropping all terms involving $\frac{1}{\epsilon_1}$, and then adding:-

$$\frac{12}{(2\delta)^3} + \frac{2}{\epsilon_1^2 2\delta} - \frac{2}{(\epsilon_1 + 2\delta)^2 2\delta} - \frac{4}{(\epsilon_1 + 2\delta)^3} + \frac{4(\epsilon_1 + \delta)}{\epsilon_1^2 4\delta^2} + \frac{4(\epsilon_1 + \delta)}{\epsilon_1^2 (\epsilon_1 + 2\delta)^2} - \frac{4(\epsilon_1 + 3\delta)}{4\delta^2 (\epsilon_1 + 2\delta)^2} \quad 4.9$$

which terms arise as in the case of g and g' , e.g.:-

$$\frac{-4}{\epsilon_1 (\epsilon_1 + 2\delta) 2\delta} + \frac{4}{\epsilon_1 (-\epsilon_1 + 2\delta) 2\delta} = \frac{8}{(\epsilon_1 + 2\delta)(-\epsilon_1 + 2\delta) 2\delta} \rightarrow \frac{8}{(2\delta)^2} \text{ as } \epsilon_1 \rightarrow 0$$

As regards cases where the non-degenerate theory becomes invalid because $\epsilon_1 + 2\delta$ is small, only 11 out of the 166 states involved in 4.7 are found to fall on this category. However, if non-degenerate theory is applied in these cases, it is found that they contribute about one-third of the calculated value of K_1 . It was therefore considered essential to carry out a degenerate perturbation calculation ($\epsilon_1 + 2\delta = 0$) as in the case of g and g' . Again the difficulty arises that only the state corresponding to the energy $E_3 + \delta$ will be unoccupied and it must therefore be considered separately. A modified matrix of 0, based on the wave functions $\psi_1^+, \psi_2^+, \frac{1}{\sqrt{2}}(\psi_3^+ - e^{ik} \psi_4^+), \frac{1}{\sqrt{2}}(\psi_1^- + e^{ik} \psi_3^-), \psi_2^-, \psi_4^-$, where $k' + i\beta_2' = R e^{ik}$, must be used and the fourth order perturbation calculation is exceedingly complicated. Unfortunately the results are unsatisfactory as once again terms such as $\frac{\alpha_3^2}{R}, \frac{\alpha_3^4}{R^2}$ etc. arise and no satisfactory means of averaging such terms over the 48 equivalent states has as yet been devised. Another point is that even these formulae are invalid, if $R=0$, which is possible for certain directions of the external field. In the circumstances a value of K_1 was calculated, using the non-degenerate formulae even when $\epsilon_1 + 2\delta$ became small, the final value obtained being

regarded as merely an indication of the order of magnitude of K_1 .

(d) Calculation of K_1 for Nickel.

In order to proceed with the calculation of K_1 for Ni it was necessary to calculate the $A_{\mu\nu}$ and $J_{\mu\nu}$ for each state involved in the summation 4.7. The $A_{\mu\nu}$ were evaluated from the formulae 4.5 using the solutions of the cubic secular equation from Part I and the same value of δ as used in the case of g and g'. For the $J_{\mu\nu}$ the coefficients a_m were evaluated from the cubic secular determinant of Part I together with the

corresponding solutions of the cubic secular equation, e.g.:-

$$a_{11} = C \begin{vmatrix} H_{11} - E_1 & H_{12} \\ H_{12} & H_{11} - E_1 \end{vmatrix}, a_{12} = C \begin{vmatrix} H_{12} & H_{11} \\ H_{11} - E_1 & H_{12} \end{vmatrix}, a_{13} = C \begin{vmatrix} H_{11} & H_{12} - E_1 \\ H_{12} & H_{11} \end{vmatrix}$$

the constant C being then chosen so that $a_{11}^2 + a_{12}^2 + a_{13}^2 = 1$. In each case it was checked that $\sum_n a_{\mu n} a_{\nu n} = 0$, i.e. that the matrix $\{a_{\mu n}\}$ was unitary orthogonal.

Using the value $\delta = 236 \text{ eV}$ as before and $n = 9.25 \times 10^{22}$ atoms per c.c., the result obtained was:-

$$K_1 = -2.043 \times 10^{-3} A^4 \text{ ergs/c.c.}$$

If A is measured in cm.⁻¹ substitution of the value 630 cm.^{-1} for the spin-orbit parameter gives:-

$$K_1 = -3.22 \times 10^8 \text{ ergs/c.c.}$$

(e) Comments.

As already stated the best available experimental figure for the first anisotropy coefficient at 0°K for Ni is -8×10^5 ergs/c.c. so that, even allowing for the possible effect of using non-degenerate perturbation theory for certain states for which it is invalid, the figure obtained here is about 100

times too large. Possible reasons for this will be considered later.

Brooks obtained a rough estimate for K_1 of -8×10^5 ergs/e.e., in good agreement with experiment and his arguments will now be considered in order to discover the reasons for the much larger figure obtained here. Firstly he assumes that the coefficients $a_{\tau n}$ ($\tau \neq n$) and hence the $J_{\mu\nu}$ are small so that one can take $1 - 5J_{\mu\nu} \sim 1$. In the present calculation it was found that $1 - 5J_{\mu\nu}$ varied from -1.8 to $+1.0$ with an average value of ~ 0.7 ; this point would actually increase the discrepancy between Brooks' and the present values for K_1 , but it is relatively unimportant. With his assumption Brooks then obtains $K_1 = -\sum (A_{12} + A_{23} + A_{13})$ where δ in expressions 4.5 is to be replaced by $-\delta$ and summation is to be carried out over all magnetic states, i.e. occupied but unpaired. Since he asserts that these states will have their spins parallel to the field and that δ is negative for them, this means that δ is to be treated as a positive quantity in 4.5. The result is therefore the same as obtained here but his argument appears unnecessarily complicated and erroneous to some extent. To recapitulate the argument used here:-

- (i) The magnetic states will have a negative exchange energy but will have spins antiparallel to the field.
- (ii) By the diagonal sum rule:- $\sum_{\text{states}} E_{\text{ex.}} = - \sum_{\text{unocc. states}} E_{\text{ex.}}$
- (iii) Treating δ throughout as the magnitude of the exchange energy, i.e. positive, the unoccupied states will be those corresponding to the highest energies, i.e. $E_i + \delta$.

Replacing "unpaired spins" by "unoccupied states" in Brooks'

argument, for most unoccupied states both ϵ_1 and ϵ_2 will be positive, since these states are those of highest band energy, in which expressions 4.5 are all positive and hence the sign of K_1 for Ni is bound to be negative at low temperatures. Brooks then makes his very rough estimate of K_1 on the following assumptions.

(I) $\Delta = 630 \text{ cm.}^{-1}$, using Coulomb's estimate as here.

(II) $\sigma = 4000 \text{ cm.}^{-1}$. Brooks states that the work of Stoner (1938a) indicates that the exchange energy cannot be much less than the bandwidth if ferromagnetism is to occur at all. In fact Stoner's criterion is that $\sigma > 2^{1/2} \epsilon_0$ (taking $J = 1$), where ϵ_0 is the energy difference between the top of the Fermi distribution and the top of the band; in the case of Ni ferromagnetism should therefore certainly be possible when the exchange energy is considerably less than the bandwidth. In fact Brooks' figure for 2σ , presumably based on Slater's $N(E)$ curve for Ni, is less than one-sixth of the bandwidth, which is certainly reasonable. Taking the same proportion of the bandwidth obtained in Part I, Brooks' estimate would have been about 2000 cm.^{-1} , which is very nearly the same as that used here.

(III) As an average value for ϵ_1 and ϵ_2 Brooks takes $10,000 \text{ cm.}^{-1}$, one-fifth of Slater's bandwidth. This is actually rather a low average value and one based on part I would be even worse. Strict comparison with the calculation here is, however, impossible since the assumption $\epsilon_1 = \epsilon_2$ entirely alters the character of expressions 4.5 for the $A_{\mu\nu}$.

Strictly speaking Brooks' estimate of K_1 is far too approximate for its agreement with experiment, even as to order

of magnitude, to have any significance but it can be said that part of the discrepancy between his value and the one obtained here is due to an overestimate of δ by use of Slater's $H(E)$ curve, which, in the writer's opinion, is too wide.

The various approximations and assumptions made in arriving at the above numerical values of g, g' and K , for H_1 , and their probable effect, will now be considered.

(i) As already stated, the validity of the assumption that the perturbation $\mathcal{E}$ represents interatomic exchange only depends on the magnitude of the spin-orbit coupling. It can be seen from Chapter III that the effect of spin-orbit interaction on the quantisation of spin of an atom is very small; the only states greatly affected are those for which $\epsilon_i + 2\sigma$ is small and these are small in number. Hence the interatomic forces are unlikely to affect this quantization appreciably, i.e. to affect the intraatomic exchange already considered in calculating free atomic wave functions so that this assumption regarding $\mathcal{E}$ appears valid.

(ii) For certain wave vectors two band wave functions $\psi_k, \psi_{k'}$ are very similar linear combinations of the atomic functions, e.g. $\frac{1}{\sqrt{2}}(\phi_i \pm \phi_j)$, so that the off-diagonal elements of the exchange operator would be comparable with the diagonal ones. Since, however, in such cases $\delta \ll E_i \sim E_j$, the effect of neglecting these elements should not be large. It will, however, be comparable with the spin-orbit effect since $\delta \sim A$. Since such cases are infrequent and contribute little to g, g' and K , (again because $A \ll E_i \sim E_j$), the usual diagonal approximation to the exchange energy is

considered reasonable.

(iii) The neglect of spin-other orbit interaction in forming the operator $\hat{O}$ will be considered in (x).

(iv) In calculating the matrix elements $\langle n' \underline{m}'_s | \hat{O} | n \underline{m}_s \rangle$ terms of the form $e^{-i a g \cdot \frac{1}{2}} \int \phi_n^+ (\underline{s} - a \underline{g}) f(\underline{r}) \underline{s} \cdot \underline{L} \phi_n(\underline{r}) d\tau$ were neglected, as stated, these, without the factor $f(\underline{r})$, would be non-orthogonality integrals. Neglect of the latter in Part I was shown to introduce an error of $\sim 8\%$ so that, since $f(\underline{r}) \sim \frac{1}{r^k}$ where $k > 3$, the error introduced here would not appear to be large although the diagonal elements of $\hat{O}$ would no longer be zero.

(v) The order in which the various perturbations are taken is worth considering. Both Λ and δ are much smaller than the free atom energy level separations and would therefore not affect these levels or the corresponding wave functions appreciably. Since only summations over the Fermi distribution are of physical interest on the collective electron model and since, by the diagonal sum rule $\sum_{occ} = - \sum_{unocc}$, $\mathcal{E}$ and $\hat{O}$ may be considered as small perturbing operators compared with the effect of the crystal field because the effect of the latter is much bigger than δ or Λ for all the unoccupied states. Finally, although Λ and δ , $\hat{O}$ may be considered as a smaller perturbing operator than $\mathcal{E}$ since it has zero diagonal matrix elements. The cases, where this argument breaks down, i.e., $\epsilon_i = 0$ and $\epsilon_i + 2\delta \sim 0$, have been dealt with; the latter is considered again in (xii).

(vi) As mentioned already in Chapter III, the use of Peierls' method of gauge transformation in the presence of a magnetic field, in order to calculate the magnetic energy from the field.

free Fermi distribution, is only strictly valid under conditions not fulfilled here. The first condition is equivalent to the field being small and the temperature not too low, whereas all calculations here have been applicable to very low temperatures only and the effective field will not be small in a ferromagnetic. Ignoring this condition a further magnetic energy term arises from the fact that the electrons move from atom to atom. This term is smaller, the tighter the binding of the electrons considered ($\propto$ bandwidth); it may become large if the curvature of the field-free energy surfaces in $\underline{k}$ -space becomes large. Since, however, this curvature is sometimes positive and sometimes negative in the region concerned, it is not considered that the effect on g or g' would be very great.

(vii) Again in the final derivation of $(n' | H_n | n)$ non-orthogonality integrals have been neglected. Their inclusion would increase the calculated values of both g and g' , probably by $\sim 5\%$.

(viii) The effect of using the "cubic band" for all calculations and the assumption that all 0.6 holes occur in it will be discussed in Chapter VI.

(ix) The use of graphical methods of integration in evaluating g, g' and K_1 appears justified in view of other approximations. From a study of the energy variations in the region of the B.E. considered it seems probable that the effect has been an overestimate in the values of $g-2, 2-g'$ and K_1 , but it is unlikely to be large.

(x) The use of Condonit's estimate of the spin-orbit parameter A is not really valid in the present case and therefore all

results have also been given in terms of A . This estimate was made from spectroscopic data for a free atom, assuming Russell-Saunders coupling; it actually corresponds to an electron having spin-orbit interaction energy $A/2$ when travelling in its orbit in the free atom but not interacting with other orbits. In fact the energy will be less than this because of such interaction; also the field, in which the electron moves, will be smaller in the metal than in the free atom, both due to increased screening by the conduction electrons and because the electron moves from atom to atom. For all these reasons the effective value of A relevant to the present problem would be smaller than Coulson's estimate, thereby reducing the calculated values of $\alpha'_{s,2}$ and K_1 .

(xi) As regards the value used for δ it is gratifying that the full calculation of Part I gives a value in good agreement with other theoretical estimates. The reasons for using a false value in the present work have already been given in detail.

Unfortunately these calculations prove rather sensitive to the value of δ owing to the necessity of considering states, for which $\epsilon_1 + 2\delta$ becomes very small. Assuming J is only just unity at 0°K, such states must occur, in which case the spin-orbit interaction will distort the Fermi surface considerably. The only satisfactory solution of the difficulty would be to include spin-orbit interaction in the band calculation although then it would appear necessary for consistency to include also the exchange effect at the same stage.

(xii) As the suggestion above would increase the complexity of the problem greatly, it has not been investigated. The consideration

of the case $\varepsilon_1 + 2\delta = 0$ by degenerate perturbation theory can only be regarded as a makeshift and even then it has not provided a practical solution of the problem so far. Some idea of the effect of this difficulty can, however, be obtained by considering the contribution of the relevant states to the calculated values of K_1 and the $O(\Lambda^2)$ corrections to g and g' .

	<u>contribution.</u>
$O(\Lambda^2)$ correction to $\Sigma(\tau L_H + 2S_H \tau)$	60%
$O(\Lambda^2)$ correction to $\Sigma(\tau L_H + S_H \tau)$	65%
K_1	54%

If these contributions are ignored, the values obtained are $g = 2.18$, $g' = 1.01$ and $K_1 = -2.12 \times 10^8$ ergs/c.c. It is considered very unlikely that the sign of the contributions from the states concerned will be changed in any more exact calculation so that these figures may be regarded as upper limits for g and g' and a lower limit for $|K_1|$. In the circumstances agreement with experiment is unlikely to be greatly affected by the approximation made here.

(xiii) As regards the anisotropy coefficient further terms in $(\alpha_H^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_H^2)$ would occur in higher orders of perturbation theory. Since these would contain a factor of Λ^6 or even a higher power, it is not considered that the calculated value of K_1 would be affected significantly by their inclusion.

It is obviously very difficult to consider separately the effects of all the approximations mentioned above, since in several cases they are not independent of one another. Further discussion will be deferred to Chapter VI.

Chapter V.

Discussion of Remainder of Brooks' Paper.

(a) Sign of K_1 for Iron.

Brooks' deductions are based on the approximate matrix $\{a_{nn}\}$ given here as 2.1. Using this and taking $\bar{\epsilon}_3$ as the energy level corresponding to the approximate solution $+\epsilon$ obtained by Jones and Matt (1937), then the $J_{\mu\nu}$ of expression 4.6 are:-

$$J_{12} = R \quad ; \quad J_{23} = \frac{1}{2}(1-R) \quad ; \quad J_{13} = R \quad 5.1$$

where $R = \frac{a^2 b^2 + b^2 c^2 + c^2 a^2}{\epsilon^4}$, with an error $\sim \frac{abc}{\epsilon^3}$ in the case of J_{12} and J_{13} and $\sim \frac{a^2 b^2 c^2}{\epsilon^6}$ in the case of J_{23} . Brooks has J_{13} and J_{23} interchanged but for consistency with the rest of his paper they should be as above. Since the other two energy levels correspond to solutions 0 and $-\epsilon$, one has $\epsilon_1 = \epsilon$; $\epsilon_2 = 2\epsilon$. Substituting in expression 4.6, this gives:-

$$K_1 = \frac{-A^4 \delta}{12\epsilon^4(\epsilon+\delta)^2(\epsilon+2\delta)^2} \left\{ (7+5R)\epsilon^4 + 16\epsilon\delta + 8\delta^4 \right\} - \frac{A^4 \delta^2}{12\epsilon^3(\epsilon+\delta)^3(\epsilon+2\delta)^2} \left\{ (26+30R)\epsilon^4 + \dots \right\}$$

The maximum value of R for any wave vector is $\frac{1}{3}$ and so, taking $R = \frac{1}{3}$ as an average value and assuming $\delta \ll \epsilon$, this becomes:-

$$K_1 \approx \frac{-4A^4 \delta^2}{\epsilon^4(\epsilon+2\delta)^2} \left\{ \frac{1}{6\delta} + \frac{2}{3\epsilon} \right\} \quad 5.2$$

Brooks obtains this expression but with a positive sign; assuming that most unpaired electrons lie in the corresponding energy band, he deduces that his expression is positive for positive ϵ and δ and therefore that K_1 should be positive for Fe. This argument is open to criticism as in the case of Ni Brooks states that δ is a negative quantity for the unpaired electrons.

Following the arguments used here for Ni, $\sum_{occ} = -\sum_{unocc}$ and most unoccupied states will lie in the $E_j + \delta$ band, for which both ϵ and δ will be positive. It follows at once from 5.2 that K_1 will

probably be positive for Fe.

(b) Discussion of Alloys and Temperature Variation of K .

Brooks points out that it might appear at first that the theory indicates that the sign of K is related to the crystal structure of the metal concerned, whereas experimental observation on alloy systems suggest a much closer correlation to the number of free spins per atom. He is able to suggest a qualitative explanation of this. Briefly, on adding Fe (with 2.2 holes per atom in the d band) to Ni the average number of holes per atom in the d band of Ni increases and that of Fe decreases due to loss of d electrons by the Ni atoms to the Fe. If the new holes in the Ni band appear in regions where $(1-5J_{\mu\nu})$ is negative, then K for the alloy may become positive. This suggestion is confirmed by the present work although, of course, more holes would appear in the $E_L + \delta$ band, for which the $A_{\mu\nu}$ may also be negative. Also the contribution to K from the Fe atoms may become negative during this process although it is most unlikely in view of (a) above. Brooks, however, suggests that there will be some tendency in this direction, as the number of holes per atom decreases for the Fe atoms, owing to the increased effect of next-nearest neighbours for states near the top of the d band. The effect of such next-nearest neighbours can be compared with the case of the simple cubic, for which K is easily shown to be negative.

Brooks attempted some quantitative verification of this theory for alloys but without success. With the improved theoretical data now available, another attempt would appear worth while.

Finally Brooks attempted to obtain a theoretical expression for the temperature variation of K_1 by expressing K_1 as a function of the magnetization, presumably by putting $\mathcal{E} = k\theta J$, but the result gave far too slow a variation. No attempt has been made here to investigate this matter.

Chapter VI.

Extension of Theory to Complete d Band.

Possibly the worst approximation in the above theory, as Brooks admits, is the neglect of the Γ_2 band, i.e. that one need only consider the d band arising from the Γ_2 level, i.e. from the three atomic wave functions ϕ_1, ϕ_2 and ϕ_3 . As already mentioned the approximation is unnecessary for an analytic solution of the problem but unfortunately the computational labour involved in translating that theory into numerical values of physical quantities becomes prohibitive.

(a) Derivation of the Spin-Orbit Secular Equation.

The derivation of a secular equation similar to 2.12 can be carried out in exactly the same way as before. Unfortunately, however, it seems impossible to find any device comparable with the change of axes from (x, y, z) to (x', y', z') , which will simplify the matrix elements. The same approximations with regard to exchange energy, the spin-orbit operator and neglect of non-orthogonality-type integrals are made as before. With the addition of the two wave functions:-

$$\phi_4 = \frac{1}{2} \frac{x^2 - y^2}{r^2} F(r) \quad ; \quad \phi_5 = \frac{1}{2\sqrt{3}} \frac{3z^2 - r^2}{r^2} F(r)$$

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} (\phi_1, \phi_2, \phi_3, \phi_4, \phi_5) = i \begin{pmatrix} \sqrt{3}\phi_5 + \phi_4 & -\phi_3 & \phi_2 & -\phi_1 & -\sqrt{3}\phi_1 \\ \phi_3 & -\sqrt{3}\phi_5 + \phi_4 & -\phi_1 & -\phi_2 & \sqrt{3}\phi_2 \\ -\phi_2 & \phi_1 & -2\phi_4 & 2\phi_3 & 0 \end{pmatrix} \quad 6.1$$

Then:-

$$\left(n \frac{1}{2} | \underline{S} \cdot \underline{L} | n' \frac{1}{2} \right) = \begin{pmatrix} 0 & i & 0 & 0 & 0 \\ -i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2i & 0 \\ 0 & 0 & -2i & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} = - \left(n \frac{1}{2} | \underline{S} \cdot \underline{L} | n' \frac{1}{2} \right) \quad 6.2$$

$$(n' \frac{1}{2} | \underline{S} \cdot \underline{L} | n \frac{1}{2}) = \begin{pmatrix} 0 & 0 & -1 & -i & -\sqrt{3}i \\ 0 & 0 & i & -1 & \sqrt{3} \\ 1 & -i & 0 & 0 & 0 \\ i & 1 & 0 & 0 & 0 \\ \sqrt{3}i & -\sqrt{3} & 0 & 0 & 0 \end{pmatrix}$$

$$(n' \frac{1}{2} | \underline{S} \cdot \underline{L} | n' \frac{1}{2}) = \begin{pmatrix} 0 & 0 & 1 & -i & -\sqrt{3}i \\ 0 & 0 & i & 1 & -\sqrt{3} \\ -1 & -i & 0 & 0 & 0 \\ i & -1 & 0 & 0 & 0 \\ \sqrt{3}i & \sqrt{3} & 0 & 0 & 0 \end{pmatrix}$$

6.2

Hence for the band wave functions ψ_r :-

$$\frac{1}{A} (r k m_s | O | r' k m_s) = \begin{pmatrix} iA & B+iC \\ -B+iC & -iA \end{pmatrix} \begin{matrix} m_s = \frac{1}{2} \\ m_s = -\frac{1}{2} \end{matrix}$$

6.3

$$\text{where: } A_{rr'} = (a_{r1} a_{r'2} - a_{r2} a_{r'1}) + 2(a_{r3} a_{r'4} - a_{r4} a_{r'3})$$

$$B_{rr'} = -(a_{r1} a_{r'3} - a_{r3} a_{r'1}) - (a_{r2} a_{r'4} - a_{r4} a_{r'2}) + \sqrt{3}(a_{r2} a_{r'5} - a_{r5} a_{r'2})$$

6.4

$$C_{rr'} = -(a_{r1} a_{r'4} - a_{r4} a_{r'1}) - \sqrt{3}(a_{r1} a_{r'5} - a_{r5} a_{r'1}) + (a_{r2} a_{r'3} - a_{r3} a_{r'2})$$

Note that $\{a_{rn}\}$ is now a 5×5 matrix so that 6.4 cannot be

simplified as before. Quantizing the spin along the direction

$$(e, \phi) :- \psi_r'(\frac{1}{2}) = \cos \frac{\theta}{2} \psi_r(\frac{1}{2}) + \sin \frac{\theta}{2} e^{i\phi} \psi_r(-\frac{1}{2})$$

$$\psi_r'(-\frac{1}{2}) = \sin \frac{\theta}{2} e^{-i\phi} \psi_r(\frac{1}{2}) - \cos \frac{\theta}{2} \psi_r(-\frac{1}{2})$$

so that the elements of the spin-orbit secular equation are

finally:-

$$\frac{1}{A} (r k \frac{1}{2} | O | r k \frac{1}{2}) = i(A_{rr'} \cos \theta + B_{rr'} \sin \theta \sin \phi + C_{rr'} \sin \theta \cos \phi) = \frac{1}{A} (r k -\frac{1}{2} | O | r k -\frac{1}{2}) \quad 6.5$$

$$\frac{1}{A} (r k \frac{1}{2} | O | r k -\frac{1}{2}) = e^{i\phi} [-B_{rr'} \cos \phi + C_{rr'} \sin \phi + i(A_{rr'} \sin \theta - B_{rr'} \cos \theta \sin \phi - C_{rr'} \cos \theta \cos \phi)]$$

$$\frac{1}{A} (r k -\frac{1}{2} | O | r k \frac{1}{2}) = e^{i\phi} [B_{rr'} \cos \phi - C_{rr'} \sin \phi + i(A_{rr'} \sin \theta - B_{rr'} \cos \theta \sin \phi - C_{rr'} \cos \theta \cos \phi)]$$

(b) Derivation of g and g' Factors.

The same approximations with regard to gauge transformation

and neglect of non-orthogonality integrals are made as before.

Then to $O(A)$ perturbation theory gives for the wave function

corresponding level $E_1 + \delta$ of the secular equation:-

$$\Psi_1^+ = \psi_1^+ + \frac{iA(A_{21}\alpha_2 + B_{21}\alpha_y + C_{21}\alpha_x)}{\epsilon_2} \psi_2^+ + \frac{iA(A_{31}\alpha_3 + B_{31}\alpha_y + C_{31}\alpha_x)}{\epsilon_3} \psi_3^+ + \frac{iA(A_{41}\alpha_4 + B_{41}\alpha_y + C_{41}\alpha_x)}{\epsilon_4} \psi_4^+ + \frac{iA(A_{51}\alpha_5 + B_{51}\alpha_y + C_{51}\alpha_x)}{\epsilon_5} \psi_5^+ + \frac{A[B_{21}\alpha_y + C_{21}\alpha_x - i(A_{21}\beta_2 + B_{21}\beta_y + C_{21}\beta_x)]}{\epsilon_2 + 2\delta} \psi_2^- + \dots \quad 6.6$$

where $\epsilon_i = E_i - E_1$, $\beta_i = \cos\theta_i$ etc., and the phase factors $e^{\pm i\phi}$ have been dropped as before. It is easily shown that:-

$$\begin{aligned} \int \psi_1^+ L_H \psi_1^+ d\tau &= 0 & \int \psi_2^+ L_H \psi_2^+ d\tau &= 0 \\ \int \psi_1^+ L_H \psi_2^+ d\tau &= -i\hbar(A_{21}\alpha_2 + B_{21}\alpha_y + C_{21}\alpha_x) = -\int \psi_2^+ L_H \psi_1^+ d\tau \\ \therefore (1 + |L_H|1^+) &= 2A\hbar \sum_{r=2}^5 \frac{(A_{r1}\alpha_r + B_{r1}\alpha_y + C_{r1}\alpha_x)^2}{\epsilon_r} + O(A^4) \end{aligned} \quad 6.7$$

Considering the equivalent state $\underline{k}' = (k_y, k_x, k_z)$, it is found that:-

$$\psi_2^{+'} = a_{r3}\phi_1^+ + a_{r1}\phi_2^+ + a_{r2}\phi_3^+ - \frac{1}{2}(a_{r4} - \sqrt{3}a_{r5})\phi_4^+ - \frac{1}{2}(\sqrt{3}a_{r4} + a_{r5})\phi_5^+$$

so that:- $A_{rr'}' = B_{rr'}$; $B_{rr'}' = C_{rr'}$; $C_{rr'}' = A_{rr'}$

and this state gives:-

$$(1 + |L_H|1^+)' = 2A\hbar \sum_{r=2}^5 \frac{(B_{r1}\alpha_2 + C_{r1}\alpha_y + A_{r1}\alpha_x)^2}{\epsilon_r} + O(A^4)$$

Similarly considering the other equivalent states, the average of 6.7 over all 48 such states is:-

$$(1 + |L_H|1^+)_{AV} = \frac{2}{3}A\hbar \sum_{r=2}^5 \frac{A_{r1}^2 + B_{r1}^2 + C_{r1}^2}{\epsilon_r} + O(A^4) \quad 6.8$$

Unfortunately $A_{rr'}^2 + B_{rr'}^2 + C_{rr'}^2 \neq 1$ so that this cannot be further simplified. As before:-

$$(\tau^+ | S_{11} | \tau^+) = \frac{\hbar}{2} + O(A^4) \quad 6.9$$

Finally, summing over the unoccupied states in the B.Z.:-

$$g = 2 + \frac{1}{0.6} \frac{4}{3} A \sum_{\text{unocc. } r=2}^5 \frac{A_{r1}^2 + B_{r1}^2 + C_{r1}^2}{\epsilon_r} + O(A^4) \quad 6.10$$

$$g' = \frac{0.6 + \frac{2}{3} A \sum_{\text{unocc. } r=2}^5 \frac{A_{r1}^2 + B_{r1}^2 + C_{r1}^2}{\epsilon_r}}{0.3 + \frac{2}{3} A \sum_{\text{unocc. } r=2}^5 \frac{A_{r1}^2 + B_{r1}^2 + C_{r1}^2}{\epsilon_r}} + O(A^4) \quad 6.11$$

For a degenerate case of the type $\varepsilon_L = 0$ a new matrix for σ must be constructed, using wave functions $\frac{1}{\sqrt{2}}(\psi_1^+ - i\psi_1^-)$, $\frac{1}{\sqrt{2}}(\psi_2^+ - i\psi_2^-)$, $\frac{1}{\sqrt{2}}(\psi_1^- + i\psi_1^+)$ in place of ψ_1^+ , ψ_2^+ , ψ_1^- and ψ_2^- respectively. It can then be shown that:- $(1^+|L_H|1^+) + (2^+|L_H|2^+) = \lim_{\varepsilon_L \rightarrow 0} [(1^+|L_H|1^+) + (2^+|L_H|2^+)]$ and that:- $(1^+|S_H|1^+) = (2^+|S_H|2^+)$

so that the same procedure can be adopted as before for such states, i.e. the terms in $\frac{1}{\varepsilon_L}$ are simply ignored. Again this justifies the use of the non-degenerate formulae for states where there is near-degeneracy of this type. Owing to the unsatisfactory nature of the investigation of degeneracy of the type $\varepsilon_L + 2\sigma = 0$ previously carried out (Chapters III and IV), it was not considered profitable to do so here as yet.

(e) Theory of Anisotropy Coefficient K_1 .

Considering the fourth order perturbation correction to the energy level $E_j + \delta$ for a non-degenerate case, the first term of the expression 4.1 gives:-

$$-A^4 \left\{ \frac{X_{11}^2}{\varepsilon_1^2} + \frac{X_{12}^2}{\varepsilon_2^2} + \frac{X_{14}^2}{\varepsilon_4^2} + \frac{X_{15}^2}{\varepsilon_5^2} + \frac{Y_{12}^2 + Z_{12}^2}{(\varepsilon_1 + 2\sigma)^2} + \frac{Y_{13}^2 + Z_{13}^2}{(\varepsilon_3 + 2\sigma)^2} + \frac{Y_{14}^2 + Z_{14}^2}{(\varepsilon_4 + 2\sigma)^2} + \frac{Y_{15}^2 + Z_{15}^2}{(\varepsilon_5 + 2\sigma)^2} \right\} \quad 6.12$$

$$\times \left\{ \frac{X_{11}^2}{\varepsilon_1^2} + \frac{X_{12}^2}{\varepsilon_2^2} + \frac{X_{14}^2}{\varepsilon_4^2} + \frac{X_{15}^2}{\varepsilon_5^2} + \frac{Y_{12}^2 + Z_{12}^2}{\varepsilon_1 + 2\sigma} + \frac{Y_{13}^2 + Z_{13}^2}{\varepsilon_3 + 2\sigma} + \frac{Y_{14}^2 + Z_{14}^2}{\varepsilon_4 + 2\sigma} + \frac{Y_{15}^2 + Z_{15}^2}{\varepsilon_5 + 2\sigma} \right\}$$

where:- $X_{rr'} = A_{rr'}\alpha_j + B_{rr'}\alpha_y + C_{rr'}\alpha_x$

$Y_{rr'} = B_{rr'}\gamma_j + C_{rr'}\gamma_x$; $Z_{rr'} = A_{rr'}\beta_j + B_{rr'}\beta_y + C_{rr'}\beta_x$

Also:- $Y_{rr'}^2 + Z_{rr'}^2 = A_{rr'}^2(1 - \alpha_j^2) + B_{rr'}^2(1 - \alpha_y^2) + C_{rr'}^2(1 - \alpha_x^2) - 2A_{rr'}B_{rr'}\alpha_j\alpha_y - 2B_{rr'}C_{rr'}\alpha_y\alpha_x - 2C_{rr'}A_{rr'}\alpha_j\alpha_x$

Putting $\alpha_i^2 = \alpha_i^2(1 - \alpha_j^2 - \alpha_k^2)$ and retaining only terms in $\alpha_i^2\alpha_j^2$.6.12

becomes:-

$A^4 (A_{xy}\alpha_x^2\alpha_y^2 + A_{yz}\alpha_y^2\alpha_z^2 + A_{zx}\alpha_z^2\alpha_x^2)$

where:- $A_{xy} = \left\{ \sum_{r=2}^5 \frac{B_{1r}^2 - C_{1r}^2}{\varepsilon_r^2} - \sum_{r=2}^5 \frac{B_{1r}^2 - C_{1r}^2}{(\varepsilon_r + 2\sigma)^2} \right\} \left\{ \sum_{r=2}^5 \frac{(B_{1r}^2 - C_{1r}^2)(\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_r + 2\sigma})}{\varepsilon_r^2} \right\} \quad 6.13$

$$- 4 \left\{ \sum_{r=2}^5 B_{1r} C_{1r} \left(\frac{1}{\varepsilon_r^2} - \frac{1}{(\varepsilon_r + 2\sigma)^2} \right) \right\} \left\{ \sum_{r=2}^5 B_{1r} C_{1r} \left(\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_r + 2\sigma} \right) \right\}$$

and similarly for A_{yz} and A_{xz} . Summing over the 48 equivalent states the average contribution from this term is:-

$$K_{11} (\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2) \quad 6.14$$

$$\text{where:- } K_{11} = \frac{1}{3} \sum_{r,r'} (2G_{rr'}^2 - 10H_{rr'}) \left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_r + 2\delta} \right)^2 \left(\frac{1}{\epsilon_{r'}} + \frac{1}{\epsilon_{r'} + \delta} \right)$$

$$+ \frac{1}{3} \sum_{r,r',r''} (5L_{rr'} - G_{rr'} G_{rr''} - 2M_{rr'}) \left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_r + 2\delta} \right) \left(\frac{1}{\epsilon_{r'}} - \frac{1}{\epsilon_{r'} + 2\delta} \right) \left(\frac{1}{\epsilon_{r''}} + \frac{1}{\epsilon_{r''} + \delta} \right) \quad 6.15$$

$$\text{where:- } G_{rr'} = A_{rr'}^2 + B_{rr'}^2 + C_{rr'}^2; H_{rr'} = A_{rr'}^2 B_{rr'}^2 + B_{rr'}^2 C_{rr'}^2 + C_{rr'}^2 A_{rr'}^2 \quad 6.16$$

$$L_{rr'} = A_{rr'}^2 A_{rr'}^2 + B_{rr'}^2 B_{rr'}^2 + C_{rr'}^2 C_{rr'}^2; M_{rr'} = A_{rr'} A_{rr'} + B_{rr'} B_{rr'} + C_{rr'} C_{rr'}$$

The second term of the expression 4.1 gives A^* times:-

$$\begin{aligned} & \frac{iX_{12}}{\epsilon_2} \left\{ \frac{iX_{13} - iX_{23} - iX_{12}}{\epsilon_3 \epsilon_2} + \frac{iX_{13} - iX_{14} - iX_{14}}{\epsilon_3 \epsilon_4} + \frac{iX_{13} - iX_{15} - iX_{15}}{\epsilon_3 \epsilon_5} + \frac{iX_{13} (Y_{12} + iZ_{12}) (-Y_{12} + iZ_{12})}{\epsilon_3 (\epsilon_2 + 2\delta)} \right. \\ & + \frac{iX_{13} (-Y_{14} - iZ_{14}) (-Y_{14} + iZ_{14})}{\epsilon_3 (\epsilon_4 + 2\delta)} + \frac{iX_{13} (-Y_{15} - iZ_{15}) (-Y_{15} + iZ_{15})}{\epsilon_3 (\epsilon_5 + 2\delta)} + \text{similar sets of terms} \\ & \text{beginning with } iX_{24}, iX_{25}, (-Y_{23} - iZ_{23}), (-Y_{24} - iZ_{24}) \text{ and } (-Y_{25} - iZ_{25}) \\ & + \frac{(Y_{12} + iZ_{12}) (Y_{12} - iZ_{12}) - iX_{12}}{2\delta \epsilon_2} + \frac{(Y_{13} + iZ_{13}) (Y_{13} - iZ_{13}) - iX_{13}}{2\delta \epsilon_3} + \frac{(Y_{14} + iZ_{14}) (Y_{14} - iZ_{14}) - iX_{14}}{2\delta \epsilon_4} \\ & + \frac{(Y_{15} + iZ_{15}) (Y_{15} - iZ_{15}) - iX_{15}}{2\delta \epsilon_5} + \frac{(Y_{12} + iZ_{12}) (-iX_{12} - (-Y_{12} + iZ_{12})) + (Y_{12} + iZ_{12}) (-iX_{13} - (-Y_{13} + iZ_{13}))}{2\delta (\epsilon_2 + 2\delta)} \\ & + \frac{(Y_{12} + iZ_{12}) (-iX_{14} - (-Y_{14} + iZ_{14})) + (Y_{12} + iZ_{12}) (-iX_{15} - (-Y_{15} + iZ_{15}))}{2\delta (\epsilon_2 + 2\delta)} \left. \right\} + \text{seven similar groups of terms} \end{aligned} \quad 6.17$$

$$\begin{aligned} \text{Now:- } (Y + iZ)(Y - iZ) &= [B\gamma_y + C\gamma_z + i(A\beta_y + B\beta_z + C\beta_n)] [B'\gamma_y + C'\gamma_z - i(A'\beta_y + B'\beta_z + C'\beta_n)] \\ &= AA'(1 - \alpha_z^2) + BB'(1 - \alpha_y^2) + CC'(1 - \alpha_x^2) - AB'(\alpha_y \alpha_z + i\alpha_x) - BB'(\alpha_z \alpha_x + i\alpha_y) \\ &\quad - CA'(\alpha_x \alpha_y + i\alpha_z) - A'B(\alpha_y \alpha_z - i\alpha_x) - B'C(\alpha_z \alpha_x - i\alpha_y) - C'A(\alpha_x \alpha_y - i\alpha_z) \end{aligned}$$

Dropping the terms, which are of too low a degree in the α_i to be of interest, i.e. retaining only those which will contribute to the coefficient of $(\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2)$, this may be written:-

$$-(A\alpha_z + B\alpha_y + C\alpha_x)(A'\alpha_z + B'\alpha_y + C'\alpha_x)$$

Denoting "the coefficient of" by $[\quad]$, expansion of 6.17 gives the following terms:-

$$\begin{aligned}
 (1) \left[\frac{1}{\epsilon_1^2 \epsilon_2} \right] &= - \left[\frac{1}{\epsilon_1^2 (\epsilon_2 + 2\sigma)} \right] = \left[\frac{1}{\epsilon_2 (\epsilon_1 + 2\sigma)^2} \right] = - \left[\frac{1}{(\epsilon_2 + 2\sigma)^2 (\epsilon_1 + 2\sigma)} \right] = - \frac{1}{2} \left[\frac{1}{\epsilon_2 \epsilon_1 (\epsilon_1 + 2\sigma)} \right] = \frac{1}{2} \left[\frac{1}{\epsilon_1 (\epsilon_1 + 2\sigma) (\epsilon_2 + 2\sigma)} \right] \\
 &= X_{11}^2 X_{22}^2 = (A_{12} \alpha_x + B_{12} \alpha_y + C_{12} \alpha_z) (A_{23} \alpha_x + B_{23} \alpha_y + C_{23} \alpha_z)^2 \\
 &= (B_{12}^2 C_{23}^2 + C_{12}^2 B_{23}^2 + 4 B_{12} C_{12} B_{23} C_{23} - B_{12}^2 B_{23}^2 - C_{12}^2 C_{23}^2) \alpha_x^2 \alpha_y^2 + \dots + \\
 &\quad + \text{terms of other symmetry.}
 \end{aligned}$$

The average coefficient for the 48 equivalent states can then be put in the form:-

$$\begin{aligned}
 &\frac{1}{3} (G_{12} G_{23} + 2 M_{23}^2 - 5 L_{12}) (\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2) \\
 (11) \left[\frac{1}{\epsilon_1 \epsilon_2 \epsilon_3} \right] &= - \left[\frac{1}{\epsilon_2 \epsilon_3 (\epsilon_1 + 2\sigma)} \right] = - \left[\frac{1}{\epsilon_1 \epsilon_3 (\epsilon_2 + 2\sigma)} \right] = - \left[\frac{1}{\epsilon_1 \epsilon_2 (\epsilon_3 + 2\sigma)} \right] = \left[\frac{1}{\epsilon_2 (\epsilon_1 + 2\sigma) (\epsilon_3 + 2\sigma)} \right] = \left[\frac{1}{\epsilon_3 (\epsilon_1 + 2\sigma) (\epsilon_2 + 2\sigma)} \right] \\
 &= \left[\frac{1}{\epsilon_2 (\epsilon_1 + 2\sigma) (\epsilon_3 + 2\sigma)} \right] = - \left[\frac{1}{(\epsilon_1 + 2\sigma) (\epsilon_2 + 2\sigma) (\epsilon_3 + 2\sigma)} \right] = -2 X_{12} X_{23} X_{31} + 2 X_{12} X_{24} X_{31} + 2 X_{13} X_{23} X_{14} X_{34}
 \end{aligned}$$

Proceeding as before, the average coefficient can be put in the form:-

$$\begin{aligned}
 &\frac{1}{3} P_{234} (\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2) \\
 \text{where:- } P_{234} &= 2 \left[M_{12} M_{13} + M_{12} M_{14} + M_{13} M_{24} + M_{13} M_{25} + M_{14} M_{23} + M_{13} M_{24} + M_{14} M_{23} - M_{12} M_{14} \right. \\
 &\quad \left. - M_{12} M_{15} - M_{13} M_{23} - 5 N_{12} \gamma_4 - 5 N_{13} \gamma_5 + 5 N_{12} \gamma_4 \right] \\
 \text{and:- } N_{12} \gamma_4 &= A_{12} A_{24} A_{14} A_{13} + B_{12} B_{24} B_{14} B_{13} + C_{12} C_{24} C_{14} C_{13}, \text{ for instance.}
 \end{aligned}$$

$$(111) \left[\frac{1}{2\sigma \epsilon_1^2} \right] = - \frac{1}{2} \left[\frac{1}{2\sigma \epsilon_1 (\epsilon_1 + 2\sigma)} \right] = \left[\frac{1}{2\sigma (\epsilon_1 + 2\sigma)^2} \right] = - X_{11}^2$$

Proceeding as before, the average coefficient can be put in the form:-

$$(1v) \left[\frac{1}{2\sigma \epsilon_1 \epsilon_2} \right] = - \left[\frac{1}{2\sigma \epsilon_2 (\epsilon_1 + 2\sigma)} \right] = - \left[\frac{1}{2\sigma \epsilon_1 (\epsilon_2 + 2\sigma)} \right] = \left[\frac{1}{2\sigma (\epsilon_1 + 2\sigma) (\epsilon_2 + 2\sigma)} \right] = -2 X_{12}^2 X_{13}^2$$

Proceeding as before, the average coefficient can be put in the form:-

Collecting all terms together and including 6.15, the final expression for the anisotropy coefficient is:-

$$\begin{aligned}
 K_1 &= \frac{A^2}{3} \left\{ \sum_{r=2}^5 (2G_{1r}^2 - 10H_{1r}) \left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_r + 2\sigma} \right)^2 \left(\frac{1}{\epsilon_r} + \frac{1}{\epsilon_r + 2\sigma} + \frac{1}{2\sigma} \right) \right. \\
 &\quad + \sum_{r < r'}^5 (5L_{rr'} - G_{1r} G_{1r'} - 2M_{rr'}^2) \left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_r + 2\sigma} \right) \left(\frac{1}{\epsilon_{r'}} - \frac{1}{\epsilon_{r'} + 2\sigma} \right) \left(\frac{1}{\epsilon_r} + \frac{1}{\epsilon_{r'}} + \frac{1}{\epsilon_r + 2\sigma} + \frac{1}{\epsilon_{r'} + 2\sigma} + \frac{2}{2\sigma} \right) \\
 &\quad + \sum_{r=2}^5 \sum_{r' \neq r}^5 (G_{1r} G_{1r'} + 2M_{rr'}^2 - 5L_{rr'}) \left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_r + 2\sigma} \right)^2 \left(\frac{1}{\epsilon_{r'}} - \frac{1}{\epsilon_{r'} + 2\sigma} \right) \\
 &\quad \left. + \sum_{r < r' < r''}^5 P_{rr'r''} \left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_r + 2\sigma} \right) \left(\frac{1}{\epsilon_{r'}} - \frac{1}{\epsilon_{r'} + 2\sigma} \right) \left(\frac{1}{\epsilon_{r''}} - \frac{1}{\epsilon_{r''} + 2\sigma} \right) \right\}
 \end{aligned}$$

as a check on this result consider the case when only the three energy bands E_1, E_2, E_3 are of interest as in chapters III and IV.

Then:- $G_{11} = A_{11}^2 + B_{11}^2 + C_{11}^2 = |a_{11}a_{11}|^2 + |a_{11}a_{21}|^2 + |a_{11}a_{31}|^2 = a_{11}^2 + a_{21}^2 + a_{31}^2 = 1$

Similarly:- $G_{12} = G_{21} = 1$

$$\begin{aligned} H_{12} &= A_{11}^2 B_{12}^2 + B_{11}^2 C_{12}^2 + C_{11}^2 A_{12}^2 = a_{11}^2 a_{12}^2 + a_{21}^2 a_{22}^2 + a_{31}^2 a_{32}^2 \\ &= a_{11}^2 (1 - a_{11}^2 - a_{12}^2) + a_{21}^2 (1 - a_{11}^2 - a_{22}^2) + a_{31}^2 (1 - a_{11}^2 - a_{32}^2) \\ &= 1 - H_{12} - (a_{11}^4 + a_{21}^4 + a_{31}^4) = 1 - H_{12} - a_{11}^4 (1 - a_{11}^2 - a_{12}^2) - a_{21}^4 (1 - a_{11}^2 - a_{22}^2) - a_{31}^4 (1 - a_{11}^2 - a_{32}^2) \\ &= 1 - H_{12} - 1 + J_{12} + J_{22} \end{aligned}$$

$H_{12} = \frac{1}{2} (J_{12} + J_{22})$; similarly $H_{13} = \frac{1}{2} (J_{12} + J_{22})$

$$L_{12} = A_{11}^2 A_{13}^2 + B_{11}^2 B_{13}^2 + C_{11}^2 C_{13}^2 = a_{11}^2 a_{13}^2 + a_{21}^2 a_{23}^2 + a_{31}^2 a_{33}^2 = J_{23}$$

Similarly:- $L_{23} = J_{13}$ and $L_{13} = J_{22}$

$$M_{12} = A_{11} A_{13} + B_{11} B_{13} + C_{11} C_{13} = -a_{11} a_{23} - a_{21} a_{13} - a_{31} a_{11} = 0 = M_{12} = M_{13}$$

$$P_{11} = 0$$

Hence 6.18 reduces to:-

$$\begin{aligned} K_1 &= \frac{A^4}{3} \left\{ (2 - 5J_{23} - 5J_{13}) \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_1 + 2\delta} \right)^2 \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_1 + 2\delta} + \frac{1}{2\delta} \right) \right. \\ &\quad + (2 - 5J_{12} - 5J_{22}) \left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_2 + 2\delta} \right)^2 \left(\frac{1}{\epsilon_2} + \frac{1}{\epsilon_2 + 2\delta} + \frac{1}{2\delta} \right) \\ &\quad + (5J_{23} - 1) \left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_2 + 2\delta} \right) \left(\frac{1}{\epsilon_3} - \frac{1}{\epsilon_3 + 2\delta} \right) \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} + \frac{1}{\epsilon_1 + 2\delta} + \frac{1}{\epsilon_2 + 2\delta} + \frac{2}{2\delta} \right) \\ &\quad \left. + (1 - 5J_{13}) \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_1 + 2\delta} \right)^2 \left(\frac{1}{\epsilon_3} - \frac{1}{\epsilon_3 + 2\delta} \right) + (1 - 5J_{12}) \left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_2 + 2\delta} \right)^2 \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_1 + 2\delta} \right) \right\} \\ &= \frac{A^4}{3} \left\{ (1 - 5J_{23}) \left[\frac{1}{2\delta} \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_3} - \frac{1}{\epsilon_1 + 2\delta} + \frac{1}{\epsilon_3 + 2\delta} \right)^2 \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_3} - \frac{1}{\epsilon_1 + 2\delta} + \frac{1}{\epsilon_3 + 2\delta} \right) \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_3} - \frac{1}{\epsilon_1 + 2\delta} + \frac{1}{\epsilon_3 + 2\delta} \right) \right] \right. \\ &\quad + (1 - 5J_{12}) \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_3} + \frac{1}{2\delta} - \frac{1}{\epsilon_1 + 2\delta} + \frac{1}{\epsilon_3 + 2\delta} \right) \left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_2 + 2\delta} \right)^2 \\ &\quad \left. + (1 - 5J_{13}) \left(\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} + \frac{1}{2\delta} - \frac{1}{\epsilon_1 + 2\delta} + \frac{1}{\epsilon_2 + 2\delta} \right) \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_1 + 2\delta} \right)^2 \right\} \end{aligned}$$

which corresponds exactly to 4.6.

As regards points of degeneracy in the B.Z., the case of $\epsilon_2 + 2\delta = 0$ has not been considered at all but a certain amount of investigation has been carried out in the case of $\epsilon_2 = 0$. Starting from the modified matrix for 0 (as for g and g' ; see (b) above),

the algebraic work required to obtain a formula for the fourth order perturbation is almost prohibitive. From all that has gone before it would be expected that the sum of the contributions from the states arising from the degenerate levels $E_1 + \delta$, $E_2 + \delta$ would be the same as that obtained by using the non-degenerate formula 6.18 in the limit as $\delta \rightarrow 0$; as before the two states may be considered together as they will either be both occupied or both unoccupied. So far it has only been possible to check the coefficient of $\frac{1}{\epsilon^2}$. In the non-degenerate case this would be for $\frac{1}{\epsilon^2}$

$$\frac{A^4}{3} [2G_{13}^2 - 10H_{13} + 2G_{23}^2 - 10H_{23}] \quad 6.19$$

while the degenerate theory gives:-

$$\frac{A^4}{3} (2G_{13}^2 - 10H_{13} + 2G_{23}^2 - 10H_{23} - 2G_{13}G_{23} - 4M_{23}^2 + 10L_{13} + G_{12}G_{13} + 2M_{13}^2 - 5L_{12} + G_{12}G_{23} + 2M_{12}^2 - 5L_{11}) \quad 6.20$$

These are not in general identical but all such points of degeneracy so far encountered have occurred on the (100) axis.

For such a point $a_1 = a_2 = a_3 = 1; a_{rr'} = 0$ ($r, r' = 1, 2, 3; r \neq r'$);

$$a_{rr'} = 0 \quad (r = 1, 2, 3; r' = 4, 5 \text{ and } r = 4, 5; r' = 1, 2, 3).$$

Then:-

$$G_{12} = G_{13} = G_{23} = 1$$

and all L's and M's in 6.20 are zero. Hence 6.20 and 6.19 become identical.

(d) Discussion.

Owing to the complicated nature of the formulae, particularly that for K_1 , it is not very easy to estimate the effect of their use in calculating g, g' and K_1 on the values already obtained. However, some general points are worth noting. The Fermi surface occurs at a considerably higher energy value in the complete (quintic) energy band than that used in Chapters III and IV, where all 0-6 holes were assumed to occur in the "cubic" band.

- (i) The relevant estimate of δ to be used is therefore $\sim 1\text{eV}$ (see Chapter III), i.e. less than half the value used before.
- (ii) More unoccupied states occur in the E_1 band than before and of these a greater proportion lie well away from the (100) axis than before.
- (iii) Rather fewer such states occur in the E_2 band than before and all are near the centres of the square faces of the B.Z.
- (iv) A few unoccupied states occur near the centres of the square faces for the E_3 band.
- (v) Apart from actual degeneracy for certain states on the (100) axis, ε_2 is very small for some states near the centres of the square faces. These did not occur before because the E_4 and E_5 bands of the approximate calculation were completely ignored.
- (vi) Completely degenerate states ($\varepsilon_2 = 0$) also occur for the same reason at other points than on the (100) axis.
- (vii) Otherwise the ε_i for the unoccupied states involved in the calculations will on the whole be a little larger than those used before, owing to the general "spreading" effect on the eigenvalues observed in the exact solution of the quintic secular equation as compared with the approximate one.

Any further deductions at this stage would be too hypothetical to be considered seriously. It seems possible that the $G_{\tau\tau'}$ will generally be < 1 but on the other hand there will be four terms in every summation over τ for two before, which could mean that the calculated values of g and g' will be little affected. This might also be said of K , since factors of the form

$$\left(\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_r + 2\delta} \right) = \frac{2\delta}{\varepsilon_r(\varepsilon_r + 2\delta)} \text{ will be reduced by a factor } \sim \frac{1}{2} \text{ for most}$$

states but again there are considerably more terms in the expression 6.18 than before.

Chapter VII.

Conclusion.

The purposes of the second part of this thesis have been twofold. Firstly some test against experiment of the calculations of Part I was desired, apart from those which could be made directly from the density of states curve. Secondly the test chosen seemed one, which would not prove overdifficult from a computational point of view, and of considerable interest in that the only theory of ferromagnetic anisotropy so far proposed on the collective electron model had never been carried through to a quantitative stage. In the course of the work attempts have been made to clarify this theory, the assumptions involved and difficulties which arise in its quantitative application, a few minor errors in Brooks' original derivation being corrected during this process, and it has also been possible to extend the theory formally to remove what is probably its crudest approximation.

As regards the numerical results obtained, there seems no particular reason to ignore the $O(\lambda^2)$ terms in the case of g and g' so that agreement with experiment here is not very good, since any theory would be expected to give results with the same order of agreement. The calculations have not led to any suggestion of an explanation of the differences between g -2 and 2 - g' ; the fault here appears to lie with the general theory of the gyromagnetic and ferromagnetic resonance effects and not in their particular interpretation of the collective electron model of a metal. It should be noted, however, that the

straightforward use of Seier's method of gauge transformation in this interpretation seems open to strong criticism, particularly in any future application of the formulae derived in Chapter VI, since the energy surfaces for the exact solution of the quintic secular equation exhibit a number of points of high curvature.

The value obtained for the first anisotropy coefficient K , for Ni is rather large as compared with experiment but this is not considered very significant owing to the uncertainty in the value to be used for the spin-orbit coupling factor A . However, it would be necessary to use a value about $\frac{1}{4}$ that of Coulomb's estimate in order to obtain agreement for K , with experiment; such a large change in A in going from the free atom to a metal, to which the tight-binding approximation is applicable, seems unlikely. It is worth noting that certain Japanese results (see Van Vleck 1937) give a rather larger value for K , for Ni than the experimental figure quoted here, e.g. -3×10^6 ergs/c.c. at liquid hydrogen temperatures, although these figures seem to be ignored in current literature on the subject.

Although, as already stated, it has been possible to carry out a formal extension of Brooks' theory to include the effect of all the d electrons of a ferromagnetic, no numerical calculations have been attempted. Apart from the complicated nature of the formulae obtained, the most laborious stage of such a calculation would lie in the evaluation of the transformation matrix $\{a_{kn}\}$. For any general wave vector $\underline{k}$ this would involve the evaluation of 25 4×4 determinants and there would

be about 120 wave vectors, for which this would be necessary. In the circumstances such a calculation does not appear justified by the slight improvement likely in the values obtained for g, g' and κ . However, some indication of the changes in these values obtainable by use of the more accurate theory can be obtained by its application to certain particular wave vectors, e.g. on the (100) axis of the B.Z.

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*Calculation of the Density of States Curve for the 3d Electrons
in Nickel.*

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It is the purpose of this letter to present some preliminary results of calculations of the density of states, $N(E)$, for the 3d electrons in a face-centred cubic lattice, using the approximation of tight binding. The calculations are applied in the main to nickel. The final results have an important bearing on the physical properties of transition metals, such as magnetic, electrical and thermal properties. Comparison may be made with the results of analogous calculations by Krutter (1935) and Slater (1936), who employed the cellular approximation.

The details of the tight binding approximation are well known (see, for example, Mott and Jones 1936). The atomic wave functions which have been used, and which correspond to the fivefold degenerate 3d level of the isolated atom, are

$$\begin{aligned}\phi_1 &= a_1 x y f(r)/r^2, & \phi_2 &= a_2 y z f(r)/r^2, & \phi_3 &= a_3 z x f(r)/r^2, \\ \phi_4 &= a_4 (x^2 - y^2) f(r)/r^2, & \phi_5 &= a_5 (3z^2 - r^2) f(r)/r^2, & . & . & .\end{aligned}\quad (1)$$

where $f(r)$ is the normalized radial function of the isolated atom and the a_1 are normalizing constants for the angular functions. Using (1) Bloch type functions may be constructed and the energy calculated from the determinantal equation

$$|H_{mn} - E\delta_{mn}| = 0, \quad m=1 \dots 5, \quad n=1 \dots 5. \quad . \quad . \quad . \quad (2)$$

The elements H_{mn} may be expressed in the general form

$$H_{mn} = \sum_{l=1}^3 A_{mn}^{(l)} \eta_{mn}^{(l)}(\mathbf{k}). \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here the $\eta_{mn}^{(l)}$ are functions of the three Cartesian components of the reduced wave vector $\mathbf{k}$, expressible in terms of circular functions of $\frac{1}{2}ak_x$, $\frac{1}{2}ak_y$, $\frac{1}{2}ak_z$, where a is the lattice constant. The coefficients $A_{mn}^{(l)}$ have the general form

$$A_{mn}^{(l)} = \int \phi_i^*(\mathbf{r} - \mathbf{R}) \Delta V \phi_j(\mathbf{r} - \mathbf{R}') d\tau, \quad . \quad . \quad . \quad . \quad (4)$$

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where $\mathbf{R}$, $\mathbf{R}'$ refer to the position of a central atom and one of its nearest neighbours, and where ΔV is the difference in the potential due to an atom when isolated and when in interaction with its nearest neighbours in the metal. Owing to the symmetry properties of the angular functions in (1) some of the coefficients vanish and the others are interdependent, such that only six independent coefficients had to be calculated. For this purpose the most suitable available values of $f(r)$ in (1) and of $V(r)$, the potential due to an isolated atom, were taken to be those of Hartree and Hartree (1936) for Cu^+ with exchange. These could be approximated to closely by simple algebraical expressions, involving exponentials. The atomic polyhedron was taken to be spherical and the assumption made that $\Delta V=0$ inside the central polyhedron and that outside it $\Delta V=V(|\mathbf{r}-\mathbf{R}'|)$. The integrations in (4) were carried out using prolate spheroidal coordinates. The resulting algebraical expressions for the coefficients were evaluated using the appropriate value of the interatomic distance. The values of the six independent coefficients range from 0.033 eV. to 0.260 eV., and these values, as that for the total width of the 3d band, are of such an order of magnitude as to justify the use of the tight binding approximation in this case.

With the H_{mn} known at all points in the Brillouin zone the energy may be calculated by solving (2). The functions $\eta_{mn}^{(0)}$ are, however, quite complicated, and hence it was decided, *in the first place*, to neglect arbitrarily certain of the non-diagonal elements such that the quintic equation (2) breaks into a cubic (arising from the atomic functions ϕ_1 , ϕ_2 and ϕ_3) and a quadratic (arising from ϕ_4 and ϕ_5). This approximation also underlies the calculations of Jones and Mott (1937) on the body-centred cubic lattice and is implicit in much of the work of Brooks (1940) on ferromagnetic anisotropy. Calculations are now proceeding which aim at solving the complete quintic in the energy range of interest for nickel, near the top of the band. Certain results may, however, be obtained at once, and, in addition, such comparison as may be made gives very close agreement with experiment using the curve which has been calculated so far. It is believed that although inclusion of the remaining H_{mn} may distort the energy surfaces derived from the two independent equations, the effect on the final $N(E)$ curve is less serious. The highest energies are found, in any case, to correspond to regions of the zone where the neglected H_{mn} are small. Finally the energy values which have already been computed may, in many cases, be used as first approximations to the roots of the complete quintic.

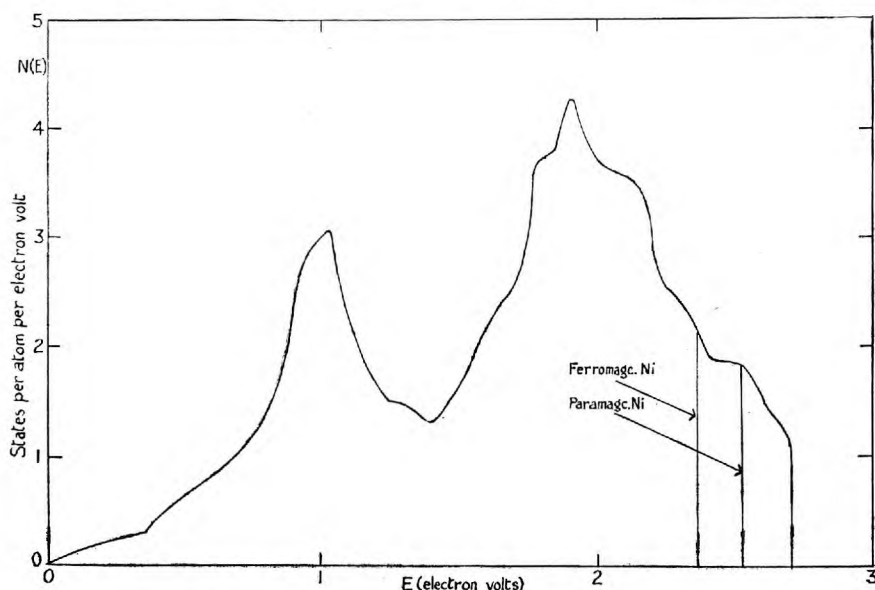
The two resulting determinantal equations were solved in the range $k_x, k_y, k_z > 0$ at all points of a lattice formed by taking intervals of $\pi/6a$, Cardan's method being used to solve some 500 cubics. (In the cellular approximation it was possible to calculate the energies at only very much fewer points in the zone). Constant energy contours were constructed in the planes $k_z = v\pi/6a$ ($v=0 \dots 12$) for each of the five solutions. Finally $N(E)$ curves were calculated by graphical integration.

A check on this stage of the calculation is provided by the fact that the area under each of the five curves corresponds to one electronic state per atom. The resulting provisional $N(E)$ curve, the sum of the five constituent curves, is shown in the figure.

The following deductions of particular interest may be made :

(1) The total width of the $3d$ band is 2.70 eV. This result is independent of the neglect of the non-diagonal elements mentioned. The value is about half that given by Slater (1936), with whose $N(E)$ curve the present curve may be compared.

(2) The value of the degeneracy temperature for nickel calculated for 0.3 vacant states per atom, corresponding to the right-hand vertical line in the figure, is 2.04×10^3 deg. K., in very close agreement with the value deduced by Wohlfarth (1949) from the magnetic and thermal properties.



Provisional density of states curve for nickel.

E , electronic energy in eV., measured from zero at the bottom of the band.

$N(E)$, density of states, such that the total area under the curve corresponds to five states per atom of either spin. Fermi limits for paramagnetic, ferromagnetic nickel as shown.

(3) The linear low temperature electronic heat coefficient, γ , for ferromagnetic nickel (left-hand vertical line) is deduced to be $1.15 \times 10^{-3} \text{ cal mol.}^{-1} \text{ deg}^{-2}$. The observed value is 1.74×10^{-3} , but as this includes a contribution due to the conduction electrons, the significant value for comparison is somewhat lower, possibly 1.5×10^{-3} .

(4) A completely general result concerning the degeneracy character at the centre of the zone, $\mathbf{k}=0$, states that here the five energy levels split into a threefold and a twofold degenerate level, separated, in general,

by a finite gap. This result is completely verified in the present case, the gap being found to be 0.88 eV., again independently of the neglect of the non-diagonal elements mentioned. In calculations using the cellular method, on the other hand, the degeneracy at $\mathbf{k}=0$ is found to be almost invariably fivefold—a result of the approximations used in the method.

It is hoped to publish fuller details when the effect of the approximation indicated above has been more completely investigated. The necessary calculations are, however, so troublesome that it was felt that a preliminary account of work already completed may be of interest.

We are indebted to Professor H. Jones for his most helpful advice, and one of us (G. C. F.) to London University for a postgraduate studentship.

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Density of States Curve for the 3d Electrons in Nickel

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ABSTRACT. A calculation is made of the energy density of electronic states for the 3d electrons in metallic nickel, using the approximation of tight binding. The early stages of the calculations and preliminary results have been previously summarized by Fletcher and Wohlfarth in 1951. The theoretical basis of the approximation is outlined and the validity of the underlying assumptions examined. The required overlap integrals are evaluated and the secular equation for the energy as a function of wave vector is solved exactly over the energy range of interest for nickel. The density of states curve is computed graphically. Among results of physical interest obtained are : bandwidth 2.7_0 ev, degeneracy temperature $1.4_5 \times 10^3$ deg K, low temperature electronic heat coefficient γ $1.6_9 \times 10^{-3}$ cal.mol $^{-1}$ deg $^{-2}$ (compared with the experimental value of 1.74×10^{-3}). The results are compared with those obtained by the cellular method of approximation used by Krutter in 1935, and Slater in 1936.

§1. INTRODUCTION

THE transition metals are of particular interest in the theory of metals, since they display anomalous electronic properties, which are only explicable on the assumption that the energy density of electronic states $N(E)$ for certain critical values of energy E is much larger than for other metals (Mott 1936 a, b). Results deduced from the only previous calculation of $N(E)$ for the 3d electrons in nickel (Krutter 1935, Slater 1936) do not agree very well with experiment and in the present work a re-calculation has been made using the approximation of tight binding (T.B.) (Bloch 1928 and others). The early stages of the calculations and preliminary results have previously been summarized (Fletcher and Wohlfarth 1951, to be referred to as I), and the purpose of the present paper is to give details of the complete work, together with a critical examination of the underlying assumptions and a discussion of the results obtained. Approximate wave functions for an electron in the metal were formed from the five atomic 3d functions and the resulting fifth-order secular equation has been solved exactly, whereas previously it has been the practice to make certain arbitrary approximations for the sake of simplicity (e.g. I, and Jones and Mott 1937). These approximations are shown to be invalid. In proceeding with the solution of this equation, numerical calculations have been made for the first time of the overlap integrals occurring in the matrix elements of energy. A feature of the calculation is the occurrence of the correct energy degeneracies as predicted by group theory. Certain results of physical interest are discussed in §4.

§2. THEORY OF THE APPROXIMATION

The complete theory of the T.B. approximation has been given by a number of authors (e.g. Mott and Jones 1936) and will not be repeated here. Bloch wave functions are built up from suitable atomic functions; those used here correspond to the five-fold degenerate 3d level of the isolated atom, i.e.

$$\left. \begin{aligned} \phi_1 &= (15/4\pi)^{1/2} xyf(r)/r^2, & \phi_2 &= (15/4\pi)^{1/2} yzf(r)/r^2 \\ \phi_3 &= (15/4\pi)^{1/2} xzf(r)/r^2, & \phi_4 &= (15/16\pi)^{1/2} (x^2 - y^2)f(r)/r^2 \\ \phi_5 &= (5/16\pi)^{1/2} (3z^2 - r^2)f(r)/r^2 \end{aligned} \right\} \dots\dots (1)$$

where $f(r)$ is the normalized radial function of the isolated atom and the numerical factors are normalizing constants for the angular functions. From (1) the functions

$$\psi_{nk} = \sum_{\mathbf{l}} \exp(i\mathbf{l} \cdot \mathbf{k}) \phi_n(\mathbf{r} - \mathbf{al}), \quad n = 1 \dots 5 \quad \dots\dots(2)$$

(where $\mathbf{k}$ is the wave-vector and $\mathbf{al}$ the position of any atom in the crystal lattice, summation being over all atoms) are constructed and may be shown to be of the correct Bloch form $\exp(i\mathbf{k} \cdot \mathbf{r})u_k(\mathbf{r})$, where $u_k(\mathbf{r})$ has the periodicity of the lattice. For a cubic lattice a is simply the lattice constant and l_x, l_y, l_z may be integral or half-integral. Finally, the zero-order wave function for an electron in the crystal is assumed to be a linear combination of the functions (2)

$$\Psi_n(\mathbf{k}; \mathbf{r}) = \sum_m a_{nm}(\mathbf{k}) \psi_{mk}(\mathbf{r}). \quad \dots\dots(3)$$

If $H = -(\hbar^2/2m)\nabla^2 + V(\mathbf{r})$ denotes the Hamiltonian and E the energy for the electron in the crystal, then Ψ_n must satisfy

$$(H - E)\Psi_n = 0. \quad \dots\dots(4)$$

If the non-orthogonality of the ψ_{nk} with respect to n is neglected, an approximation to be discussed later, it is easily shown that E must satisfy the secular determinantal equation

$$|H_{nm} - E\delta_{nm}| = 0, \quad m = 1 \dots 5; \quad n = 1 \dots 5, \quad \dots\dots(5)$$

where $H_{nm} = [\int \psi_{nk}^* H \psi_{mk} d\tau] / \alpha_n \alpha_m$ and $\alpha_n^2 = \int \psi_{nk}^* \psi_{nk} d\tau$. It can readily be shown that

$$\alpha_n^2 = N \sum_{\mathbf{l}} \exp(-i\mathbf{l} \cdot \mathbf{k}) \int \phi_n^*(\mathbf{r} - \mathbf{al}) \phi_n(\mathbf{r}) d\tau \simeq N, \quad \dots\dots(6)$$

where N is the total number of atoms in the crystal, on the assumption that the contributions to (6) from all other atoms ($\mathbf{l} \neq 0$) is negligible compared with that from the central atom ($\mathbf{l} = 0$). Finally, H_{nm} can be expressed in the form

$$H_{nm} = (\mathcal{E}_0 + C)\delta_{nm} + \sum_{\mathbf{l} \neq 0} \exp(-i\mathbf{l} \cdot \mathbf{k}) \int \phi_n^*(\mathbf{r} - \mathbf{al})(V - U)\phi_m(\mathbf{r}) d\tau, \quad \dots\dots(7)$$

where U is the potential due to an isolated atom at $\mathbf{l} = 0$ and $\mathcal{E}_0$ is the energy of a 3d electron in the field of such an atom. The constant C , termed the self-energy of the central atom, will be defined below. For convenience, energies may be measured above and below the constant value $\mathcal{E}_0 + C$. With the assumptions to be discussed below, the matrix elements H_{nm} are then found to have the following explicit values

$$\left. \begin{aligned} H_{11} &= -4A_1 \cos \xi \cos \eta + 4A_2 (\cos \eta \cos \zeta + \cos \zeta \cos \xi) \\ H_{22} &= -4A_1 \cos \eta \cos \zeta + 4A_2 (\cos \zeta \cos \xi + \cos \xi \cos \eta) \\ H_{33} &= -4A_1 \cos \zeta \cos \xi + 4A_2 (\cos \xi \cos \eta + \cos \eta \cos \zeta) \\ H_{44} &= 4A_4 \cos \xi \cos \eta - 4A_5 (\cos \eta \cos \zeta + \cos \zeta \cos \xi) \\ H_{55} &= -(4/3)(A_4 + 4A_5) \cos \xi \cos \eta + (4/3)(2A_4 - A_5)(\cos \eta \cos \zeta + \cos \zeta \cos \xi) \\ H_{12} &= H_{21} = -4A_3 \sin \zeta \sin \xi; \quad H_{23} = H_{32} = -4A_3 \sin \xi \sin \eta \\ H_{31} &= H_{13} = -4A_3 \sin \eta \sin \zeta; \quad H_{14} = H_{41} = 0 \\ H_{24} &= H_{42} = -4A_6 \sin \eta \sin \zeta; \quad H_{34} = H_{43} = 4A_6 \sin \zeta \sin \xi \\ H_{15} &= H_{51} = -(8/3^{1/2})A_6 \sin \xi \sin \eta; \quad H_{25} = H_{52} = (4/3^{1/2})A_6 \sin \eta \sin \zeta \\ H_{35} &= H_{53} = (4/3^{1/2})A_6 \sin \zeta \sin \xi \\ H_{45} &= H_{54} = (4/3^{1/2})(A_4 + A_5)(\cos \eta \cos \zeta - \cos \zeta \cos \xi) \end{aligned} \right\} \quad \dots\dots(8)$$

where $\xi = \frac{1}{2}ak_x$; $\eta = \frac{1}{2}ak_y$; $\zeta = \frac{1}{2}ak_z$ and

$$\left. \begin{aligned} A_1 &= - \int \phi_1^*(x - \frac{1}{2}a, y - \frac{1}{2}a, z)(V - U)\phi_1(x, y, z) d\tau \\ A_2 &= \int \phi_1^*(x, y - \frac{1}{2}a, z - \frac{1}{2}a)(V - U)\phi_1(x, y, z) d\tau \\ A_3 &= \int \phi_1^*(x - \frac{1}{2}a, y, z - \frac{1}{2}a)(V - U)\phi_2(x, y, z) d\tau \\ A_4 &= \int \phi_4^*(x - \frac{1}{2}a, y - \frac{1}{2}a, z)(V - U)\phi_4(x, y, z) d\tau \\ A_5 &= - \int \phi_4^*(x, y - \frac{1}{2}a, z - \frac{1}{2}a)(V - U)\phi_4(x, y, z) d\tau \\ A_6 &= \int \phi_2^*(x, y - \frac{1}{2}a, z - \frac{1}{2}a)(V - U)\phi_4(x, y, z) d\tau. \end{aligned} \right\} \dots\dots(9)$$

The assumptions inherent in the above treatment will now be briefly considered.

(i) The fundamental assumption of 'tight binding' is that the atoms in the crystal are far enough apart for interaction between them to be small. It is this interaction that causes the discrete energy levels of the isolated atom to broaden into bands of allowed energy for the crystal, and the assumption can only be justified on the grounds of consistency if the widths obtained for these bands are comparatively small. The value of 2.7₀ ev obtained for the bandwidth in the present calculation satisfies this criterion on comparison with bandwidths obtained for electrons farther from the atomic nucleus and therefore affected to a greater extent by neighbouring atoms in the crystal.

(ii) The non-orthogonality of the ψ_{nk} with respect to n is neglected, that is, the approximation is made that

$$\sum_{l \neq l'} \sum \exp \{ia(l - l') \cdot \mathbf{k}\} \int \phi_n^*(\mathbf{r} - a\mathbf{l}')\phi_m(\mathbf{r} - a\mathbf{l}) d\tau = 0 \quad (n \neq m). \quad \dots(10)$$

This approximation is linked up with another mentioned above, viz. that $\alpha_n^2 \simeq N$ and it is convenient to consider them together. As far as the derivation of eqns. (5) and (7) is concerned the neglect of non-orthogonality may be expressed in the alternative form

$$\begin{aligned} \int \psi_{nk}^* \psi_{mk} d\tau &\ll \int \psi_{nk}^* \psi_{nk} d\tau \quad (n \neq m) \quad \dots\dots(11) \\ \text{or } \sum_l \sum_{l'} \exp \{ia(l - l') \cdot \mathbf{k}\} \int \phi_n^*(\mathbf{r} - a\mathbf{l}')\phi_m(\mathbf{r} - a\mathbf{l}) d\tau \\ &\ll \sum_l \sum_{l'} \exp \{ia(l - l') \cdot \mathbf{k}\} \int \phi_n^*(\mathbf{r} - a\mathbf{l}')\phi_n(\mathbf{r} - a\mathbf{l}) d\tau \\ \text{or } \sum_{l \neq l'} \sum \exp \{ia(l - l') \cdot \mathbf{k}\} \int \phi_n^*(\mathbf{r} - a\mathbf{l}')\phi_m(\mathbf{r} - a\mathbf{l}) d\tau \\ &\ll N + \sum_{l \neq l'} \sum \exp \{ia(l - l') \cdot \mathbf{k}\} \int \phi_n^*(\mathbf{r} - a\mathbf{l}')\phi_n(\mathbf{r} - a\mathbf{l}) d\tau. \quad \dots\dots(12) \end{aligned}$$

The integrals involved will obviously be much greater for nearest neighbours than for other pairs of atoms; considering nearest neighbours only for $n=1$, $m=2$, for example, a calculation gave for the left- and right-hand sides of (12) respectively the values

$$-0.028N \sin \zeta \sin \xi \text{ and } N[1 + 0.08 \cos \xi \cos \eta - 0.02 (\cos \eta \cos \zeta + \cos \zeta \cos \xi)]$$

so that both approximations appear to be reasonable. It is stressed that, at least in the present problem, the actual orthogonality of the ψ_{nk} is immaterial, provided the inequality (12) is obeyed.

(iii) It is assumed in deriving (7) that

$$\int \phi_n^*(\mathbf{r})(V-U)\phi_m(\mathbf{r}) d\tau = C\delta_{nm}. \quad \dots\dots(13)$$

Now $V-U$ is an even function of $x, y, z, x-y$ or $x+y$ because of the symmetry of the lattice and hence, from considerations of the parity of $\phi_n^*\phi_m$ with respect to one or other of these variables, it is easily shown that $\int \phi_n^*(\mathbf{r})(V-U)\phi_m(\mathbf{r}) d\tau = 0$ ($n \neq m$). Also $V-U$ must be symmetrical in x, y and z so that $\int \phi_n^*(\mathbf{r})(V-U)\phi_n(\mathbf{r}) d\tau$ will have the same value for $n=1, 2$ and 3 . An approximate calculation shows that the absolute values of this integral for $n=4$ and 5 are slightly less than that for $n=1, 2$ and 3 as would be expected since ϕ_1, ϕ_2 and ϕ_3 have antinodes in the directions of nearest neighbours while ϕ_4, ϕ_5 have antinodes in the directions of next nearest neighbours. Owing to the assumption (see §3) that $V=U$ for $r < a/2^{3/2}$, however, the differences are very small and the assumption expressed in (13) is unlikely to introduce any serious error.

(iv) The usual assumption was made that the major contribution to the H_{nm} arises from nearest neighbouring atoms and only these were considered. Any given atom in the face-centred cubic lattice has twelve nearest neighbours given by $\mathbf{l} = (\pm \frac{1}{2}, \pm \frac{1}{2}, 0), (\pm \frac{1}{2}, 0, \pm \frac{1}{2}), (0, \pm \frac{1}{2}, \pm \frac{1}{2})$ and six next nearest given by $\mathbf{l} = (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)$. It seems probable, therefore, that the latter will also make a fairly large contribution, since they are only $\sqrt{2}$ times as far away as the nearest neighbours. This approximation seems the most likely to introduce serious error but is unavoidable without seriously increasing the complexity of the expressions for the H_{nm} and hence of the calculation.

§3. DETAILS OF COMPUTATION

In order to calculate the numerical values of the coefficients A_i some assumption must be made regarding the radial wave function $f(r)$ and the potential $V-U$. For the latter it was assumed that (i) $V=U$ within a sphere about the central atom of radius A equal to half the distance between nearest neighbours ($A=a/2^{3/2}$) (Mott and Jones 1936, p. 67), and (ii) $U=0$ elsewhere. For V outside this sphere an atomic potential centred on the nearest neighbour was used, which should be a good approximation in the regions where the product of the two wave functions is large. Since the atomic wave functions and potential have not been calculated for Ni, Hartree and Hartree's figures for Cu^+ with exchange (1936) were used, as this ion contains the same number of electrons as the Ni atom. For ease of computation as close a fit as possible was made to these values by explicit algebraic expressions. With primed symbols referring to the nearest neighbour, the range $r' < 2A/5$ was found to be relatively unimportant and the expressions

$$f(r') = 85.88r'^2 \exp(-5r') + 1.979r'^2 \exp(-2r') \quad \dots\dots(14)$$

$$V(r') = -\{1 + 28 \exp(-3r')\}/r' \quad \dots\dots(15)$$

were obtained (V is in atomic units). Integration was carried out over all space T less the atomic sphere τ of the central atom. Within this range

$$f(r) = 1.979r^2 \exp(-2r) \quad \dots\dots(16)$$

is a sufficiently good approximation, while for integration over τ it was also assumed that $f(r') = 1.979r'^2 \exp(-2r')$ and $V(r') = -1/r'$. Although the $r'^2 \exp(-5r')$ term would not be small in integrating over τ , it must be omitted as it has been neglected in integrating over T . Thus for instance

$$A_1 \propto \int [1.979 \exp(-2r) \{1 + 28 \exp(-3r')\} \\ \times \{85.88 \exp(-5r') + 1.979 \exp(-2r')\} xyx'y'/r'] dT \\ - \int [1.979 \exp(-2r) \times 1.979 \exp(-2r') xyx'y'/r'] d\tau. \dots\dots(17)$$

In carrying out the integrations, prolate spheroidal coordinates with the central atom and nearest neighbour as foci were used. The values obtained for the A_i may then be put in the convenient form

$$A_1 = 0.1928E_0, A_2 = 0.0572E_0, A_3 = 0.0776E_0, A_4 = 0.1348E_0, \\ A_5 = 0.0247E_0, A_6 = 0.0862E_0, \dots\dots(18)$$

$$\text{where} \quad E_0 = 4(A_1 + A_2) = 1.349 \text{ ev.} \quad \dots\dots(19)$$

A qualitative consideration of the various approximations indicated above shows that their effects on the A_i are all likely to be small, some being additive and some subtractive. Their total effect appears negligible compared with that arising from neglect of next-nearest neighbours.

Owing to the difficulty in solving a fifth order equation with coefficients as complex as (5), it was decided as a first approximation to neglect arbitrarily H_{nm} for $n=1, 2, 3$; $m=4, 5$, as has been done by previous workers (e.g. Jones and Mott 1937), and solve the resulting cubic and quadratic equations. Details of this work have already been given in I. Apart from giving correctly the total width of the band (2.70 ev) which is unaffected by the neglected terms, this preliminary calculation served to reduce greatly the work involved in solving the complete quintic equation and also demonstrated the effect of neglecting the above terms (see §4).

From a study of the $N(E)$ curve obtained in I it was decided to calculate the more exact curve over the range of energy values $0.5 < E/E_0 < 0.771$ ($2.35 < E < 2.70$ ev for diagram in I), a complete calculation being excessively laborious and unnecessary for most purposes. In effect only those solutions of (5) were found, which fell within this range; further reference to the previous calculation indicated in what regions of the Brillouin zone such solutions were likely to be found.

Along certain directions in $\mathbf{k}$ -space it is found that the secular eqn. (5) can be solved exactly as follows. Solutions marked * are identical with those obtained in I.

$$(100) \text{ direction. } E_{1,2} = 4A_2 + 4(A_2 - A_1) \cos \xi \quad *$$

$$E_3 = -4A_1 + 8A_2 \cos \xi \quad *$$

$$E_4 = 4A_4 - 8A_5 \cos \xi \quad *$$

$$E_5 = (4/3)[-A_4 - 4A_5 + (4A_4 - 2A_5) \cos \xi] \quad *$$

$$(110) \text{ direction. } E_1 = 4A_4 \cos^2 \xi - 8A_5 \cos \xi \quad *$$

$$E_{2,3} = 4A_2 \cos^2 \xi + 4(A_2 - A_1) \cos \xi \pm 4A_3 \sin^2 \xi \quad *$$

E_4 and E_5 given by

$$E^2 + [(4A_1 + 16A_5/3 + 4A_4/3)q^2 + (8A_5/3 - 16A_4/3 - 8A_2)q]E \\ + (16q^2/3)[(4A_1A_5 + A_1A_4)q^2 - (8A_2A_5 + 2A_2A_4 + 4A_1A_4 - 2A_1A_5)q \\ + (8A_2A_4 - 4A_2A_5)] - 64A_6^2p^4/3 = 0$$

where $p = \sin \xi$; $q = \cos \xi$.

$$(111) \text{ direction.. } E_1 = 4[(2A_3 + 2A_2 - A_1) \cos^2 \xi - 2A_3]. \quad *$$

The other four roots occur in two doubly-degenerate pairs given by

$$E^2 - 4[(2A_2 - A_1 + A_4 - 2A_5 - A_3) \cos^2 \xi + A_3]E \\ + 16\{[(A_4 - 2A_5)(2A_2 - A_1 - A_3) - 2A_6^2] \cos^4 \xi \\ + [A_3(A_4 - 2A_5) + 4A_6^2] \cos^2 \xi - 2A_6^2\} = 0.$$

$$\xi = \pi; \zeta = 0 \text{ direction. } E_{1,2} = \pm 4(A_1 + A_2) \cos \eta - 4A_2 \quad *$$

$$E_3 = 4A_1 \quad *$$

$$E_{4,5} = (4/3)[2A_5 - A_4 \pm 2(A_4 + A_5)(1 + 3 \cos^2 \eta)^{1/2}]. \quad *$$

The general effect of solving the quintic equation exactly, that is the effect of including the elements H_{nm} neglected in I, is to separate the solutions from each other and to remove some of the points of degeneracy which occurred in I and which were accidents of that approximation.

Returning to a consideration of eqn. (5) for a general vector $\mathbf{k}$, various methods have been devised for solving such an equation, either in its determinantal or expanded form. Investigation of these methods showed, however, that none was suitable in the present case owing to the complexity of the H_{nm} and the fact that the roots of (5) are not, in general, well separated. An estimate of the required solution for a given vector $\mathbf{k}$ was therefore made from the approximate solutions already obtained in I. This was substituted in the determinant, which was evaluated, a correction was applied to the solution and the process repeated until a solution correct to three decimal places was obtained. The symmetry of eqn. (5) reduced considerably the region of the Brillouin zone to be investigated, and in all some 270 roots were obtained by the above method and checked at symmetrically equivalent points.

For each wave vector $\mathbf{k}$, eqn. (5) has five roots, and a major problem is that of collecting these roots into five sets, each set belonging to one Brillouin zone and having an associated energy band. As a first step the energy degeneracies arising from symmetry considerations, reality of the Hamiltonian and accidental degeneracy may be investigated as indicated by Bouckaert, Smoluchowski and Wigner (1936) and by Herring (1937).

Following the arguments of the above papers the following deductions regarding degeneracy can be made for the present case.

(a) Due to symmetry there should be one triply degenerate level and one doubly degenerate level at $\mathbf{k} = 0$. A double degeneracy, arising from the former, should occur along the (100) direction and two along the (111) direction. There is no other symmetry degeneracy apart from a double degeneracy at the point $\mathbf{k} = (2\pi/a, \pi/a, 0)$.

(b) If the Hamiltonian of a problem is real, it is possible for degeneracy, additional to that due to symmetry, to occur between a wave function and its complex conjugate. For a face-centred cubic crystal it is easily shown that no degeneracy of this type can occur.

(c) In addition to the above, various points of accidental degeneracy must occur in the present case. Their prediction, however, depends on a knowledge of the relative energies of the five wave functions Ψ_n (which will, in general, have different symmetry properties) for certain special wave vectors, e.g. $\mathbf{k} = (0, 0, 0)$, $(2\pi/a, 0, 0)$, etc., so that most of these degeneracies are probably a result of the approximations of the calculation. They are indicated in fig. 1.

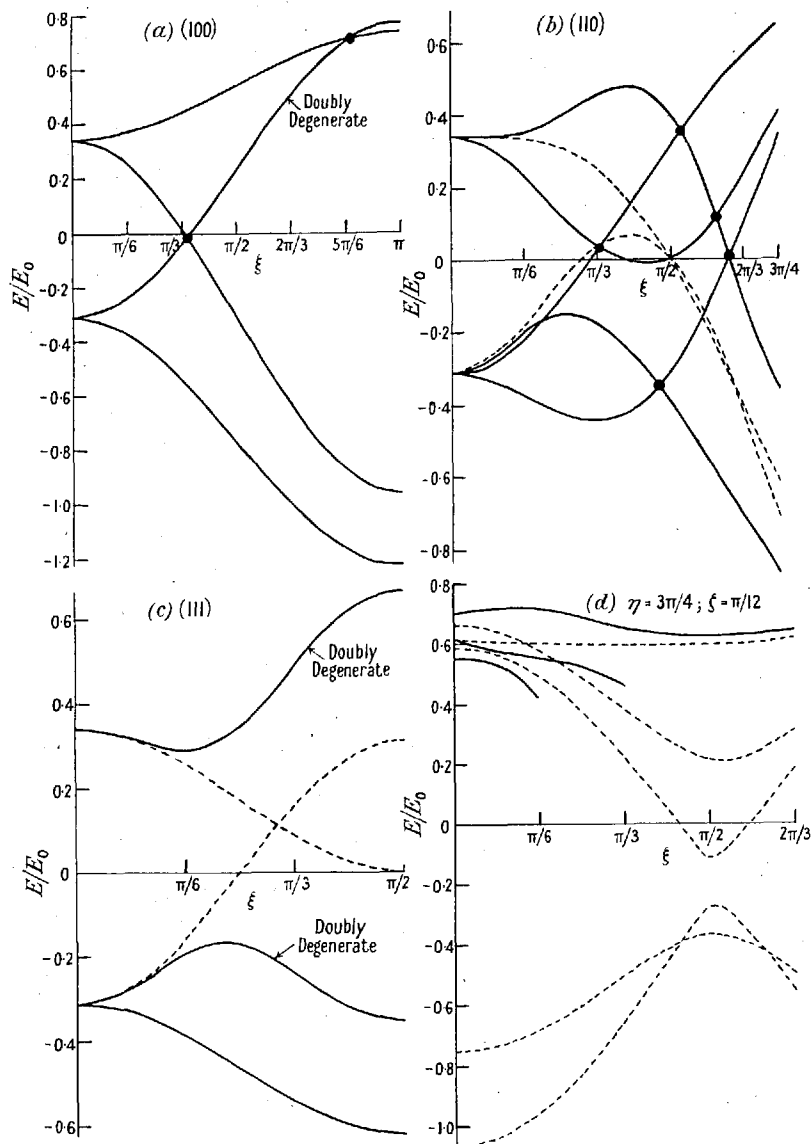


Fig. 1. Variation of energy with wave vector along certain directions in $\mathbf{k}$ -space. Broken curves indicate approximate solutions obtained in I. $\circ$ Predicted points of accidental degeneracy.

(d) The normal derivative of E vanishes over the square faces of the Brillouin zone and along every line joining two opposite corners of a hexagonal face. E must have six-fold rotational symmetry over each hexagonal face.

From the solutions of eqn. (5), curves showing the variation of E with $\mathbf{k}$ were drawn for each value of k_y , and each value of k_z from 0 to $2\pi/a$ at intervals of $\pi/6a$. Only one other point of accidental degeneracy (see fig. 1(b)) was discovered, apart from those predicted. Attempts to collect the energy values into sets, as mentioned above, indicated quite conclusively that there is only one possible way of doing this. Solutions must be interchanged at all points

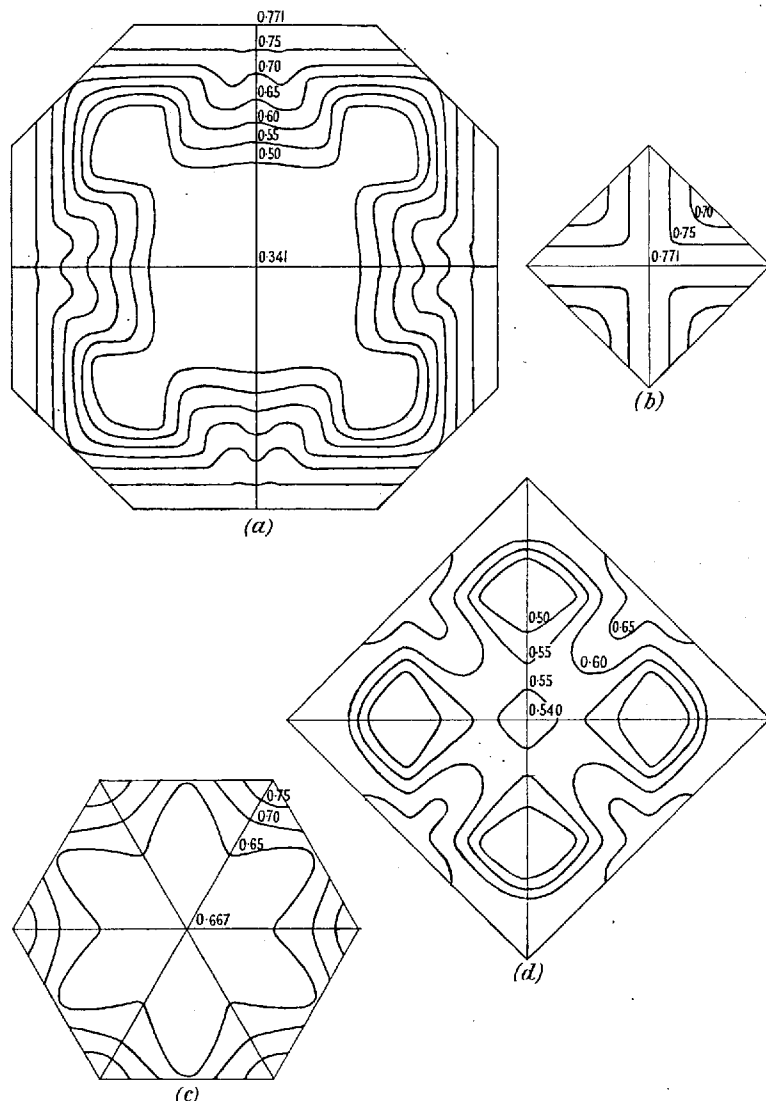


Fig. 2. Contours of constant energy for certain planes of the Brillouin zone for the high energy set of solutions of (5) drawn at energy intervals of $0.05 E_0$. (a) $\xi=0$ plane. (b) Square face ($\xi=\pi$). (c) Hexagonal face. (d) $\xi=\pi/2$ plane.

of accidental degeneracy in such a way that for every value of $\mathbf{k}$ the highest energy value belongs to Brillouin zone I, the next highest to Brillouin zone II, and so on. This is a perfectly valid procedure (Bouckaert, Smoluchowski and Wigner 1936), and the resulting discontinuities in $\text{grad } E$ do not affect $N(E)$ since on any given surface of constant energy of $\mathbf{k}$ -space such discontinuities occur only at isolated points and not over an area.

As in the previous calculation in I constant energy contours were drawn in the planes $k_z = \nu\pi/6a$ ($\nu = 0 \dots 12$) at intervals of $0.025 E_0$ for each of the three sets of energy values involved in the energy range considered. Examples of the $(E, \mathbf{k})$ curves and the constant energy contours are shown in figs. 1 and 2.

It follows directly from the definition of $N(E)$ that

$$N(E) \propto \iint \frac{dS}{|\text{grad } E|},$$

integrating over the surface in $\mathbf{k}$ -space for which the energy has the constant value E . To avoid numerical integration in three variables the approximation $N(E) \propto \Delta K / \Delta E \propto \Delta K$ was made, where ΔK is the volume of $\mathbf{k}$ -space enclosed between the surfaces of energies E and $E + \Delta E$, the value so obtained for $N(E)$ being assumed to be that for $E + \frac{1}{2}\Delta E$. This indicates the method used for calculating an $N(E)$ curve for each set of energy values, the volumes ΔK being

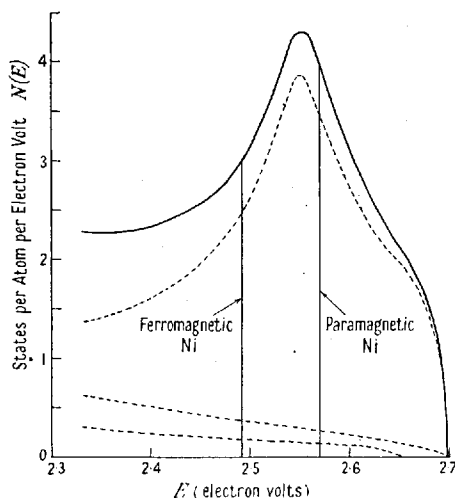


Fig. 3. Density of states curve for nickel. E , electronic energy in eV, measured from zero at the bottom of the band. $N(E)$, density of states, such that the total area under the (complete) curve corresponds to 5 states of either spin. Fermi limit for paramagnetic, ferromagnetic nickel as shown. ----- Constituent $N(E)$ curves.

obtained by graphical integration. It was not possible to check this stage of the calculation, as was done in I, by measuring the areas under the $N(E)$ curves, since they are incomplete, but any error introduced is unlikely to be greater than in the previous calculation, viz. of the order of 1%. Finally, the total $N(E)$ curve over the relevant energy range was obtained by adding the three constituent curves and is shown in fig. 3.

§ 4. RESULTS AND DISCUSSION

(a) The total width of the 3d band is 2.70 eV, as obtained already in I, since the highest and lowest energy values occur when $\mathbf{k} = (2\pi/a, 0, 0)$ for which $H_{nm} = 0$ ($n = 1, 2, 3$; $m = 4, 5$). On comparison of fig. 3 with the curve obtained in I it is seen that the right-hand peak has moved to a higher energy value nearly at the top of the band. This is readily understood on reference to fig. 1. Consider the (111) direction in particular, since here the effect of the previously neglected elements H_{nm} is greatest. Fig. 1(c) then shows clearly that the result of including these elements is to force the higher solutions of eqn. (5) to still

higher energy values and the lower ones to lower values, i.e. to increase the number of states near the limits of the band and decrease the number near the middle. This suggests also, therefore, that the left-hand peak of the $N(E)$ curve would occur nearer the bottom of the band than in I. The $N(E)$ curve would then resemble that given by Slater (1936), but there are important differences between the two curves. The width of Slater's curve is twice that obtained here and the height of his peak only about half that of fig. 3. The effect of these differences is illustrated below.

(b) From fig. 3 the energy difference ϵ_0 between the top of the band and the right-hand vertical line, which corresponds to 0.3 vacant states per atom, is 0.125 eV. Then by definition the degeneracy temperature for nickel is $T = (e/kc) \times 10^8 \times 0.125 = 1.4_5 \times 10^3$ °K.

This compares with 1600°K and 2400°K deduced by Wohlfarth (1949) from the magnetic and thermal properties respectively, and about 2000°K deduced as above from Slater's curve. Although the present value does not compare so favourably with Wohlfarth's figures as does Slater's value or that deduced in I, this is to be expected, since Wohlfarth's calculations were based on the assumption of a parabolic band form, to which Slater's $N(E)$ curve and that in I approximate far more closely than does the present curve.

(c) The electronic property, which provides the simplest check on an $N(E)$ curve as calculated here, is the electronic contribution to the specific heat. From Stoner (1936), the linear, low temperature, electronic heat coefficient γ is given by $\gamma = 2.835 \times 10^{-4} R N(E)_0$, where R is the universal gas constant and $N(E)_0$ is the density of states for one direction of spin at the Fermi limit. For a paramagnetic, one can assume zero magnetization at absolute zero so that the lowest states are completely filled by pairs of electrons of opposite spins. In the case of ferromagnetic nickel and cobalt, however, Wohlfarth (1949) has shown that there must be almost complete magnetization at very low temperatures. Thus, for nickel, 5 states per atom of one spin (+) are fully occupied and only 4.4 states per atom of the other spin (−), instead of 4.7 states of each spin. The only electrons which can take part in the specific heat process are those of (−) spin near the top of this unfilled band. The area under the curve of fig. 3 corresponds to 5 electronic states per atom so that the relevant value of $N(E)_0$ is given by the left-hand vertical line, the area to the right of which corresponds to 0.6 state per atom, i.e. this is the Fermi limit in the unfilled (−) spin band. The resulting value obtained for γ is $1.6_9 \times 10^{-3}$ cal mol^{−1} deg^{−2} as compared with an observed value of 1.74×10^{-3} , and one of 1.1×10^{-3} deduced from Slater's $N(E)$ curve. A suitable value for comparison purposes would be somewhat lower than 1.74×10^{-3} , since this figure includes contributions from the s electrons and from d→s transitions (Wohlfarth 1948, 1949), possibly 1.5×10^{-3} . The very close agreement obtained here, however, must be regarded as somewhat fortuitous, owing to the approximations made and the fact that the Fermi limit occurs at a steeply sloping part of the $N(E)$ curve so that any error in its position would introduce a comparatively large error in γ .

It may also be noted, by comparison with I, that consideration of the previously neglected elements H_{nm} has brought the theoretical value of γ into closer agreement with experiment; these elements have been neglected in previous calculations of a similar nature to the present one (Jones and Mott 1937). A more interesting point, however, is that the 'ferromagnetic Fermi limit' now falls to

the left of the band peak. If this does in fact occur, then a number of theoretical calculations of other electronic properties, based on a parabolic variation of $N(E)$ with E at the Fermi limit, would appear to be in need of revision.

(d) As mentioned in §3(a) a triple and a double degeneracy should occur between the wave functions at $\mathbf{k}=0$. This is confirmed in the present calculation with an energy separation between the two degenerate levels of 0.88 eV. In all applications of the cellular method, however, five-fold degeneracy is obtained at the centre of the Brillouin zone, a result due to the method of approximation.

(e) Returning to a general consideration of the $N(E)$ curve, Wohlfarth (1951) points out that the collective electron treatment of ferromagnetism was originally developed by Stoner (1938, 1939, 1948, 1951) for a 'parabolic' energy band, for which $N(E) \propto (E_M - E)^{1/2}$, where E_M is the upper energy limit of the band. Wohlfarth carries out similar calculations for a 'rectangular' energy band, for which $N(E)$ is constant, and shows that the observed values of several electronic properties of nickel lie between the values calculated for parabolic and rectangular bands. Use of a band form intermediate between these two might therefore be expected to yield results in good agreement with experiment. The present curve may therefore be of use as a basis for a new calculation of suitable electronic properties for nickel.

Another problem, to which the present work is related, is that of ferromagnetic anisotropy. The view has been put forward that this is due to spin-orbit coupling and Brooks (1940) has treated the problem theoretically on these lines, using 'tight-binding' wave functions and obtaining qualitative agreement with experiment for iron and nickel. In his treatment, however, the matrix elements H_{nm} ($n=1, 2, 3$; $m=4, 5$) are neglected (as in I), whereas it has been shown here that this approximation is not a valid one. It is possible, therefore, that the results obtained by Brooks would be considerably modified if these elements were taken into consideration.

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