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MULTI-BAND ELECTRICAL CONDUCTION

By
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ABSTRACT

Scattering amplitudes arising from lattice vibrations are calculated for electrons in a transition metal, with special reference to nickel. The potential in the crystal is treated as a deformable potential, with corrections to adjust the zero of potential and to include effects of the redistribution of charge during lattice vibration.

The distinction between normal and Umklapp processes is not a sharp one when a deformable potential is assumed. Rather, the scattering gradually takes on more of an Umklapp character as the wave length of the phonon decreases.

The 4s electrons are treated in the weak binding and 3p electrons in the strong binding approximation. For s-s scattering, the Umklapp amplitude is larger than normal amplitude by roughly the ratio (kinetic energy at the bottom of the band) / (Fermi energy), or about 8. This makes back-scattering unreasonably likely, and indicates that the method is probably not accurate for large angle scattering. Scattering amplitudes for s-d scattering are of the same order as for s-s scattering in the forward direction. The dependence of s-d amplitude on the various angles is explored.

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I. INTRODUCTION

The electrical conductivity of monovalent metals is fairly well understood. The more common multivalent metals are more complicated, and less theoretical work has been done on them. The object of this investigation is to study the electrical conductivity of metals for a simple case of a multivalent metal such as nickel whose conduction electrons are of two types. One type may be characterized as behaving under external forces as if it had an effective mass several times greater than the free electron mass, the other type having a mass nearly equal to the free electron mass. When an external electric field is applied, the 4s electrons, which have the smaller mass, are accelerated proportionally more than the 3d electrons, which have the larger mass. Thus, the 4s electrons contribute most of the electric current.

The external electric field accelerates an electron until the electron suffers a collision. Collisions can be between electrons or can be caused by any lack of periodicity in the metal. Examples of the latter are impurities, defects, grain boundaries, and thermal vibrations of the ionic cores. At ordinary temperatures, thermal vibrations provide the most important process limiting conduction. This will be the process considered in this investigation.

The probability of a collision involves two factors: one, the probability of making a transition to a given final state, and two, the density of the final states. The 4s electrons, which carry most of the current, can scatter into either 4s states or 3d states. These are the only states that are possible from energy requirements. The density of 3d states is much larger than that of 4s states so 4s to 3d scattering is the dominant one in limiting transport phenomena in metals of the type of nickel, provided that the transition probability into a 3d state is comparable with that into a 4s state.

In the presentation of this work, first a survey of metallic conduction is given showing the relation of the probability of scattering with the conduction process. Then, the probability for 4s to 4s scattering is discussed. The probability for 4s to 3d scattering is then calculated and the probability of the two types of scattering compared with each other and with other workers' results.

II. LITERATURE SURVEY

Houston[1] and Bloch[2] have investigated, on the basis of quantum mechanics, the way in which electrons interact with a crystal lattice when an external electric field is applied. Brillouin,[3] and Sommerfeld and Bethe,[4] assumed with Bloch that as ionic cores vibrate, the electric potential deforms with the crystal without changing magnitude. This type of potential is called deformable. Nordheim[5] objected to this assumption because he believed that the most important contribution to the potential is near the ionic core. He assumed that the potential consisted of the sum of ionic potentials located at displaced ion sites. Bardeen[6] performed a self-consistent calculation taking into account ionic potentials located at ion sites and the potential change due to redistribution of conduction electrons when ions are displaced from their equilibrium positions. Bardeen's method is better justified than either the deformable potential or the rigid core potential of Nordheim, but it is only suitable for monovalent metals with nearly free electrons. Of the two methods, the deformable potential predicts s - s scattering more nearly like that calculated by Bardeen than does the rigid core potential. Thus the deformable potential will be used in this work.

Mott[7] was the first to suggest that the reduced conductivity of transition metals could be attributed to s electrons' being able to scatter into d states as well as s states. He estimated that the probability of s - s scattering between definite initial and final states would be about the same as that of s - d scattering.

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[1] W. V. Houston, Z. Physik 48, 449 (1928); Phys. Rev. 34, 279 (1929).

[2] F. Bloch, Z. Physik 52, 555 (1928); 59, 208 (1930).

[3] L. Brillouin, Quantenstatistik (Julius Springer, Berlin, 1931).

[4] A. Sommerfeld and H. A. Bethe, Handbuch der Physik, Vol. 24, Part 2 (Julius Springer, Berlin, 1933) p. 499.

[5] L. Nordheim, Ann. Physik 9, 607 (1931).

[6] J. Bardeen, Phys. Rev. 52, 688 (1937).

[7] N. F. Mott, Proc. Phys. Soc. (London) 47, 571 (1935); Proc. Roy. Soc. (London) A153, 699 (1936).

Wilson[8] used the estimate of Mott for s - d scattering to calculate the conductivity of transition metals.

The importance of electron - electron scattering was recognized by Baber.[9] He found that the resistivity of transition metals should have a small T^2 dependent term added to the usual formula, as is observed in platinum. Electron - electron collisions will not affect resistivity in metals where all conduction electrons have the same effective mass, as in this case the current carried by two electrons is proportional to the crystal momentum, and thus is unchanged by the collision.

The idea that conduction electrons can redistribute to equalize the Fermi energy and thus produce an additional potential was developed by Landauer,[10] Dexter,[11] and Hunter and Nabarro.[12]

Bhatia[13] and Ziman[14] discussed the effect of Umklapp scattering processes on the temperature dependence of resistance of monovalent metals.

III. SURVEY OF METALLIC CONDUCTION

The fundamental property of crystalline structures is their translational symmetry. Thus in a one-electron approximation, each electron would find itself in a periodic potential. According to Bloch,[2] wave functions for an electron in a periodic potential can be put in the form

$$\psi(\vec{r}, \vec{k}) = N^{-\frac{1}{2}} \exp(i\vec{k} \cdot \vec{r})\, U(\vec{r}, \vec{k}), \qquad (3.1)$$

where $U(\vec{r}, \vec{k})$ has the periodicity of the crystal in the variable $\vec{r}$, the electron coordinate, and is normalized in a cell containing one atom. N is the number of atoms in the crystal. In this work, one atom per unit

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[8] A. H. Wilson, Proc. Roy. Soc. (London) A167, 580 (1938).

[9] W. G. Baber, Proc. Roy. Soc. (London) A158, 383 (1937).

[10] R. Landauer, Phys. Rev. 82, 520 (1951).

[11] D. L. Dexter, Phys. Rev. 86, 770 (1952).

[12] S. C. Hunter and F. R. Nabarro, Proc. Roy. Soc. (London) A220, 542 (1953).

[13] A. B. Bhatia, Proc. Phys. Soc. (London) A65, 188 (1952).

[14] J. M. Ziman, Proc. Roy. Soc. (London) A226, 436 (1954).

cell will be assumed. The vector $\vec{k}$ is called the propagation vector, and $\hbar\vec{k}$ the crystal momentum; $\hbar$ is Planck's constant divided by 2π. The energy of the state will be a function of $\vec{k}$.

It is well known[15] that the mean velocity of an electron in a Bloch state is given by

$$v_i = (\hbar/im)\int\psi^*(\partial\psi/\partial x_i)d\tau = \partial E(\vec{k})/\partial\hbar k_i \quad . \qquad (3.2)$$

If an electrostatic force is applied, Houston[16] has shown that as a wave packet progresses, the time derivative of the crystal momentum is equal to that force, that is

$$d(\hbar\vec{k})/dt = \vec{F}, \qquad (3.3)$$

where $\vec{F}$ is the external force. It is a basic law of all mechanics that the time rate of change of momentum is equal to the force; for electrons subject to periodic potentials, as well as external forces, the time rate of change of crystal momentum is equal to the external force. An effective mass can be defined in a manner analogous with Newton's law. For

$$dv_i/dt = dv_i/d(\hbar k_j) \ d(\hbar k_j)dt, \qquad (3.4)$$

so if one defines the effective mass by

$$(1/m)_{ij} = dv_i/d(\hbar k_j) = d^2E(\vec{k})/d(\hbar k_i)d(\hbar k_j), \qquad (3.5)$$

(by equation (3.2)), then the equation of motion will appear in its familiar form

$$dv_i/dt = (1/m)_{ij}\ F_j; \qquad (3.6)$$

however, 1/m is a symmetric tensor. Equation (3.6) follows from Houston's theorem, equation (3.3).

Sommerfeld and Bethe[4] give an extended formulation of the electrical conduction calculation, so only a brief résumé of their discussion will be given. If $f(\vec{k}\ell, t)$ is the probability, at time t, that the state of band ℓ with propagation vector $\vec{k}$, be occupied, then for a steady state

$$(\partial f/\partial t)_{\text{field}} + (\partial f/\partial t)_{\text{collisions}} = 0. \qquad (3.7)$$

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[15] F. Seitz, The Modern Theory of Solids (McGraw-Hill Book Company, Inc., New York, 1940) p. 316.

[16] W. V. Houston, Phys. Rev. 57, 184 (1940).

In a uniform electric field in the x direction, E_x, one has

$$(\partial f/\partial t)_{\text{field}} = eE_x\,(\partial f/\partial(\hbar k_x)) = eE_x\,v_x\,(df_o/dE). \qquad (3.8)$$

The first equality is again Houston's theorem; the second is obtained by the approximation of replacing f by f_o, the equilibrium value, which depends on k_x only through $E(\vec{k})$. The charge of an electron is -e. Thus the equation for f, the Boltzmann equation, is as follows:

$$-e\,E_x\,v_x\,(df_o/dE) = (\partial f/\partial t)_{\text{collisions}}. \qquad (3.9)$$

The electric current is the sum of the currents of every state,

$$J_x = -2\Sigma(\ell)\int e v_x\, f(\vec{k}\ell)\, d\vec{k}/(2\pi)^3; \qquad (3.10)$$

the factor 2 accounts for the two spin orientations, and the factor $(\frac{1}{2}\pi)^3$ arises from the density of states in k- space.

In order to calculate $(\partial f/\partial t)_{\text{collisions}}$, one must first calculate $\mathcal{W}(\vec{k}\ell, \vec{k}'\ell')$, the probability per unit time that an electron in state $\vec{k}\ell$ makes a transition to a state $\vec{k}'\ell'$. For sufficiently long times this is equal to

$$\mathcal{W}(i,\ f) = (2\pi/\hbar)\left|\int \psi_f^* V_p\, \psi_i\, d\tau\right|^2 \delta(E_i - E_f), \qquad (3.11)$$

where i indexes the initial state, and f the final state. V_p is the perturbing potential causing the transition. The expression $\delta(E_i - E_f)$ is delta function of the difference of the initial and final energies.

Once $\mathcal{W}(\vec{k}\ell, \vec{k}'\ell')$ is known, $(\partial f/\partial t)_{\text{collisions}}$ may be determined in the following manner. The product of $f(\vec{k}\ell)$, the probability that state $\vec{k}\ell$ be occupied, times $\mathcal{W}(\vec{k}\ell, \vec{k}'\ell')$, times $\{1 - f(\vec{k}'\ell')\}$, the probability that state $\vec{k}'\ell'$ be empty, is the probability per unit time that an electron makes a transition from state $\vec{k}\ell$ to state $\vec{k}'\ell'$. This product summed over bands ℓ' and integrated over $\vec{k}'$ gives the net loss per unit time from state $\vec{k}\ell$. The net gain per unit time can be similarly expressed. $(\partial f/\partial t)_{\text{collisions}}$ is the difference, thus

$$\begin{aligned}&(\partial f(\vec{k}\ell)/\partial t)_{\text{collisions}} = \\ &\Sigma(\ell')\int\Big[\mathcal{W}(\vec{k}'\ell', \vec{k}\ell)\, f(\vec{k}'\ell')\, \{1 - f(\vec{k}\ell)\} \\ &-\mathcal{W}(\vec{k}\ell, \vec{k}'\ell')\, f(\vec{k}\ell)\, \{1 - f(\vec{k}'\ell')\}\Big]\, d\vec{k}'/(2\pi)^3. \end{aligned} \qquad (3.12)$$

Substituting equation (3.12) for the right hand side of equation (3.9), one obtains the Boltzmann equation for $f(\vec{k}\ell, t)$. To determine the current and thus the conductivity, the solution to the Boltzmann equation must be substituted into the expression for the current, equation (3.10). Before this formidable task can be started, the transition amplitude for scattering, must be found.

$$\int \psi_f^*\, V_p\, \psi_i\, d\tau \qquad (3.13)$$

The object of the present investigation is to make a more quantitative estimate of integral (3.13) for s - d scattering than that of Mott[7] and to study the relation between s - s and s - d scattering. In particular, it is of interest to show the importance of shear modes on electronic scattering, and to study the angular dependence of scattering, facets that have been ignored for the most part in previous work.

Nickel was chosen as an example because information on its wave functions and energy bands is available from recent work of several investigators.[17-18]

IV. THE SCATTERING AMPLITUDE

The scattering amplitude for the perturbation V_p is given by integral (3.13). In this case the perturbation V_p is the difference between the potential in a static, perfectly periodic crystal lattice and the potential in a crystal lattice where the ionic cores are in thermal vibration.

If one considers the potential energy of a crystal as a function of the displacement of ionic cores from their equilibrium positions, and makes a Taylor's series expansion of the energy in terms of these displacements, the first non-constant terms will be the quadratic terms. The linear terms will be zero from the equilibrium condition. For small displacements, quadratic terms give a good approximation to the energy. Then "normal modes", that is traveling plane wave motion, can exist in which each ion undergoes a motion with definite phase relationship to the other ions. In a normal mode the displacement of the ion with equilibrium position at $\vec{R}_n$ is given by

$$\vec{S}_n = N^{-\frac{1}{2}} a \hat{\mathcal{E}} \cos(\vec{q} \cdot \vec{R}_n - \omega t + \delta), \tag{4.1}$$

where for each propagation vector $\vec{q}$, there are three polarizations $\hat{\mathcal{E}}$ and in general three frequencies ω. The polarization vectors for these three modes are mutually perpendicular. For long wave lengths in an isotropic medium, one mode is longitudinal, the other two transverse. In a longitudinal mode, the propagation vector is parallel to the polarization vector; in each transverse mode it is perpendicular. The amplitude factor, $N^{-\frac{1}{2}} a$, is picked for convenience.

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[17] G. C. Fletcher, Proc. Phys. Soc. (London) A65, 192 (1952).

[18] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

Any general motion of the ions can be represented as a linear combination of normal modes (phonons). The phonons can be quantized and form a Bose-Einstein system. The displacement $\vec{S_n}$ of the ion at $\vec{R_n}$ can be written in general as

$$\vec{S_n} = N^{-\frac{1}{2}} \Sigma(q,j)\, \hat{\varepsilon}_{qj} \{a_{qj} \exp(i\vec{q}\cdot\vec{R_n}) + a^*_{qj} \exp(-i\vec{q}\cdot\vec{R_n})\}, \qquad (4.2)$$

where a_{qj} is the destruction operator for a phonon in the qj th mode, and a^*_{qj} is the creation operator for a phonon in the qj th mode. If N_{qj} is the number of phonons in the qj th mode, and M is the mass of an ion, the operators have the following transition amplitudes:

$$(N_{qj} - 1|a_{qj}|N_{qj}) = (\hbar N_{qj}/2M\omega_{qj})^{\frac{1}{2}}, \qquad (4.3)$$

$$(N_{qj} + 1|a^*_{qj}|N_{qj}) = (\hbar(N_{qj} + 1)/2M\omega_{qj})^{\frac{1}{2}} . \qquad (4.4)$$

Equation (4.3) is the matrix element of a_{qj} connecting the initial state, with N_{qj} phonons in the qj th mode, and the final state, with $N_{qj} - 1$ phonons in the same mode, the content of all other modes remaining the same. Equation (4.4) has a similar interpretation. The matrix elements of the a's between all other types of states are zero, thus the content of one mode can change by only one phonon at a time. For thermal equilibrium of the phonons, the average number in the qj th mode, $\bar{N}_{qj}$, is given by the usual formula, that is

$$\bar{N}_{qj} = \{\exp(\hbar\omega_{qj}/kT) - 1\}^{-1} , \qquad (4.5)$$

where k is Boltzmann's constant, and T is the temperature.

For high temperatures

$$\bar{N}_{qj} \approx kT/\hbar\omega_{qj} , \qquad (4.6)$$

and thus

$$(N_{qj} - 1|a_{qj}|N_{qj}) \approx (N_{qj} + 1|a^*_{qj}|N_{qj}) \approx (kT/2M)^{\frac{1}{2}}/\omega_{qj} . \qquad (4.7)$$

For elastic waves in isotropic materials, and elastic waves traveling along principal directions of cubic crystals, waves separate into longitudinal and transverse modes. In general, longitudinal waves will have a velocity, v_ℓ, greater than that of transverse waves, v_t. For many materials[19]

$$v_\ell / v_t \approx 3^{\frac{1}{2}}. \qquad (4.8)$$

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[19] G. Joos, Theoretical Physics (Hafner Publishing Co., New York, 1950), second edition, p. 180.

Since

$$\omega = v\ q, \tag{4.9}$$

the amplitude of transverse waves is greater than that of longitudinal waves with the same $\vec{q}$ by about a factor of $3^{\frac{1}{2}}$.

For the general case of elastic waves in a crystal with one atom per primitive cell, there will be waves of three different (and perpendicular) polarizations for each propagation vector $\vec{q}$. These waves will not in general be separable into longitudinal and transverse waves. The waves of all three polarizations may contribute to scattering between the same initial and final state. Because the phase relations between them are random, the total transition probability will be obtained from the sum of the squares of the transition amplitude for each mode. In the present work, the elastic waves will be treated as if one polarization is longitudinal and two are transverse for each wave vector. And the amplitude of the transverse waves will accordingly be taken as $3^{\frac{1}{2}}$ times the amplitude of the longitudinal wave.

As shown in Appendix A, the perturbation of electrons by the lattice vibrations can be considered as a sum of perturbations, one for each mode. Only modes of a single q will scatter an electron between a given initial and final state, so the perturbation potential due to only a single mode need be considered. Thus the scattering process is that of an inelastic collision, an electron absorbing or emitting a phonon, and changing its energy and crystal momentum so as to conserve both energy and crystal momentum of the system of electron plus phonons. The conservation of energy arises in the time dependent perturbation theory, and the conservation of crystal momentum is demonstrated later in this section.

Bloch,[2] in his early work on the conductivity of metals, assumed that the potential in a deformed metallic crystal is deformable; that is, the potential in the deformed crystal $V_{def.}(\vec{r})$ is given by

$$V_{def.}(\vec{r}) = V\{\vec{r} - \vec{S}(\vec{r})\}, \tag{4.10}$$

where the deformation consists of taking a point at $\vec{r}$ to a point at $\vec{r} + \vec{S}(\vec{r})$. Thus the potential in the deformed crystal at the new point is equal to potential of the undeformed crystal at the old point. Following Bloch, in this work it is assumed that the fine structure of the potential is as given by equation (4.10), but slowly varying functions of the local state of strain of the crystal are added to the potential for two reasons. The first of these is that even in a homogeneously deformed crystal the total electronic energy does not change to first order in strain. With a correct potential, this stationary property is automatic; in an approximate potential it provides a method of adjusting the zero of potential. The second reason is that in an inhomogeneous deformation, some redistribution of charge takes place to keep the Fermi level constant throughout the crystal.

Appendix B derives the function of strain that must be added to equation (4.10) to have the total binding energy independent of strain to first order. The potential in a homogeneously deformed crystal, $V_h(\vec{r})$, is then given by

$$V_h(\vec{r}) = V\{\overrightarrow{r - S}(\vec{r})\} + (2/3) \ \{(KE)_F - (2/5)\zeta\} \Delta(r), \qquad (4.11)$$

where Δ is the dilatation (that is, the volume increase per unit volume). $(KE)_F$ is the average kinetic energy at the Fermi level, defined by equation (B.24). The Fermi energy for the undeformed crystal ζ , is the difference in energy between the highest occupied state and the lowest occupied state of the conduction band. A normal band has been assumed, that is, one in which the energy above the bottom of the band is proportional to k^2.

For sinusoidal deformations, as is shown in Appendix C in a manner similar to that used by Hunter and Nabarro,[12] the potential in the deformed crystal can be obtained by adding to the potential of a homogeneously deformed crystal, deformed with the local deformation, the potential

$$- (DE_F/D\Delta)\, \Delta(\vec{r}) \ (1 + \chi q^2)^{-1} , \qquad (4.12)$$

due to redistributed charge. Here $(DE_F/D\Delta)$ is the derivative of the Fermi energy with respect to dilatation keeping the crystal everywhere electrically neutral. $\vec{q}$ is the propagation vector of the sinusoidal deformation. For a band in normal form, χ is given by

$$\chi = (\pi \hbar^2/4m^* \ k_F \ e^2) \ = \pi a_0 \ m/4k_F \ m^* , \qquad (4.13)$$

where k_F is the k of electrons with the Fermi energy, and m^* is the effective mass. a_0 is the radius of the first Bohr orbit, $a_0 = \hbar^2/me^2$. $DE_F/D\Delta$ is shown in Appendix B to be $- (4/15)\zeta$. If one combines equation (4.11) and term (4.12), one finds for the potential in a sinusoidally deformed crystal, $V_d(\vec{r})$, the expression

$$V_d(\vec{r}) \ = \ V\{\overrightarrow{r - S}(\vec{r})\} + \\ (2/3) \ \left[(KE)_F - (2/5) \{1 - (1 + \chi q^2)^{-1}\} \ \zeta\right] \Delta(\vec{r}). \qquad (4.14)$$

Except for very near the origin, $V\{\overrightarrow{r - S}(\vec{r})\}$ may be expanded in a Taylor's series in $\vec{S}$ keeping only the first term since $\vec{S}(\vec{r})$ is small. Thus the perturbation potential, $V_p(\vec{r})$, is as follows:

$$V_p(\vec{r}) \ = \ V_d(\vec{r}) - V(\vec{r}) = - \vec{S}(\vec{r}) \ \cdot \nabla V(\vec{r}) + C(q)\,\Delta(\vec{r}), \qquad (4.15)$$

where

$$C(q) = (2/3) \ \left[(KE)_F - (2/5) \ \{1 - (1 + \chi \, q^2)^{-1}\} \ \zeta\right] \ . \qquad (4.16)$$

Equation (4.14) is the perturbation potential in terms of a continuous deformation wave. In order to use this equation, an expression for $\vec{S}(\vec{r})$, the continuous displacement vector, is still required. Equation (4.2) gives the displacement $\vec{S}_n$ of a core from its equilibrium position $\vec{R}_n$. It seems reasonable to assume for $S(\vec{r})$ a similar form,

$$\vec{S}(\vec{r}) = N^{-\frac{1}{2}} \hat{\varepsilon}_{qj} \left\{ a_{qj} \exp(i\vec{q} \cdot \vec{r}) + a^{*}_{qj} \exp(-i\vec{q} \cdot \vec{r}) \right\}, \tag{4.17}$$

for the qj th mode. This expression certainly has the correct form when $\vec{r}$ is near a $\vec{R}_n$. It will be shown later (in section VII. B) that this expression is satisfactory for long wave lengths, but corrections must be applied for wave lengths near the minimum.

The strain tensor is defined as follows:

$$\eta_{ij} = \left\{ (\partial S_i/\partial x_j) + (\partial S_j/\partial x_i) \right\}/2, \tag{4.18}$$

while the dilatation Δ is the trace of the strain tensor, that is:

$$\Delta = \eta_{11} + \eta_{22} + \eta_{33}. \tag{4.19}$$

From equation (4.17) it is seen that the dilatation for the qj th mode is

$$\begin{aligned} \Delta(\vec{r}) = {} & N^{-\frac{1}{2}} i \hat{\varepsilon}_{qj} \cdot \vec{q} \left\{ a_{qj} \exp(i\vec{q}\cdot\vec{r}) \right. \\ & \left. - a^{*}_{qj} \exp(-i\vec{q}\cdot\vec{r}) \right\}. \end{aligned} \tag{4.20}$$

Substituting equations (3.1), (4.14) and (4.20) into equation (3.13), one can evaluate the scattering amplitude for the qj th mode as follows:

$$\begin{aligned} & \int \psi^{*}_{f} V_p \psi_i \, d\tau \\ & = N^{-3/2} a_{qj} \left\{ iC(q) \vec{q} \cdot \hat{\varepsilon}_{qj} \int \exp(i\vec{K}_{+} \cdot \vec{r}) \, U^{*}_{f} U_i \, d\tau \right. \\ & \left. - \int \exp(i\vec{K}_{+} \cdot \vec{r}) \, \hat{\varepsilon}_{qj} \cdot \nabla V(\vec{r}) \, U^{*}_{f} U_i \, d\tau \right\} \\ & - N^{-3/2} a^{*}_{qj} \left\{ iC(q) \vec{q} \cdot \hat{\varepsilon}_{qj} \int \exp(i\vec{K}_{-} \cdot \vec{r}) \, U^{*}_{f} U_i \, d\tau \right. \\ & \left. + \int \exp(i\vec{K}_{-} \cdot \vec{r}) \, \hat{\varepsilon}_{qj} \cdot \nabla V(\vec{r}) \, U^{*}_{f} U_i \, d\tau \right\}, \end{aligned} \tag{4.21}$$

where $\vec{K}_{\pm} = \vec{k}_i \pm \vec{q} - \vec{k}_f$.

All these integrals are of the form $N^{-1} \int \exp(i\vec{K} \cdot \vec{r}) \, F(\vec{r}) \, d\tau$, where $F(\vec{r})$ has the periodicity of the lattice, i.e., $F(\overrightarrow{r - R_n}) = F(\vec{r})$. Variables can be changed in each cell so that the integral becomes

$$\begin{aligned} & N^{-1} \Sigma(n) \exp(i\vec{K} \cdot \vec{R}_n) \int \exp\left\{ i\vec{K} \cdot (\overrightarrow{r - R_n}) \right\} F(\overrightarrow{r - R_n}) \, d\tau_n \\ & = A \, N^{-1} \Sigma(n) \exp(i\vec{K} \cdot \vec{R}_n), \end{aligned} \tag{4.22}$$

where $A = \int \exp(i\vec{K} \cdot \vec{r})\, F(\vec{r})\, d\tau_0$, an integral over the 0 th cell. The sum over the lattice can be performed along one translation vector at a time. Each is a geometric series, the ratio of terms being modulus one. Unless $\vec{K} \cdot \vec{R}_n = 2\pi m$, where for every n, m is some integer, the sum remains bounded as the size of the crystal grows indefinitely. If $\vec{K} \cdot \vec{R}_n = 2\pi m$, then the sum of the series is just the number of atoms in the crystal, and $N^{-1}\sum(n) \exp(i\vec{K} \cdot \vec{R}_n) = 1$.

Suppose $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ are the primitive vectors of a crystal, that is, the atom positions are generated by $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$, the n's being integers. Reciprocal vectors can be defined so that $\vec{b}_1 = \vec{a}_2 \times \vec{a}_3/(\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3)$ and so forth, cyclically. A reciprocal lattice is then generated by $\vec{B}_n = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$. In order that $\vec{K} \cdot \vec{R}_n = 2\pi m$, $\vec{K} = 2\pi \vec{B}_p$. Unless $k_i \pm \vec{q} - \vec{k}_f = 2\pi\vec{B}_n = \vec{K}_n$, the integral $\int \psi_f^* \; V_p \psi_i \; d\tau$ will go towards zero as the volume of the crystal increases. The reason for this is that $N^{-1}\sum(n) \exp(i\vec{K} \cdot \vec{R}_n) \rightarrow 0$ as $N \rightarrow \infty$ unless $\vec{K} = 2\pi \vec{B}_n$.

Since $\vec{k}$ and $\vec{q}$ enter only through the exponential in the form $\exp(i\vec{k} \cdot \vec{r})$, adding 2π times any reciprocal vector to $\vec{k}$ or $\vec{q}$ will not change its effect. The first Brillouin zone can be defined as that part of k-space as near the origin as 2π times any other reciprocal vector. By adding 2π times some reciprocal lattice vector, any $\vec{k}$ or $\vec{q}$ can be made to fall in this first zone. This will be assumed to be done. Since $\vec{k}_i$, $\vec{k}_f$ and $\vec{q}$ are all in this zone, $\vec{K}_n$ in the expression $\vec{k}_i \pm \vec{q} - \vec{k}_f = \vec{K}_n$ will be either the origin or a nearby K vector. If $\vec{K}_n$ is not zero, the collision is called an Umklapp process, while if $\vec{K}_n = 0$ the collision is called a normal process.

Except for the few values of $\vec{q} = \pi \vec{B}_n$, the conditions $\vec{k}_i + \vec{q} - \vec{k}_f = 2\pi\vec{B}_n$ and $\vec{k}_i - \vec{q} - \vec{k}_f = 2\pi \vec{B}_{n'}$ cannot be satisfied simultaneously by the same value of $\vec{q}$ for any given $\vec{k}_i$ and $\vec{k}_f$. We will assume the first relation to be satisfied. If $\vec{q}$ causes scattering in equation (4.21), $-\vec{q}$ would cause scattering proportional to a^*_{qj} instead of a_{qj} for scattering between states with the same propagation vectors as those considered. In the first case, that is when $\vec{q}$ causes the scattering, and the scattering amplitude is proportional to a_{qj}, the final electronic energy is greater than the initial electronic energy by the energy of a phonon. The reason is that a_{qj} destroys a phonon during the scattering process. Similarly, the final electronic energy is less than the initial electronic energy by the energy of a phonon for the case of $-\vec{q}$ causing scattering proportional to $a^*_{-q\,j}$. The first case will be carried along; the second case can be obtained from the first by inspection.

From the fact that $\vec{K}_+$ is some $\vec{K}_n$, the scattering amplitude can now be written

$$\int \psi_f^* \, V_p \, \psi_i \, d\tau = N^{-\frac{1}{2}} a_{qj} \Big\{ iC(q)\, \vec{q} \cdot \hat{\mathcal{E}}_{qj} \int \overline{U}_f^* \, U_i \, d\tau_0 - \hat{\mathcal{E}}_{qj} \cdot \int \overline{U}_f^* \, U_i \, \nabla V(\vec{r})\, d\tau_0 \Big\}, \qquad (4.23)$$

where $\bar{U}_f^* = U_f^* \exp(i\vec{K} \cdot \vec{r})$, the plus being dropped on $\vec{K}$. Since

$$\psi_f = \exp(i\vec{k}_f \cdot \vec{r}) \quad U_f = \exp\left\{i(\overrightarrow{k_f + K}) \cdot \vec{r}\right\}\bar{U}_f, \tag{4.24}$$

$\bar{U}_f$ corresponds to a $\vec{k}$ of $\vec{k}_f + \vec{K} = \vec{\bar{k}}_f$.

By partial integration, one can convert the second integral of equation (4.23) as follows:

$$\int \bar{U}_f^* \, U_i \, (\partial V(\vec{r})/\partial s) \, d\tau_o = - \int V(\vec{r}) \left\{\partial (\bar{U}_f^* \, U_i)/\partial s\right\} d\tau_o \,, \tag{4.25}$$

where s is in the direction of $\hat{\varepsilon}_{qj}$. The surface terms go out since $\bar{U}_f^*$, U_i, and $V(\vec{r})$ are periodic. ψ satisfies the Schroedinger equation

$$\left\{-(\hbar^2/2m) \nabla^2 + V(\vec{r}) - E\right\} \psi(\vec{r}, \vec{k}) = 0, \tag{4.26}$$

so U_i satisfies the equation

$$(\hbar^2/2m) \, (\nabla^2 U_i + 2i\vec{k}_i \cdot \nabla U_i - k_i^2 \, U_i) + (E_i - V) \quad U_i = 0. \tag{4.27}$$

Similarly, $\bar{U}_f^*$ satisfies the following equation:

$$(\hbar^2/2m) \, (\nabla^2 \bar{U}_f^* - 2i\vec{\bar{k}}_f \cdot \nabla \bar{U}_f^* - \bar{k}_f^2 \, \bar{U}_f^*) + (E_f - V) \, \bar{U}_f^* = 0. \tag{4.28}$$

If one multiplies equation (4.27) by $(\partial \bar{U}_f^*/\partial s)$ and equation (4.28) by $(\partial U_i/\partial s)$, and adds, the resulting equation, integrated by parts, is

$$\begin{aligned} - \int V(\vec{r}) \left\{\partial (\bar{U}_f^* \, U_i)/\partial s\right\} d\tau_o = & -(i\hbar^2/m) \quad (\vec{k}_i - \bar{k}_f) \, \cdot \\ & \int \nabla U_i \, (\partial \bar{U}_f^*/\partial s) \quad d\tau_o \quad - \left\{E_i - E_f - (\hbar^2/2m) \, (k_i^2 - \bar{k}_f^2)\right\} \\ & \int U_i \, (\partial \bar{U}_f^*/\partial s) \quad d\tau_o \, . \end{aligned} \tag{4.29}$$

The scattering amplitude can then be written as

$$\begin{aligned} \int \psi_f^* \, V_p \psi_i \, d\tau = N^{-\frac{1}{2}} \, a_{qj} \Big\{ & iC(q) \quad \vec{q} \cdot \hat{\varepsilon}_{qj} \int \bar{U}_f^* \, U_i \, d\tau_o && B_1 \\ & + \left[E_i - E_f - (\hbar^2/2m) \, (k_i^2 - \bar{k}_f^2)\right] \int U_i \, (\partial \bar{U}_f^*/\partial s) \, d\tau_o && B_2 \\ & - (\hbar^2/2m) \quad i\vec{q} \, . \quad 2\int \nabla U_i \quad (\partial \bar{U}_f^*/\partial s) \quad d\tau_o \Big\} \, . && B_3 \end{aligned} \tag{4.30}$$

Equation (4.30) will be evaluated for a 4s initial state and either 4s or 3d final states in later sections. Parts B_2 and B_3 are as derived by Bethe,[4] while B_1 is new, arising from slowly varying functions added to the deformable potential as used by Bloch[2] and Bethe.[4]

V. THE 4S BAND IN NICKEL

In order to evaluate the scattering amplitude as given by equation (4.30), the wave functions and energy values of the electrons must be found. The 4s band in nickel is similar to other s bands in metals in being weakly bound, that is the wave functions of 4s electrons have appreciable magnitude in the region between ions. A standard method of treating bands of this type, as discussed by Seitz,[20] has been used for the 4s band of nickel. The periodic part of the wave function in Bloch form, $U(\vec{r}, \vec{k})$, satisfies the equation,

$$\begin{aligned} &-\Big\{(\hbar^2/2m)\ (\nabla^2 + 2i\vec{k}\cdot\nabla - k^2) \\ &+ E(\vec{k}) - V(\vec{r})\Big\}\ U(\vec{r}, \vec{k}) = 0. \end{aligned} \tag{4.27}$$

The solution $U(\vec{r}, \vec{k})$ can be expanded in terms of $U(\vec{r}, 0)$ of all bands, by using a perturbation energy of

$$H' = -(\hbar^2/m)\ \vec{k}\cdot i\nabla + (\hbar^2/2m)\ k^2, \tag{5.1}$$

since the functions $U(\vec{r}, 0)$ form a complete set of periodic functions. Using standard non-degenerate second order perturbation theory,[21] one can expand the energy of the ℓ th band for small $\vec{k}$ as follows:

$$\begin{aligned} E_\ell(\vec{k}) &= E_\ell(0) - (\hbar^2/m)\ \vec{k}\cdot(\ell\,|\,i\nabla|\,\ell) + (\hbar^2/2m)\ k^2 \\ &+ (\hbar^4/m^2)\ \vec{k}\vec{k}\colon \Sigma(\ell')\ (\ell\,|\,i\nabla|\,\ell')\ (\ell'\,|\,i\nabla|\,\ell) \\ &\div \Big\{E_\ell(0) - E_{\ell'}(0)\Big\}, \end{aligned} \tag{5.2}$$

where

$$\int U^*_\ell\ (\vec{r}, 0)\ i\nabla U_{\ell'}(\vec{r}, 0)\ d\tau_0 = (\ell\,|\,i\nabla|\,\ell'). \tag{5.3}$$

This is only valid if the ℓ th state is non-degenerate at $\vec{k} = 0$. The effective mass of the ℓ th band at $\vec{k} = 0$ is obtained by twice differentiating

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[20] F. Seitz, *op. cit.*, p. 352.

[21] L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 149.

equation (5.2).

$$(1/m)_{pq} = \partial^2 E_{\ell}(k)/\partial(\hbar k_p)\,\partial(\hbar k_q) = (1/m)\,\delta_{pq}$$
$$+ (\hbar^2/m^2)\sum(\ell')\left\{(\ell|i\nabla_q|\ell')(\ell'|i\nabla_p|\ell) + (\ell|i\nabla_p|\ell')(\ell'|i\nabla_q|\ell)\right\}/\left\{E_{\ell}(0) - E_{\ell'}(0)\right\}. \qquad (5.4)$$

Similarly for small $\vec{k}$'s, $U_{\ell}(\vec{r}, \vec{k})$ can be expanded to first order as follows:

$$U_{\ell}(\vec{r}, \vec{k}) = U_{\ell}(\vec{r}, 0) - (\hbar^2/m)\vec{k}\cdot\sum(\ell')(\ell'|i\nabla|\ell) \times U_{\ell'}(\vec{r}, 0)/\left\{E_{\ell}(0) - E_{\ell'}(0)\right\}. \qquad (5.5)$$

As seen in equation (5.5), the energy denominator is favorable to appreciable mixing only for states of energy near $E_{\ell}(0)$. Further, solutions for $\vec{k} = 0$ can be classified according to their symmetry, and for crystals of high symmetry (such as cubic) this is very useful.[22] Wave functions arising from s states have full cubic cymmetry (Γ_1). The operator $i\nabla$ has symmetry Γ_{15}, and so in first order perturbation can connect s states only with states of symmetry Γ_{15}. These include p states, some f states, etc.

The matrix elements connecting the 4s state of nickel with the 3p state and the 4p state were estimated. The 4s wave function used was that calculated for metallic copper by Fuchs.[23] Copper and nickel have the same crystal structure, face centered cubic. The lattice constant[24] for copper at room temperature is 3.608×10^{-8} cm while that for nickel at room temperature is 3.517×10^{-8} cm. The difference between lattice constants is about three percent. The 3p wave function used was that calculated by Hartree and Hartree[25] for the Cu^+ ion. Since the 3p function of copper is tightly bound, one expects the wave function of electrons in the metal to be nearly equal to those in the free ion.

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[22] L. P. Bouckaert, R. Smoluchowski and E. Wigner, Phys. Rev. 50, 58 (1936). This paper will be denoted as BSW in later references.

[23] K. Fuchs, Proc. Roy. Soc. (London) A151, 585 (1935).

[24] C. D. Hodgman, Handbook of Chemistry and Physics (Chemical Rubber Publishing Co., Cleveland, Ohio) thirtieth edition, p. 2016.

[25] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A157, 490 (1936).

The 4p wave function was calculated by the Wigner-Seitz[26-27] method, using the potential for Cu^+ of Hartree and Hartree.[25] In this method the atomic polyhedron is approximated by a sphere of equal volume. In the face centered cube, there are four atoms, thus, for copper the volume per atom is $(3.608 \times 10^{-8}\ \mathrm{cm})^3/4 = 11.75 \times 10^{-24}\mathrm{cm}^3$. The volume of the sphere is $4\pi r_s^3/3$, so the radius $r_s = 1.41 \times 10^{-8}$ cm $= 2.7\ a_o$, where a_o, the radius of the first Bohr orbit, is $a_o = 0.528 \times 10^{-8}$ cm.

Since the potential and the region are spherical, the solution will be in terms of spherical harmonics:

$$U_{\ell m}(\vec{r}, 0) = Y_\ell^m(\theta, \varphi)\ \ R_\ell(r) = Y_\ell^m(\theta, \varphi) P_\ell(r)/r. \tag{5.6}$$

The radial part of the wave function satisfies the equation,

$$(\hbar^2/2m)\left\{d^2P_\ell(r)/dr^2 - \ell(\ell+1)\ P_\ell(r)/r^2\right\} + \left\{E - V(r)\right\}\ P_\ell(r) = 0. \tag{5.7}$$

If distances are measured in terms of the radius of the first Bohr orbit, $a_o = \hbar^2/me^2 = 0.528 \times 10^{-8}$ cm, and energies in terms of the Rydberg, that is, $e^2/2a_o$ - 13.6 eV, the above equation becomes:

$$\frac{d^2\ P_\ell(r)}{d\ r^2} + \left\{E - V(r) - \ell(\ell+1)/r^2\right\} P_\ell(r) = 0. \tag{5.8}$$

Since spherical harmonics are ortho-normal, that is:

$$\int Y_\ell^m(\theta,\varphi)\ \ Y_{\ell}^{m'}(\theta,\varphi)\ \ \sin\theta\, d\theta\, d\varphi = \delta_{\ell\ell'}\delta_{mm'}, \tag{5.9}$$

in order that $\int U^* U\, d\tau_o = 1$, the P's are normalized so that $\int_0^{r_s} P_\ell^2\, dr = 1$.

Solutions to equation (5.8) are found in the following manner. For small r, hydrogenic wave functions may be used. These are given, for example, by Pauling and Wilson.[28] This solution for small r is extended in steps by calculating the second derivative of P_ℓ from equation (5.8) for some assumed value of energy. The change of the first derivative in an interval is computed from the second derivative. In the same manner the

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[26] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).

[27] J. Bardeen, J. Chem. Phys. 6, 367 (1938).

[28] L. Pauling and E. B. Wilson, Introduction to Quantum Mechanics (McGraw-Hill Book Company, New York, 1935), p. 136.

change in P_ℓ in an interval is computed from the new value of the first derivative. With the value of the function at a new radius, a new second derivative is computed and the process continued, extending the function for increasing r. The entire process is repeated with other assumed energies until an energy is found for which the computed function satisfies the appropriate boundary conditions. In the case of p functions, since $U_p(\vec{r},o)$ is periodic in the unit cell, and odd with respect to either x, y, or z, it must vanish halfway between nearest neighbor ions. Thus, the boundary condition on $P_{4p}(r)$ is $P_{4p}(r_s) = 0$. Table 1 gives $R_{4s}(r)$, $P_{3p}(r)$, and $P_{4p}(r)$ as well as $r(dR_{4s}/dr)$ at intervals of 0.1 a_o from 0 to 2.7 a_o.

From equation (5.5), the rate at which p functions mix with s functions as $\vec{k}$ is increased is

$$-(\hbar/m)\ (p|i\nabla|s)/\{E_s(0) - E_p(0)\}. \tag{5.10}$$

The matrix element can be evaluated as follows:

$$(p_z|\partial/\partial z|s) = \int Y_1^{0*}\ Y_0\ R_p\ R_s'\ (z/r)\ \ d\tau_o = 3^{-\frac{1}{2}} \int_0^{r_s} R_p\ R_s'\ r^2\ \ dr, \tag{5.11}$$

since $Y_0 = (4\pi)^{-\frac{1}{2}}$, and $Y_1^0 = (3/4\pi)^{\frac{1}{2}}\ (z/r)$. The matrix elements were calculated from the functions in Table 1, numerically integrating with intervals of 0.1 a_o. The trapezoid rule[29] was used; that is, the integral was approximated as the sum of the integrands minus one-half the end point values of the integrand, multiplied by the interval. The matrix elements are given below:

$$\int U_{4pz}^{*}(\vec{r},o)\ \ \frac{\partial}{\partial z}\ U_{4s}(\vec{r},o)\ \ d\tau_o = 0.055/a_o, \tag{5.12}$$

$$\int U_{3pz}^{*}(\vec{r},o)\ \ \frac{\partial}{\partial z} - U_{4s}(\vec{r},o)\ \ d\tau_o = 0.31/a_o\ . \tag{5.13}$$

The 4s band of nickel has 0.6 electrons per atom so the number of states filled in the 4s band is $4\pi k_F^3/3\ \ (2\pi)^3 = 0.6N/2V$. Since $N/V = (3/4\pi)(2.7a_o)^{-3}$, $k_F = 0.58/a_o$. The energies of the three states are:

$$E_{4s}(o) = -0.8\ e^2/2a_o, \tag{5.14}$$

$$E_{3p}(o) = -7.3\ e^2/2a_o, \tag{5.15}$$

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[29] W. A. Granville, P. F. Smith, and W. R. Longley, Elements of the Differential and Integral Calculus (Ginn and Company, Boston, 1941), p. 245.

Table 1. Normalized wave functions for copper

r/a_0	R_{4s}	rR'_{4s}	P_{3p}	P_{4p}
0.1	-0.772	-3.86	0.607	0.344
0.2	-0.715	0.82	0.400	0.233
0.3	0.044	1.79	-0.249	-0.129
0.4	0.479	0.93	-0.804	-0.441
0.5	0.513	-0.12	-1.123	-0.602
0.6	0.430	-0.72	-1.235	-0.634
0.7	0.270	-1.16	-1.212	-0.564
0.8	0.099	-1.25	-1.115	-0.435
0.9	-0.044	-1.10	-0.986	-0.261
1.0	-0.148	-0.87	-0.848	-0.067
1.1	-0.219	-0.70	-0.717	0.133
1.2	-0.274	-0.61	-0.598	0.330
1.3	-0.323	-0.60	-0.494	0.501
1.4	-0.361	-0.42	-0.405	0.657
1.5	-0.384	-0.32	-0.350	0.774
1.6	-0.394	-0.23	-0.296	0.891
1.7	-0.397	-0.14	-0.236	0.942
1.8	-0.420	-0.08	-0.176	0.994
1.9	-0.422	-0.02	-0.145	0.978
2.0	-0.420	0.02	-0.114	0.963
2.1	-0.418	0.06	-0.094	0.882
2.2	-0.416	0.13	-0.073	0.801
2.3	-0.409	0.13	-0.060	0.666
2.4	-0.405	0.06	-0.047	0.531
2.5	-0.404	0.02	-0.038	0.361
2.6	-0.403	0.04	-0.030	0.191
2.7	-0.401	0.04	-0.025	0.000
E	$-0.8e^2/2a_0$		$-7.3e^2/2a_0$	$2.2e^2/2a_0$

$$E_{4p}(o) = 2.2\ e^2/2a_o, \tag{5.16}$$

so the amount of 3p and 4p states mixed with the 4s state at the Fermi level is:

$$-(\hbar^2/m)\ (3p\ |i\nabla/4s)\ \cdot\ \vec{k}_F/\left\{E_{4s}(o) - E_{3p}(o)\right\} = 0.055, \tag{5.17}$$

$$-(\hbar^2/m)\ (4p\ |i\nabla|\ 4s)\ \cdot\ \vec{k}_F/\left\{E_{4s}(o) - E_{4p}(o)\right\} = 0.021. \tag{5.18}$$

These calculations indicate that the nearby states do not mix appreciably with the 4s state.

This result is somewhat surprising because 3p states are presumably very tightly bound and thus $E_{3p}(\vec{k}) = E_{3p}(0)$. In this case the 3p functions have three-fold degeneracy, since they have Γ_{15} symmetry.[22] For state p_x and $\vec{k}$ in the k_x direction, the energy is the same expression[30] as given for the non-degenerate case, equation (5.2). Equation (5.2) applied to 3p states. says that coupling of 3p (k = 0) with other k = 0 states must cancel off $\hbar^2 k^2/2m$. 3p - 4s coupling should be the most important single contribution. The same matrix elements and energy denominators are involved as in equations (5.12) to (5.16). Evidently the 3p state gets small contributions from many different states. Similarly, one might expect many states to mix slightly with the 4s state as $\vec{k}$ is increased from k = 0.

Slater[31] has calculated one-electron energies of solids by averaging x-ray term values. Band widths have been taken from soft x-ray levels. He gives the 4s band width (ξ) of copper as 0.5 $e^2/2a_o$, and the 3p state as located 5.1 $e^2/2a_o$ below the bottom of the 4s band. In the case of nickel the respective energies are 0.4 and 4.5 $e^2/2a_o$. From the low temperature specific heat of copper its ξ is estimated to be 4.78 eV or 0.35 $e^2/2a_o$, and its effective mass to be $m^* = 1.47$ m.[32] The difference in energy of the 3p state of copper and the bottom of the 4s band as given by equation (5.14) minus equation (5.15) is 6.5 $e^2/2a_o$. These last energies are one-electron values that neglect exchange and coulomb effects, so it is not surprising that the agreement with Slater's values is not better.

In calculations of scattering amplitudes of electrons in nickel, Fuchs'[23] wave function for the k = 0 electronic state of copper will be used for $U_{4s}(\vec{r}, \vec{k})$ for all $\vec{k}$, since no one state appears to mix appreciably with $U_{4s}(\vec{r}, 0)$. The 4s effective mass used will be that from low temperature specific heat of copper, $m^* = 1.47$ m. The value of ξ that will be

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[30] L. Schiff, *op. cit.*, p. 154.

[31] J. C. Slater, Phys. Rev. *98*, 1039 (1955).

[32] F. Seitz, *op. cit.*, p. 153.

used for nickel is obtained by multiplying the value for copper from low temperature specific heat by $(0.6)^{2/3}$ since nickel has but six-tenths the number of 4s electrons that copper has. This gives a value of $\zeta = 0.25$ $e^2/2a_o$ for nickel.

The quantities χ and $(KE)_F$ that appear in equation (4.10) can now be estimated. The value of χ that will be used is

$$\chi = \pi m/4m^* a_o k_F \;= \pi/(1.47)(0.6) = 0.89, \tag{5.19}$$

and that of $(KE)_F$ is

$$(KE)_o + \zeta = 2.75\ e^2/2a_o\ , \tag{5.20}$$

where $(KE)_o$ is given following equation (7.7).

VI. THE 3D BAND OF NICKEL

Fletcher[17] has calculated the wave function and energy values of the 3d band of nickel, using the strong binding method. A Bloch function can be formed from the following combination of atomic functions,

$$\psi = N^{-\frac{1}{2}} \Sigma(n) \ \ \exp(i\vec{k} \ \cdot \ \vec{R_n}) \ \varphi(\overrightarrow{r - R}_n). \tag{6.1}$$

If each atomic function has appreciable magnitude only in its own cell, then the Bloch function will be nearly like the atomic function within that cell. Fletcher formed Bloch functions from each of the five 3d atomic functions for nickel. The atomic functions were taken in the cubic form, that is:

$$\varphi_1 - (15/4\pi)^{\frac{1}{2}}\ (xy/r2)\ R_{3d}(r), \tag{6.2}$$

$$\varphi_2 = (15/4\pi)^{\frac{1}{2}}\ (yz/r^2)\ R_{3d}(r), \tag{6.3}$$

$$\varphi_3 = (15/4\pi)^{\frac{1}{2}}\ (zx/r^2)\ R_{3d}(r), \tag{6.4}$$

$$\varphi_4 = (15/16\pi)^{\frac{1}{2}}\ \left[(x^2 - y^2\ /r^2)\right]\ R_{3d}(r), \tag{6.5}$$

$$\varphi_5 = (5/16\pi)^{\frac{1}{2}}\ \left[(3z^2 - r^2\ /r^2)\right]\ R_{3d}(r), \tag{6.6}$$

where $R_{3d}(r)$ is normalized so that $\int R^2_{3d}(r)\ r^2\ dr = 1$. Linear combinations of Bloch functions formed from these atomic functions are made so as to minimize the energy as calculated in the strong binding approximation. If $\psi = \bar{b}_t \psi^t$ where

$$\psi^t = N^{-\frac{1}{2}} \Sigma(n)\ \exp(i\vec{k} \cdot \vec{R_n})\ \varphi^t(\overrightarrow{r - R}_n), \tag{6.7}$$

then minimizing the energy is equivalent to solving the equations.

$$(H_{tt'} - E(\vec{k})\ O_{tt'})\ \bar{b}_{t'} = 0, \qquad (6.8)$$

where repeated indices are to be summed. $H_{tt'}$ is defined as

$$H_{tt'} = \int \psi^{t*}\, H \psi^{t'}\ d\tau, \qquad (6.9)$$

and $O_{tt'}$ is defined as

$$O_{tt'} = \int \psi^{t*}\, \psi^{t'}\ d\tau. \qquad (6.10)$$

Fletcher neglected the off diagonal terms of $O_{tt'}$, and numerically estimated $H_{tt'}$ taking $R_n = 0$ and $\vec{R}_n$ of the nearest neighbors into account. He approximated the Cu^+ potential of Hartree and Hartree[25] by the analytic form

$$V(r) = -\left\{1 + 28\ \exp(-3r)\right\} / r, \qquad (6.11)$$

where $V(r)$ is in atomic units and r is in units of the first Bohr radius a_0. The radial part of φ_{3d} was determined by curve fitting, using two hydrogenic radial functions. The normalized radial part of the 3d functions was given by Fletcher as

$$R_{3d}(r) = 85.88r^2\ \exp(-5r) + 1.979r^2\ \exp(-2r). \qquad (6.12)$$

Fletcher evaluated the matrix elements by keeping nearest neighbor terms and calculating interaction integrals using the functions (6.11) and (6.12). The matrix elements obtained are:

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

$$H_{22} = -4A_1 \cos\eta \ \cos\zeta + 4A_2(\cos\zeta \ \cos\xi + \cos\xi \ \cos\eta\ );$$

$$H_{33} = -4A_1 \cos\zeta \ \cos\xi + 4A_2(\cos\xi \ \cos\eta - \cos\eta \ \cos\zeta\ );$$

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

$$H_{55} = -(4/3)(A_4 + 4A_5) \cos\xi \ \cos\eta + (4/3)(2A_4 - A_5)$$
$$\quad \times\ (\cos\eta \ \cos\zeta + \cos\zeta \ \cos\xi\ );$$

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

$$H_{31} = H_{13} = -4A_3 \sin\eta \ \sin\zeta\ ;\ H_{14} = H_{41} = 0\ ;$$

$$H_{24} = H_{42} = -4A_6 \sin\eta \ \sin\zeta\ ;\ H_{34} = H_{43} = 4A_6 \sin\zeta \ \sin\xi\ ;$$

$$H_{15} = H_{51} = -(8/3^{\frac{1}{2}})A_6 \sin\xi \sin\eta ;$$

$$H_{25} = H_{52} = (4/3^{\frac{1}{2}})A_6 \sin\eta \sin\zeta ;$$

$$H_{35} = H_{53} = (4/3^{\frac{1}{2}})A_6 \sin\zeta \sin\xi ;$$

$$H_{45} = H_{54} = (4/3^{\frac{1}{2}})(A_4 + A_5)(\cos\eta \cos\zeta - \cos\zeta \cos\xi); \qquad (6.13)$$

where $\xi = ak_x/2$, $\eta = ak_y/2$, and $\zeta = ak_z/2$. a is the cube edge of the face centered cubic lattice. The interaction constants are

$$A_1 = 0.1928E_0,\ A_2 = 0.0572E_0,\ A_3 = 0.0776E_0,$$

$$A_4 = 0.1348E_0,\ A_5 = 0.0247E_0,\ A_6 = 0.0862E_0, \qquad (6.14)$$

where $E_0 = 4(A_1 + A_2) = 1.349$ eV.

Along certain directions in k-space, the secular equation (6.8) can be solved explicitly as follows:

(100) direction. $E_{1,2} = 4A_2 + 4(A_2 - A_1)\cos\xi$.

$$E_3 = -4A_1 + 8A_2\cos\xi .$$

$$E_4 = 4A_4 - 8A_5\cos\xi .$$

$$E_5 = (4/3)\left\{-A_4 - 4A_5 + (4A_4 - 2A_5)\cos\xi\right\}. \qquad (6.15)$$

(110) direction. $E_1 = 4A_4\cos^2\xi - 8A_5\cos\xi$.

$$E_{2,3} = 4A_2\cos^2\xi + 4(A_2 - A_1)\cos\xi \pm 4A_3\sin^2\xi .$$

E_4 and E_5 are given by the two roots of

$$\begin{aligned} E^2 &+ \Big[\Big\{4A_1 + (16A_5/3) + (4A_4/3)\Big\} q^2 \\ &+ (8A_5/3 - 16A_4/3 - 8A_2)q\Big] E \\ &+ (16q^2/3)\Big[(4A_1A_5 + A_1A_4)q^2 \\ &- (8A_2A_5 + 2A_2A_4 + 4A_1A_4 - 2A_1A_5)q \\ &+ (8A_2A_4 - 4A_2A_5)\Big] - 64A_6^2p^4/3 = 0, \end{aligned} \qquad (6.16)$$

where $p = \sin\xi$; $q = \cos\xi$.

(111) direction. $E_1 = 4 \left\{(2A_3 + 2A_2 - A_1)\cos^2 \xi - 2A_3\right\}$.

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

$$\begin{aligned} &E^2 - 4 \left\{(2A_2 - A_1 + A_4 - 2A_5 - A_3)\cos^2 \xi + A_3\right\} E \\ &+ 16 \Big[\left\{(A_4 - 2A_5)(2A_2 - A_1 - A_3) - 2A_6^2\right\} \cos^4 \xi \\ &+ \left\{A_3(A_4 - 2A_5) + 4A_6^2\right\} \cos^2 \xi - 2A_6^2\Big] = 0. \end{aligned} \tag{6.17}$$

$\xi = \pi$; $\zeta = 0$ direction

$$\begin{aligned} &E_{1,2} = \pm 4A(A_1 + A_2)\cos \eta - 4A_2. \\ &E_3 = 4A_1. \\ &E_{4,5} = (4/3) \left\{2A_5 - A_4 \pm 2(A_4 + A_5)(1 + 3\cos^2 \eta)^{\frac{1}{2}}\right\}. \end{aligned} \tag{6.18}$$

Electronic wave functions can be written so that the $\vec{k}$ falls within the first Brillouin zone. This zone, for a face-centered crystal, is shown in Figure 1. Following is a description of the zone.

If the lattice vectors are

$$\begin{aligned} \vec{a}_1 &= (a/2, a/2, 0), \\ \vec{a}_2 &= (a/2, 0, a/2), \\ \vec{a}_3 &= (0, a/2, a/2), \end{aligned} \tag{6.19}$$

then the reciprocal vectors are

$$\begin{aligned} \vec{b}_1 &= 1/a(1, 1, -1), \\ \vec{b}_2 &= 1/a(1, -1, 1), \\ \vec{b}_3 &= 1/a(-1, 1, 1). \end{aligned} \tag{6.20}$$

These satisfy the relation $\vec{a}_i \cdot \vec{b}_j = \delta_{ij}$. The k-space lattice is given by $\vec{K}_n = 2\pi(n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3)$, for integer n's. The nearest neighbors to the origin in k-space are for the six values of the type $n_1 = \pm 1$, $n_2 = \pm 0$, $n_3 = 0$, etc., and for the two of the type $n_1 = \pm 1$, $n_2 = \pm 1$, $n_3 = \pm 1$. For $n_1 = n_2 = n_3 = 1$, $\vec{K} = (2\pi/a)(1, 1, 1)$. A plane bisecting this vector is erected. This forms the hexagonal face of the Brillouin zone, the center of which is called L; the center of the zone is called Γ. The distance ΓL is $3^{\frac{1}{2}}\pi/a$. The next nearest neighbors are given by the six values of the type $n_1 = \pm 1$, $n_2 = \pm 1$, $n_3 = 0$. For $n_1 = 1$, $n_2 = 1$, $n_3 = 0$, $\vec{K} = 2\pi/a(2, 0, 0)$. A plane bisecting this vector is also erected. This forms the square face,

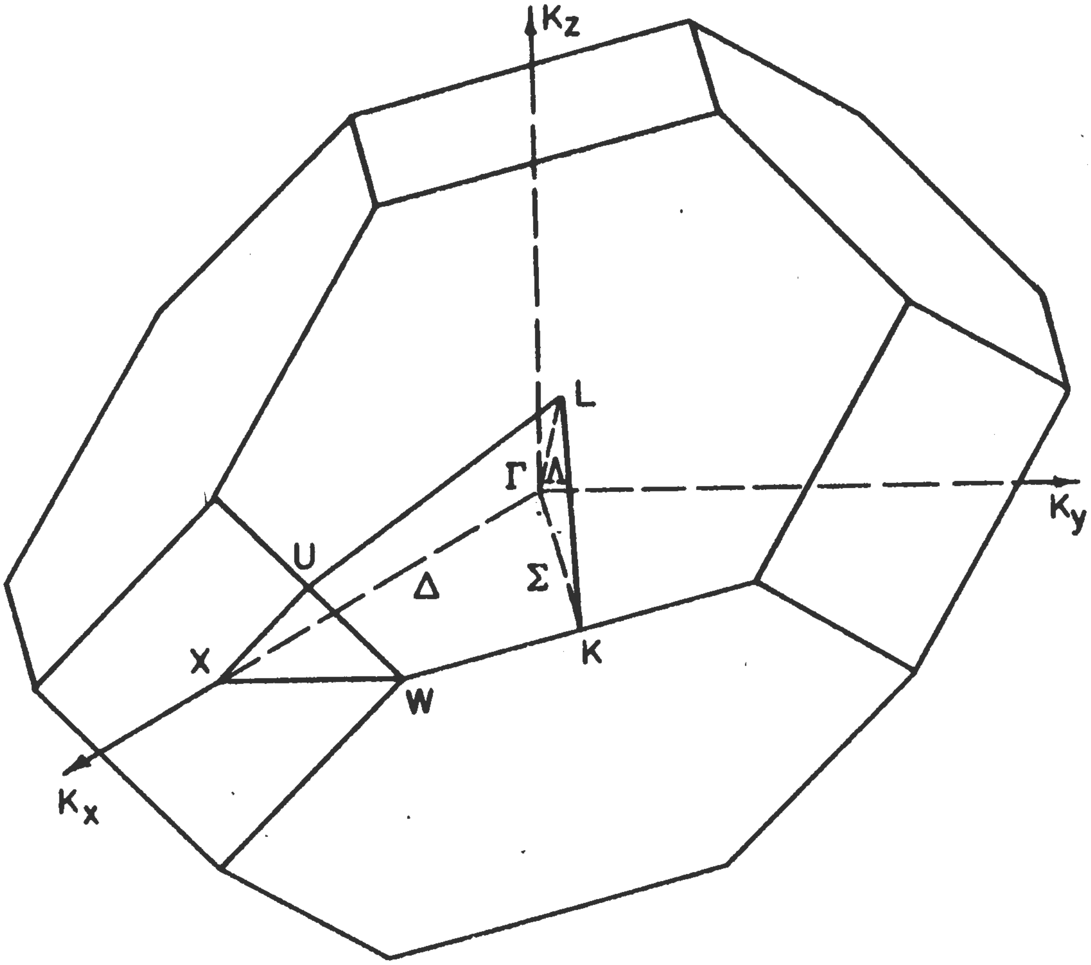

Figure 1. The Brillouin zone for a face-centered crystal. Points and lines of symmetry are labeled using the notation of BSW.[22]

the center of which is called X. The distance ΓX is $2\pi/a$. One sees that every vector in this zone is at least as near to the origin as it is to any other k-space lattice point. For copper $a = 3.608 \times 10^{-8}$ cm $= 6.84\ a_o$, so the distance $\Gamma L = 3^{1/2}\ \pi/a = 0.80/a_o$ and the distance $\Gamma X = 2\pi/a = 0.92/a_o$. If one were to approximate the first Brillouin zone by a sphere of equal volume, $(2\pi)^3$ times the reciprocal of the volume of the atomic polyhedron, the radius would be $0.90/a_o$. k-space distances are three percent larger for nickel.

When $E_{3d}(\vec{k})$ is known, equation (6.8) can be solved for $\bar{b}_t(\vec{k})$. This can be done for the special directions for which the energy values have been given. Information concerning $\bar{b}_t(\vec{k})$ for some other k's can be determined from considerations of symmetry.

Let $0(\vec{r})$ be some operation (rotation, reflection, etc.) on the points of configuration space that leave a particular point (the origin) unaltered. The corresponding operation on a function $F(\vec{r})$ is defined by

$$0\ F(\vec{r}) = F(0^{-1}\vec{r}). \qquad (6.21)$$

The set of operators 0 that leaves the potential function invariant forms a group known as the point group (referred to the point chosen as origin). Since the Laplacian is invariant to all rotations and reflections, every operator of the point group commutes with the Hamiltonian operator

$$H = -\ (\hbar^2/2m)\ \nabla^2 + V(\vec{r}). \qquad (6.22)$$

So if ψ is an eigenfunction of the Hamiltonian with energy E, 0ψ is also an eigenfunction with the same energy:

$$H\ 0\ \psi = 0\ H\ \psi = 0\ E\ \psi = E\ 0\ \psi. \qquad (6.23)$$

An operator 0 applied to a Bloch function gives

$$0\ \psi(\vec{r}, \vec{k}) = \exp(i\vec{k} \cdot 0^{-1}\ \vec{r})\ U(0^{-1}\ \vec{r}, \vec{k}). \qquad (6.24)$$

Let $0(\vec{k})$ define the same operation in k-space as the operator $0(\vec{r})$ does in configuration space. Then

$$0\ \vec{k} \cdot 0\ \vec{r} = \vec{k} \cdot \vec{r}, \qquad (6.25)$$

from which it follows that

$$0\ \psi\ (\vec{r}, \vec{k}) = \exp(i0\vec{k} \cdot \vec{r})\ U(0^{-1}\ \vec{r}, \vec{k}). \qquad (6.26)$$

Since $U(0^{-1}\ \vec{r}, \vec{k})$ is periodic in the crystal, $0\ \psi\ (\vec{r}, \vec{k})$ is a Bloch function solution with propagation vector $0\vec{k}$.

The point group referred to an atomic position in a simple face centered cubic lattice such as nickel is the full cubic group m 3 m.

That sub-group of the point group that takes $\vec{k}$ into itself or into an equivalent $\vec{k}$, that is, a $\vec{k}'$ differing from $\vec{k}$ by 2π times a reciprocal lattice vector, is called the small group of $\vec{k}$. For example, suppose $\vec{k}$ is a general point in the k_x, k_y plane. The identity operation and $z \rightarrow -z$ form the small group. Since the square of $z \rightarrow -z$ is the identity operation, $\psi(\vec{r}, \vec{k})$ can be found that are even or odd to this operation. When an operation is performed on a function in the Bloch form as given by equation (6.1), all of the $\vec{R}_n$'s can be mapped on to other $\vec{R}_n$'s, so that the transform of equation (6.1) is the same type of sum of transformed φ functions. For the odd solution, only φ_2, and φ_3, can enter, while for the even solution, φ_1, φ_4, and φ_5, can enter. Thus, wave functions whose $\vec{k}$'s lie on planes $XL\Gamma$, $LK\Gamma$, $KX\Gamma$, and XUW as shown in Figure 1, must be either even or odd to the operations $z \leftrightarrow y$, $x \leftrightarrow y$, $z \rightarrow -z$, and $x \rightarrow -x$, respectively.

Any $\vec{k}$-vector in the Brillouin zone can be generated by operating with some member of the point group on some vector in that portion of the zone included between these three planes. Thus if $\bar{b}_t(\vec{k})$ is known in this region, solutions for the whole zone are known. A plane similar to $KL\Gamma$ can be obtained as a continuation of $XL\Gamma$, a point similar to K being the intersection of the line UL and the center of a hexagonal edge. Some energy contours for this plane and the $KX\Gamma$ and XUW planes are shown in Figure 2, for the highest energy even and odd solutions. Fletcher's[17] energy values were plotted in his units on lines of high symmetry and contours drawn between them to obtain these figures.

According to Fletcher's work, the Fermi energy for ferromagnetic nickel is about 0.2 eV below the top of the 3d band, or about $0.62E_o$, and for paramagnetic nickel, is about 0.18 eV below the top of the 3d band, or about $0.67E_o$. As states with energy near that of the Fermi energy are those of interest, the energy contours plotted in Figure 2 are those for $0.6E_o$, and $0.7E_o$. A symbol such as X_5 0.771, signifies that for a $\vec{k}$ at point X, there is a wave function with symmetry classification X_5 and energy $0.771E_o$. Since wave functions of propagation vector $\vec{k}$ form a basis for an irreducible representation of the small group of $\vec{k}$, knowledge of the small group enables one to classify the symmetry of wave functions. The notation is that of BSW.[22] Figure 3 shows that portion of the Brillouin zone bounded by the planes $XL\Gamma$, $LK\Gamma$, $KX\Gamma$, and XUW. Energy contours for $E = 0.6E_o$ have been plotted to show how the constant energy lines on Figure 2 fit together in three dimensions. The signs on symmetry planes show whether the wave function is even or odd to mirroring in that plane.

Results on normal 4s to 3d scattering will involve wave functions referred to a coordinate system where polar angles are measured from $\vec{k}_{3d}$. The numbers on the axes of rotation in Figure 3 denote the absolute value of the m values of spherical harmonics appearing in the wave function in this coordinate system. For instance, on the two-fold axis Σ, the wave function Σ_2 has symmetry like $z(x - y)$. In a new coordinate system where the z' axis is in the (1 1 0) direction, the y' axis is in the (0 0 1)

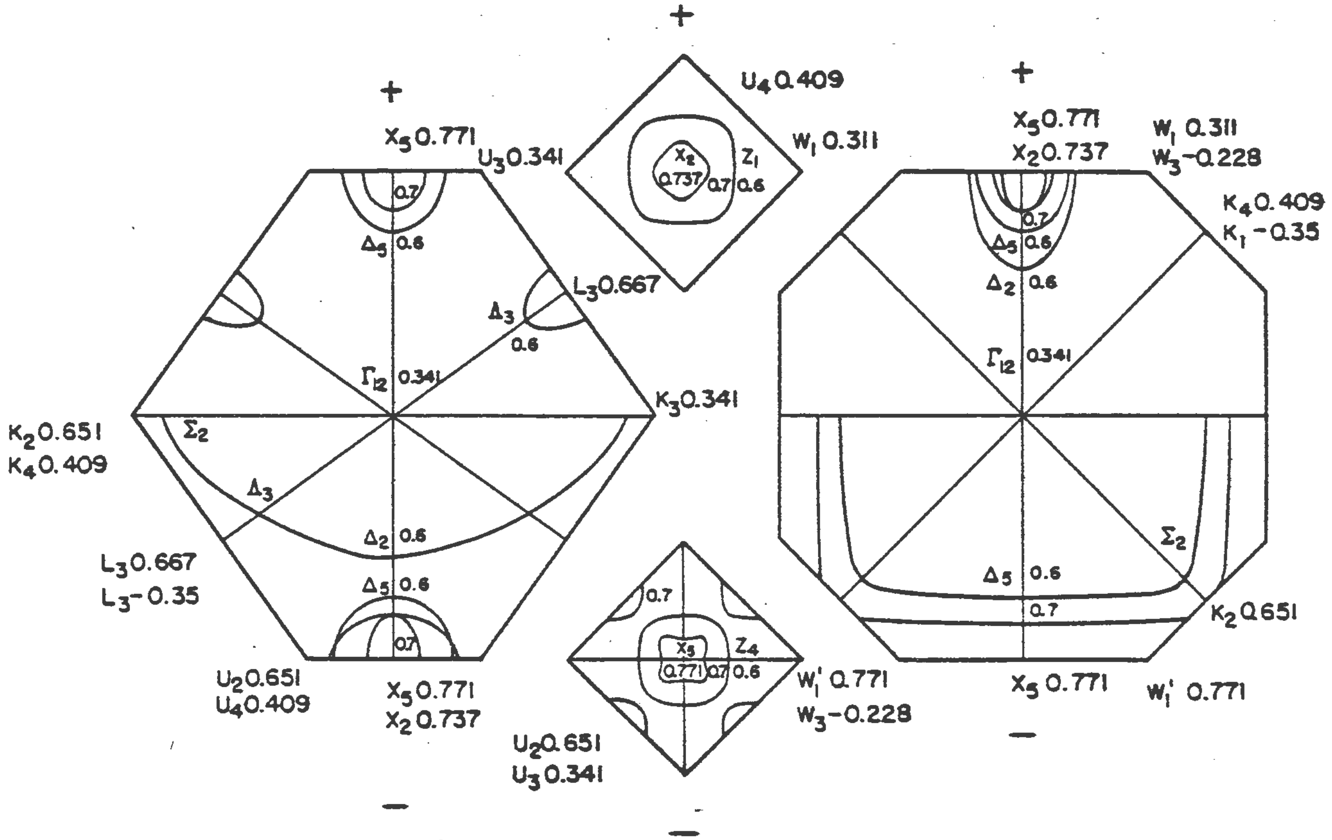

Figure 2. 3d constant energy contours for high symmetry planes of k-space of metallic face-centered nickel. Energy is given in units of $E_0 = 1.349$ eV, measured from an arbitrary zero. Wave functions for k's in the upper planes are even to mirroring, while those in the lower planes are odd. Wave function symmetry is given in the notation of BSW.[22]

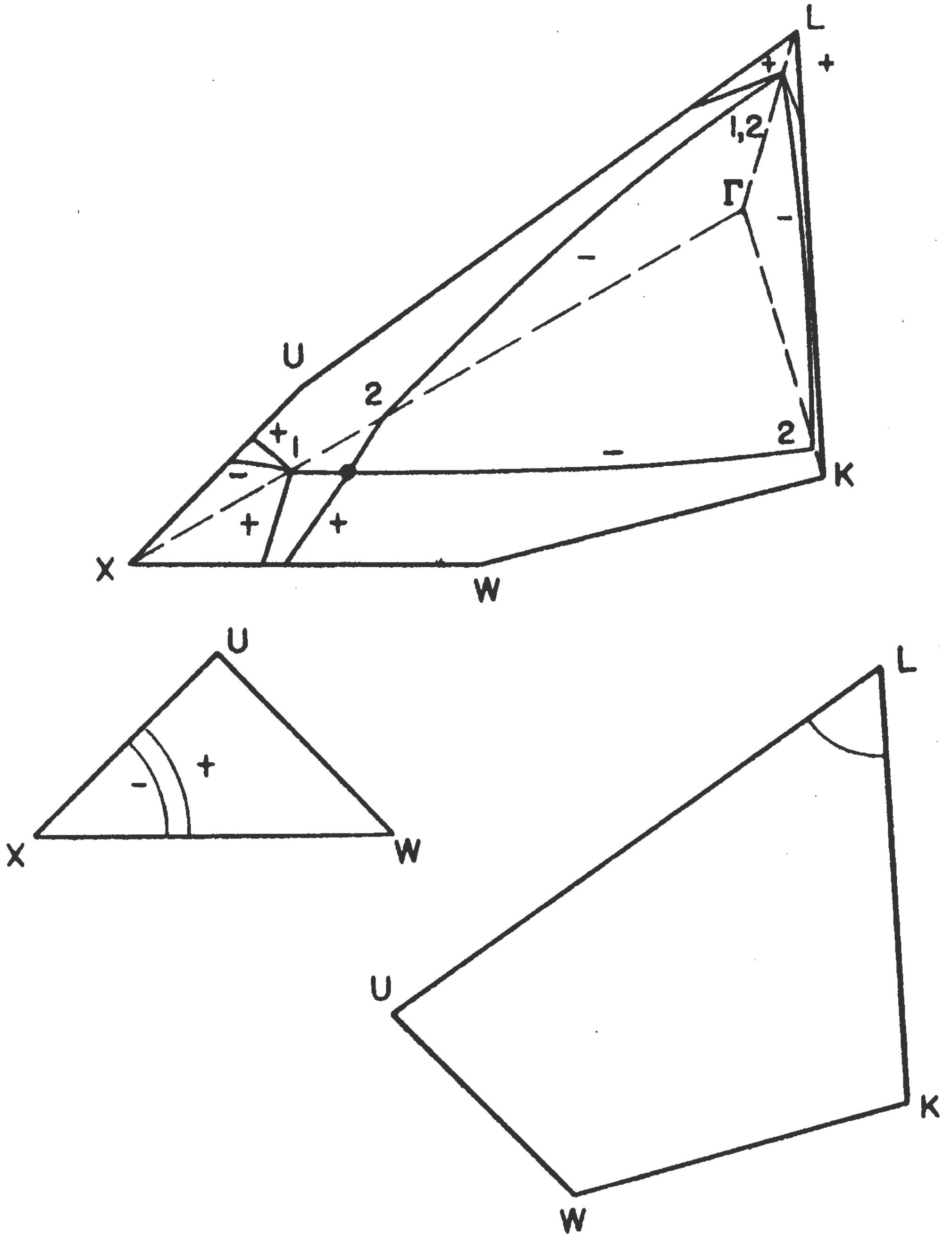

Figure 3. A portion of the 3d Brillouin zone of face-centered metallic nickel showing a $0.6E_0$ energy contour. Signs in high symmetry planes denote symmetry under mirroring. A dot signifies an accidental degeneracy. Numbers on axes of rotation denote the absolute magnitude of m values of spherical harmonics appearing in the wave function for $\vec{k}$ lying on the axis, that axis being the polar axis.

direction, and the x' axis is in the $(\bar{1}\ 1\ 0)$ direction, this wave function has symmetry like x' y'. In equations (6.2) through (6.6) for the 3d functions in polynomial form, φ_5 consists of m = 0 terms, φ_2 and φ_3 m = $\pm$ 1 terms, and φ_1 and φ_4 m = $\pm$ 2 terms. Since Σ_2 is in the form φ_1, 2 is shown on the two-fold axis.

Since m = 0 terms are even to all mirror planes including the polar axis, wave functions with even-odd mirror symmetry can never have m = 0 parts. Wave functions with even symmetry can have all five types. The m = 0 solutions have low energy in all special directions, so one would not expect them to enter appreciably in solutions for energies near the Fermi energy.

Fletcher has neglected off-diagonal terms in the over-lap integral given by equation (6.10). Since these will probably be of comparable size with respect to the off-diagonal terms of the Hamiltonian given by equation (6.9), this neglect is serious. The work of Slater and Koster[18] circumvents this difficulty by considering the atomic functions to be made orthonormal to each other by taking suitable linear combinations. Energy values and wave functions are determined at points of high symmetry by some accurate method such as the cellular method or the orthogonalized plane-wave method. The strong binding method is then used as an interpolation procedure, the constants $A_1 \ldots A_6$ being determined so as to fit the accurate calculation at points of high symmetry. Slater and Koster have used the results of Howarth's[33] cellular calculation on the 3d band of metallic copper to compare the constants that would fit Howarth's energy values at points of high symmetry. They find fairly good agreement with Fletcher's results except for one constant.

Howarth[34] has also calculated the d band of copper using Slater's [35] method of augmented plane waves. His results are completely different from those of Howarth,[33] so it seems that calculations on strongly bound electrons are very sensitive to slight changes in potential. This would make one rather unconfident of the constants as calculated by either Fletcher or Slater and Koster. On the other hand, the atomic functions used by

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[33] D. J. Howarth, Proc. Roy. Soc. (London) A220, 513 (1953).

[34] D. J. Howarth, Great Malvern, Worchester, England. (Private commuication). 1955.

[35] J. C. Slater, Phys. Rev. 92, 603 (1953).

Fletcher should be fairly reliable as only small amounts of nearby neighbors need be added to make the atomic functions ortho-normal with the nearby neighbors. Fletcher's interaction constants will be used in this work.

VII. 4S TO 4S SCATTERING

A. Normal Processes

The scattering amplitude as given by equation (4.30) will now be evaluated for scattering from one 4s state to another. As discussed in Section V, the wave function calculated by Fuchs[23] for the k = 0 state of the 4s band of metallic copper will be used for $U_{4s}(\vec{r},\vec{k})$ for nickel. First normal porcesses will be considered, that is scattering for which $K_n = 0$. The first term B_1 in equation (4.30) contributes to the scattering amplitude the following term:

$$N^{-\frac{1}{2}}\ a_{qj}\ C(q)\ i\vec{q}\cdot\ \hat{\varepsilon}_{qj} \tag{7.1}$$

since $\int U_f^* \ U_i\ d\tau_o = 1$. The second term B_2 in equation (4.30) does not contribute to scattering because the integral is zero. The reason is that the integrand is the product of an even function and an odd function, and the region of integration is even to inversion.

Since $U_{4s}(r)$ is assumed to be spherically symmetric, B_3 in equation (4.30) is

$$\begin{aligned} &-N^{-\frac{1}{2}}\ a_{qj}\ (\hbar^2/m)\ i\vec{q}\cdot\ \int \text{grad}\ U_i\ (\partial\ U_f^*/\partial\ s)\ d\tau_o \\ &= -N^{-\frac{1}{2}}\ a_{qj}\ (\hbar^2/m)\ i\vec{q}\cdot\ \hat{\varepsilon}_{qj}\int|\partial U_{4s}/\partial\ s|^2\ d\tau_o. \end{aligned} \tag{7.2}$$

The equality follows, as only the part of $\vec{q}$ in the direction of s can contribute. The integral can be related to the kinetic energy at k = 0, $(KE)_o$, by noticing that for spherically symmetric wave functions:

$$\begin{aligned} (KE)_o &= -(\hbar^2/2m)\int\psi^*\ \nabla^2\psi\ d\tau \\ &= (3\hbar^2/2m)\int|\partial\psi/\partial x|^2\ d\tau. \end{aligned} \tag{7.3}$$

The last equation comes from the use of the divergence theorem, and the fact that $\psi^*\psi$ is periodic. Thus the third term in the scattering amplitude, B_3, becomes:

$$B_3 = -\ N^{-\frac{1}{2}}\ a_{qj}\ (2/3)\ i\vec{q}\cdot\ \hat{\varepsilon}_{qj}\ (KE)_o. \tag{7.4}$$

Combining B_1 and B_3, one can write the scattering amplitude for regular 4s to 4s scattering as

$$N^{-\frac{1}{2}} a_{qj} (2/3)\, i\vec{q} \cdot \hat{\varepsilon}_{qj} \left\{(3.5) + (2/5)(1 + \chi q^2)^{-1}\right\} \zeta, \qquad (7.5)$$

since $\zeta = (KE)_F - (KE)_o$. Bethe,[4] by neglecting the effect that the total electronic energy must be independent of strain to first order, and the effect of charge redistribution, has only the term B_3, given by equation (7.4). Equation (7.5) is similar to the result of Bardeen,[6] except that it does not fall off as fast for increasing q.

The kinetic energy is given by the following expression:

$$(KE) = -(\hbar^2/2m)\int \psi^* \nabla^2 \psi \, d\tau = (\hbar^2/2m)\int |\nabla\psi|^2 \, d\tau, \qquad (7.6)$$

which can be obtained by use of the divergence theorem. The wave function at the bottom of the band is given by $\psi = Y_0 R_{4s}$ so $\nabla\psi = (\vec{r}/r)\, Y_0 (dR_{4s}/dr)$. For this case the kinetic energy is given by

$$(KE)_o = \int_0^{r_s} (\hbar^2/2m)(dR_{4s}/dr)^2 \, r^2 \, dr. \qquad (7.7)$$

This was evaluated by numerical integration for the wave function given by Fuchs, with a result of $(KE)_o = 2.80\ e^2/2a_o$. The atomic polyhedron has been approximated by a sphere as was done in Section V. This will be done in the evaluation of all integrals in this work. Steps of 0.1 a_o were too coarse for the interval nearest the origin, so a 4s wave function was calculated by the Wigner-Seitz[26] method using the Hartree and Hartree[25] potential for Cu^+, and normalized so as to join the function of Fuchs at the first maximum. The contribution to equation (7.7) of the interval from 0.0 to 0.1 a_o was integrated in finer steps. The value of $(KE)_o$ was reduced from 2.8 to 2.16 $e^2/2a_o$ by this recomputation. As an additional check, the 4s wave function was computed for the entire span by the Wigner-Seitz method. The value of $(KE)_o$ found by numerical integration for this function was 2.96 $e^2/2a_o$. The discrepancy between this value and that from Fuchs' function is due to the fact that Fuchs took exchange into account and this was not done in the computation of the wave function in this work. In the following work, a value of 2.5 $e^2/2a_o$ (34 eV) has been used for $(KE)_o$.

B. Umklapp Processes

For Umklapp processes $\vec{K}$ is a small non-vanishing $\vec{K}$ vector. The smallest is that in the (111) direction, and the next smallest is in the (100) direction. The scattering amplitude for Umklapp processes will be evaluated by substituting in equation (4.30) for the scattering amplitude. The integral appearing in B_2 can be converted into a function involving the integral appearing in B_1 as follows:

$$\begin{aligned}\int U_{4s}(\partial \bar{U}_{4s}/\partial s)d\tau_o &= -\hat{\varepsilon}_{qj} \cdot \int \exp(i\vec{K}\cdot\vec{r})\, U_{4s}\nabla U_{4s}\; d\tau_o \\ &= -\hat{\varepsilon}_{qj} \cdot \int \exp(i\vec{K}\cdot\vec{r})\nabla(U_{4s}{}^2)d\tau_o/2 \\ &= \hat{\varepsilon}_{qj} \cdot \int U_{4s}{}^2\; \nabla \exp(i\vec{K}\cdot\vec{r})\; d\tau_o/2 \\ &= i\; \hat{\varepsilon}_{qj} \cdot \vec{K} \int \bar{U}_{4s}\, U_{4s}\; d\tau_o/2, \end{aligned} \qquad (7.8)$$

where integration by parts has been done twice. Neglecting $E_i - E_f$, the energy of the phonon, one can combine parts B_1 and B_2 of the scattering amplitude as follows:

$$\begin{aligned} &B_1 + B_2 = \\ &N^{-\frac{1}{2}}\, a_{qj}\; i \left\{C(q)\; \vec{q}\cdot \hat{\varepsilon}_{qj} + \hat{\varepsilon}_{qj} \cdot \vec{K}\; (\hbar^2/2m)(\vec{k}_f{}^2 - k_i{}^2)/2 \right. \\ &\left. \int \bar{U}_{4s}\, U_{4s}\; d\tau_o \right\}. \end{aligned} \qquad (7.9)$$

Since $\vec{k}_f = \overrightarrow{k_f + K} = \overrightarrow{k_i + q}$, the expression in the brackets may be written as

$$C(q)\; \hat{\varepsilon}_{qj} \cdot \vec{q} + (\hbar^2/2m)(q^2 + 2\vec{k}_i \cdot \vec{q})(\hat{\varepsilon}_{qj} \cdot \vec{K}/2). \qquad (7.10)$$

The largest value of $C(q)$ is $(2/3)(KE)_F = 1.83\; e^2/2a_o$. Referring to Figure 6, it is seen that for Umklapp processes $\vec{k}_i$, $-\vec{k}_f$, and $\vec{q}$, are all in the general direction of $\vec{K}$. The largest value of q is about $K/2$, so the largest value of $(q^2 \pm 2\vec{k}_i \cdot \vec{q})$ is less than $3(K/2)^2$, since k_i cannot be as large as $K/2$. For $\vec{K}$ in the $(1\,1\,1)$ direction, $K = 2\pi 3^{\frac{1}{2}}/a = 1.6/a_o$, and for $\hat{\varepsilon}_{qj}$ in the direction of $\vec{q}$ and $\vec{K}$, term (7.10) is less than $(0.8/a_o)(1.83 + 1.92)\; e^2/2a_o = 3.00\; e^2/2a_o{}^2$.

Equation (D.5)* gives the value of the integral in equation (7.9) as -0.018 so the maximum absolute value of $B_1 + B_2$ for Umklapp $4s - 4s$ scattering is

$$\begin{aligned} B_1 + B_2 &= N^{-\frac{1}{2}}\, a_{qj}\; i(3.00)(0.018)\;\; e^2/2a_o{}^2 \\ &= N^{-\frac{1}{2}}\, a_{qj}\; i(0.054)\;\; e^2/2a_o{}^2. \end{aligned} \qquad (7.12)$$

Thus $B_1 + B_2$ can be neglected compared to B_3 as given by equation (D.14)* and the Umklapp $4s - 4s$ scattering amplitude is given by

$$-N^{-\frac{1}{2}}\, a_{qj}\; (2/3)\; i\vec{q} \cdot \hat{\varepsilon}_{qj}\; (0.8)\;\; (KE)_o. \qquad (7.13)$$

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*Equations (D.5) and (D.14), as well as other equations whose numbers are preceded by letters A-F, are included in the Appendices of the Ph.D. thesis by John B. Gibson. See Appendices, this report, page 47.

B_1 is large in normal 4s - 4s scattering, but is small for Umklapp 4s - 4s scattering. The reason is that B_1 is porportional to $\int U^*_{4s} U_{4s} d\tau_0$, which equals 1 for normal scattering but equals -0.018 for Umklapp scattering. B_1 and B_3 tend to cancel for normal scattering, but for Umklapp scattering B_1 is too small to, and of the wrong sign for this cancellation; thus Umklapp scattering is much greater than normal scattering.

Notice that the value of Umklapp scattering amplitude does not join continuously to the regular scattering amplitude when $\overrightarrow{k_f - k_i}$ lies on the Brillouin zone boundary, that is when normal processes end and Umklapp processes begin. In order to show this condition more clearly, a $(1\,\bar{1}\,0)$ plane intersecting the first Brillouin zone, passing through the k_z axis and the (111) direction is shown in Figure 4.

Since $\overrightarrow{k_i + q - k_f} = \overrightarrow{K_n}$, and $\vec{k_i}$, $\vec{k_f}$ and $\vec{q}$ must all be in the first zone, Umklapp cannot take place while $\overrightarrow{k_i - k_f}$ lies in the first zone. In Figure 4 the case is shown for $\overrightarrow{k_i - k_f}$ lying on the zone boundary. For this case $\vec{q}$ also lies on the zone boundary. As $\overrightarrow{k_i - k_f}$ crosses the zone boundary and Umklapp processes begin, the scattering will be continuous. The fact that the present calculations show a discontinuity in scattering amplitude is an indication of the inadequacy of the calculations as carried up to this point.

The difficulty can be understood by noting that as $\overrightarrow{k_i - k_f}$ is in the first zone and approaches the zone boundary, $\vec{q_1}$ causes scattering, while, after $\overrightarrow{k_i - k_f}$ crosses the zone boundary, $\vec{q_2}$ causes scattering. Since $\vec{q_2} = \overrightarrow{q_1 + K_n}$, the displacements of the ionic cores are the same for both waves. This is not true for the displacement of a general point as given by equation (4.17):

$$\vec{S}(\vec{r}) = N^{-\frac{1}{2}} \sum(qj)\ \hat{\varepsilon}_{qj} \left\{ a_{qj} \exp(i\vec{q}\cdot\vec{r}) + a^{*}_{qj} \exp(-i\vec{q}\cdot\vec{r}) \right\}, \qquad (4.17)$$

with $\vec{q}$ restricted to the first Brillouin zone. In fact the equation can be generalized to the form

$$\vec{S}(\vec{r}) = N^{-\frac{1}{2}} \sum(qjn)\ \hat{\varepsilon}_{qj}\ X_n \left[a_{qj} \exp(i\overrightarrow{q + K_n}\cdot\vec{r}) + a^{*}_{qj} \exp\left\{-i(\overrightarrow{q + K_n})\cdot\vec{r}\right\} \right] \qquad (7.14)$$

without in any way violating the condition that at the position of the ion cores, $\vec{S}(\vec{R_n})$ is given by equation (4.2), provided only that for the coefficients X_n,

$$\sum(n)\ X_n = 1. \qquad (7.15)$$

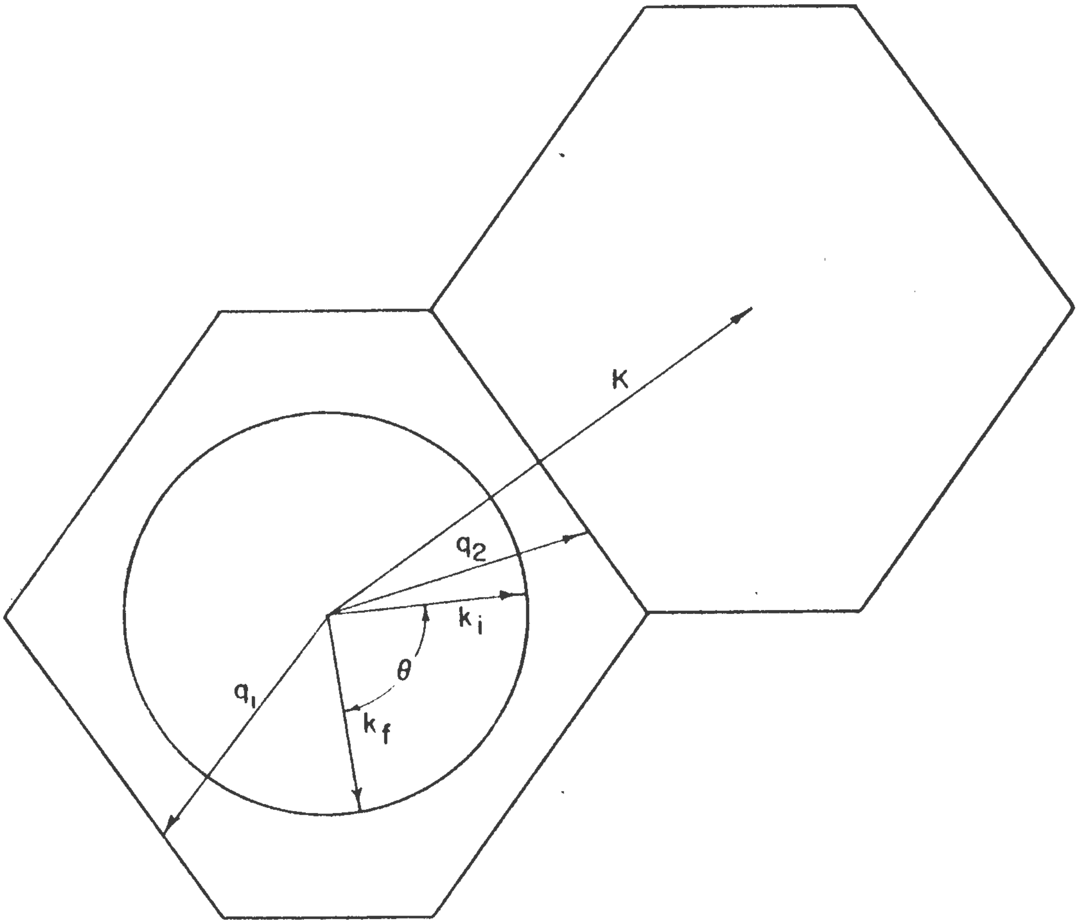

Figure 4. A plane intersecting the Brillouin zone in the (0 0 1) and (1 1 1) directions. This is the limiting case, in which scattering changes from normal to Umklapp. $\overline{q_1}$ will scatter as a normal process, while $\overline{q_2}$ will scatter as an Umklapp process. The scattering angle is θ.

Further, if the X_n are functions only of $|\vec{q} + \vec{K}_n|$, whether $\vec{q}$ is or is not in the first Brillouin zone can make no difference. Smoothness and convergence (according to equation (7.15)) are the only criteria at once available to restrict the dependence of X_n on $\vec{q} + \vec{K}_n$. In the present work the form

$$X_n \propto |\vec{q} + \vec{K}_n|^{-4} \tag{7.16}$$

is assumed.

For small $\vec{q}$, $X_0 \approx 1$, and all others are small. On the other hand, when $\vec{q}$ approaches a zone boundary and $q \approx |\vec{q} + \vec{K}_n|$, for some n, then $X_0 \approx X_n \approx 1/2$, and all others are small. Since the scattering amplitude is linear in the waves, scattering amplitudes as previously calculated may be added. Figure 5 shows the same section of the Brillouin zone as Figure 4, for the case when $\vec{k}_i - \vec{k}_f$ is in the first Brillouin zone, and Figure 6 shows the case when $\vec{k}_i - \vec{k}_f$ is outside the Brillouin zone.

As shown in Figure 5, for the case when $\vec{k}_i - \vec{k}_f$ is inside the Brillouin zone, the wave with propagation vector $\vec{q}$ scatters as a normal process proportional to $(\vec{k}_f - \vec{k}_i) \cdot \hat{\varepsilon}_{qj}$ while the wave with propagation vector $\vec{q} + \vec{K}$ scatters as an Umklapp process. The Umklapp amplitude is proportional to $(\vec{\bar{k}}_f - \vec{k}_i) \cdot \hat{\varepsilon}_{qj} = (\vec{k}_f - \vec{k}_i + \vec{K}) \cdot \hat{\varepsilon}_{qj}$. The wave with propagation $\vec{q} + \vec{K}$ must be included in the calculations along with the wave with propagation vector $\vec{q}$, as $|\vec{q} + \vec{K}|$ is fairly close in magnitude to q. Other $\vec{K}_n$'s are of very slight importance, since the corresponding vectors $\vec{q} + \vec{K}_n$ are much larger than $\vec{q}$.

In Figure 6 the case when $\vec{k}_i - \vec{k}_f$ is outside the Brillouin zone is illustrated. The wave with propagation vector $\vec{q}$ (in the first Brillouin zone) scatters as an Umklapp process proportional to $(\vec{\bar{k}}_f - \vec{k}_i) \cdot \hat{\varepsilon}_{qj} = (\vec{k}_f - \vec{k}_i + \vec{K}) \cdot \hat{\varepsilon}_{qj}$, since $\vec{\bar{k}}_f = \vec{k}_f + \vec{K}$. The wave $\vec{q} + \vec{K}_n$, where $\vec{K}_n = -\vec{K}$, scatters as a normal process proportional to $(\vec{\bar{k}}_f + \vec{K}_n - \vec{k}_f) \cdot \hat{\varepsilon}_{qj} = (\vec{k}_f - \vec{k}_i) \cdot \hat{\varepsilon}_{qj}$. Thus it is seen that the scattering amplitude is continuous when $\vec{k}_i - \vec{k}_f$ crosses the boundary of the Brillouin zone.

The scattering amplitude can be written as

$$\int \psi_f^* V_p \psi_i \, d\tau$$

$$= N^{-\frac{1}{2}} a_{qj} \, (2/3) \, i \, (\vec{k}_f - \vec{k}_i) \cdot \hat{\varepsilon}_{qj} \quad G(u), \tag{7.17}$$

where $u = \sin \theta/2 = |\vec{k}_f - \vec{k}_i|/2 k_f$. $G^2(u)$ is plotted in Figure 7 as a function of the scattering angle θ. $\vec{k}_i - \vec{k}_f$ has been assumed to be in the $\vec{K}$ direction. K has been taken as $1.8/a_o$, double the radius of the sphere whose volume equals that of the first Brillouin zone. The two waves with largest X_n have been added with relative weight factors of $(\vec{q} + \vec{K}_n)^{-4}$.

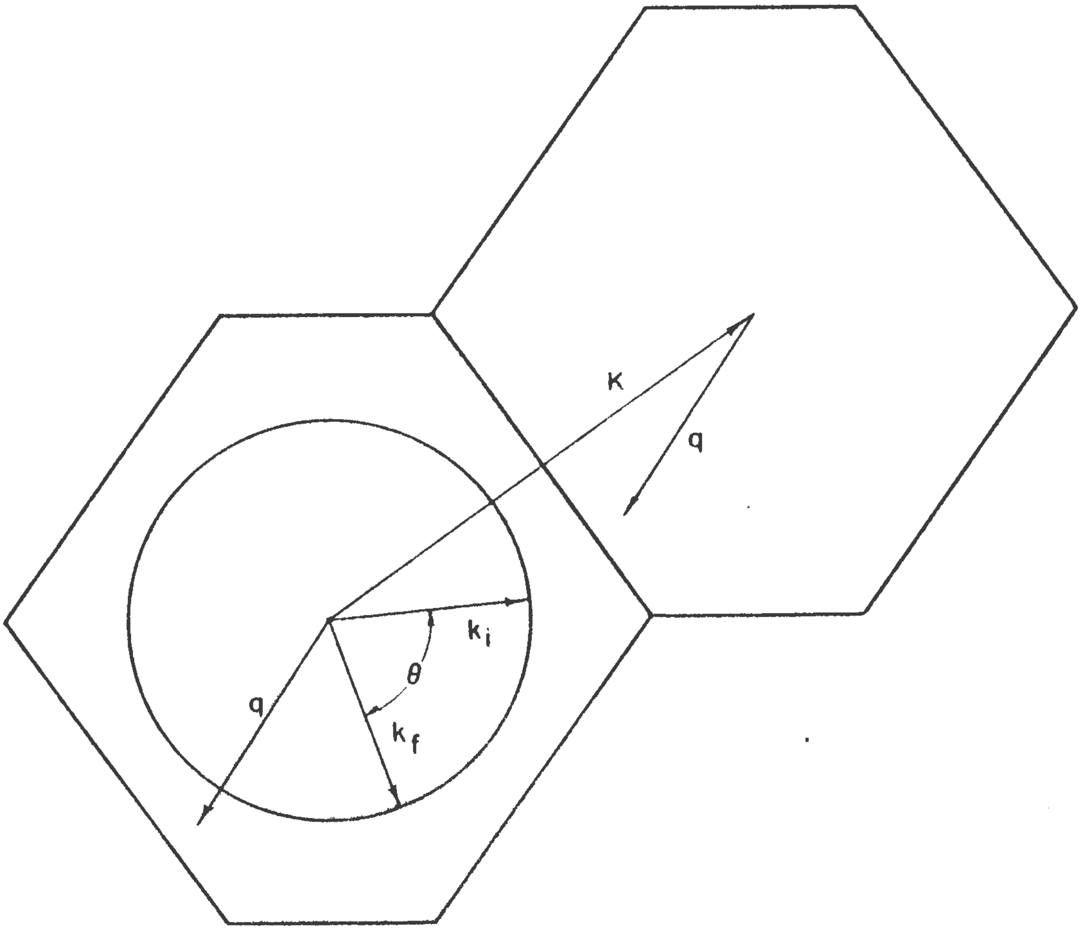

Figure 5. A plane intersecting the Brillouin zone in the (0 0 1) and (1 1 1) directions. $\overrightarrow{k_i - k_f}$ lies in the zone. $\overrightarrow{q}$ scatters as a normal process, and $\overrightarrow{q + K}$ scatters as an Umklapp process. The scattering angle is θ.

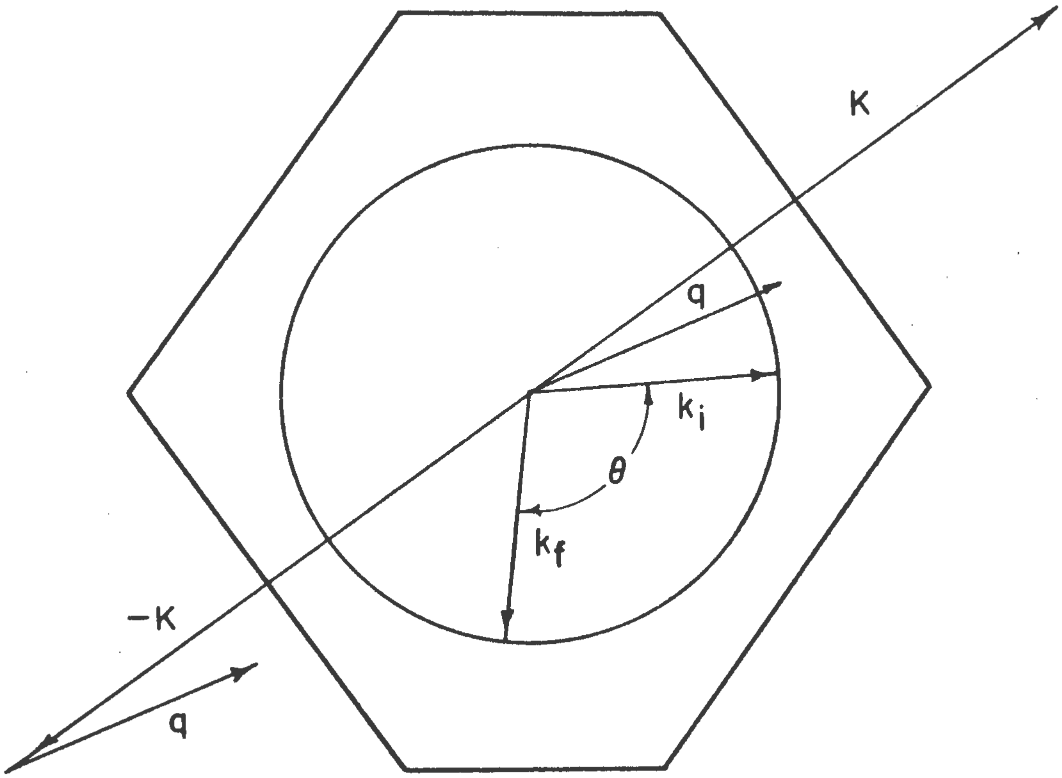

Figure 6. A plane intersecting the Brillouin zone in the (0 0 1) and (1 1 1) directions. $\overrightarrow{k_i - k_f}$ lies outside the zone. $\vec{q}$ scatters as an Umklapp process and $\overrightarrow{q - K}$ scatters as a normal process. The scattering angle is Θ. The relation between the vectors is of the form $\overrightarrow{k_f - k_i} = \overrightarrow{q - K}$.

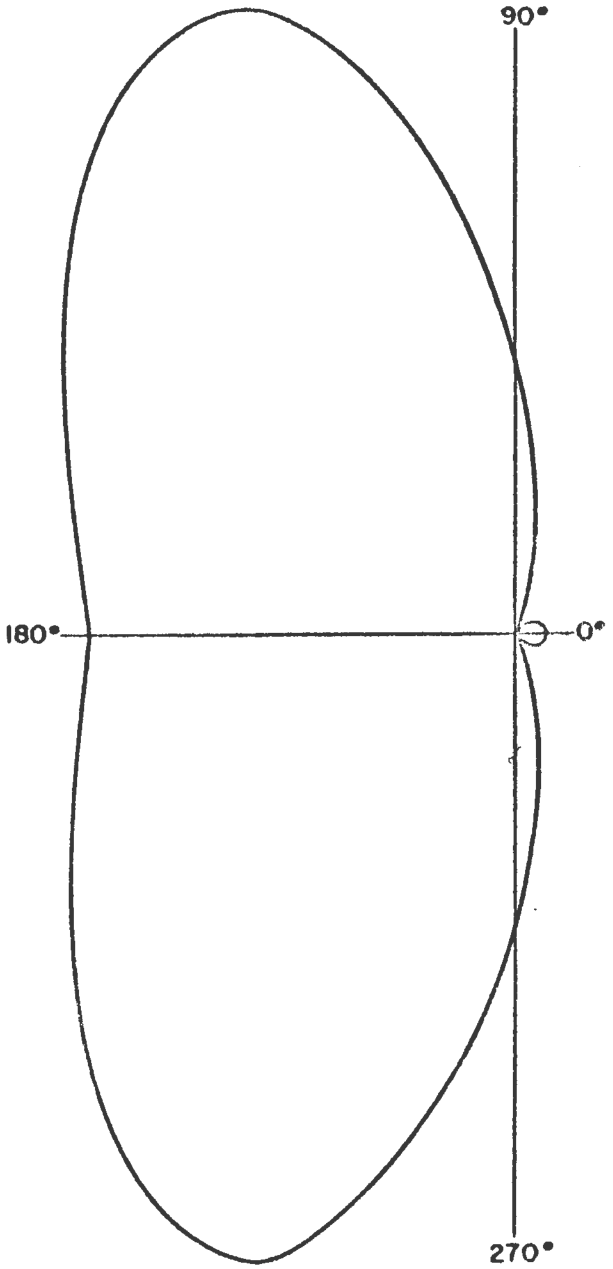

Figure 7. A polar plot of 4s to 4s scattering showing $G^2(u)$ as a function of scattering angle Θ. $u = \sin(\Theta/2)$, and $G^2(0) = 1$. $\overrightarrow{k_i - k_f}$ has been assumed to be in the $\overrightarrow{K}$ direction. Scattering from waves with propagation vectors $\overrightarrow{q + K_n}$ have been combined with relative weight factors $|\overrightarrow{q + K_n}|^{-4}$ to obtain $G(u)$.

VIII. 4S TO 3D SCATTERING

The amplitude for 4s to 3d scattering may be found by evaluating equation (4.30) for the scattering amplitude using the wave function of Fuchs[23] for $U_{4s}(\vec{r}, \vec{k})$ and the wave functions of Fletcher[17] for $\psi_{3d}(\vec{r}, \vec{k})$. It will be assumed that $\psi_{3d}(\vec{r}, \vec{k})$ is of the form:

$$\psi_{3d}(\vec{r}, \vec{k}) = N^{-\frac{1}{2}} \sum(n,m)\, b_m(\vec{k}) \exp(i\vec{k} \cdot \vec{R}_n)\, \varphi^m_{\text{atomic}}(\overrightarrow{r - R_n}), \tag{8.1}$$

where

$$\varphi^m_{\text{atomic}}(\vec{r}) = Y^m_2(\vartheta, \varphi)\, R_{3d}(r). \tag{8.2}$$

These atomic functions are expressed in a form different from those in equations (6.2) through (6.6). Since $\varphi^m_{\text{atomic}}(\vec{r})$ is small outside of the atomic polyhedron for tightly bound electrons, the main contribution to the wave function in the cell about the origin will come from the $R_n = 0$ term, and only this term will be considered.

The first term, B_1, in equation (4.30) for the scattering amplitude, is proportional to $\int \overline{U}^*_{3d}\, U_{4s}\, d\tau_o$, where $\overline{U}^*_{3d} = \exp(i\vec{K} \cdot \vec{r})\, U^*_{3d}$. In terms of $R_{3d}(r)$, $\overline{U}^*_{3d}$ is given by

$$\overline{U}^*_{3d}(\vec{r},\vec{k}) = \sum(m)\, b^*_m(\vec{k})\, Y^{m*}_2(\vartheta, \varphi) \exp(i\, \overline{k}_{3d} \cdot \vec{r}) R_{3d}(r), \tag{8.3}$$

since

$$U^*_{3d} = \exp(i\vec{k} \cdot \vec{r})\, \psi^*_{3d}(\vec{r}, \vec{k}). \tag{8.4}$$

By expanding the exponential in spherical harmonics, one can evaluate this integral as follows:

$$\int \overline{U}^*_{3d}\, U_{4s}\, d\tau_o = - \sum(m) 4\pi b^*_m(\overline{k}_{3d}) Y^{m*}_2(\Theta, \Phi) \int_0^{r_s} j_2(\overline{k}_{3d} r) R^*_{3d}\, U_{4s}\, r^2\, dr, \tag{8.5}$$

where (Θ, Φ) are the polar and azimuthal angles of $\overline{k}_{3d} = \overrightarrow{k_{3d} + K}$.

The second term, B_2, in the scattering amplitude formula equation (4.30) is proportional to $\int U_{4s}(\partial \overline{U}^*_{3d}/\partial s) d\tau_o$, where s is the direction of the polarization vector $\hat{\varepsilon}_{qj}$. Integrating once by parts, one gets $- \int \overline{U}^*_{3d}(\partial U_{4s}/\partial s) d\tau_o$. Let $\partial U_{4s}/\partial s$ be expanded in spherical harmonics as follows:

$$\partial U_{4s}/\partial s = \sum(m)\, c_m\, Y^m_1(\vartheta, \varphi)\, U'_{4s}. \tag{8.6}$$

In the same manner as before, the integral above becomes:

$$\int U_{4s}(\partial \bar{U}^{*}_{3d}/\partial s)\,d\tau_o = -\sum(m, m', \ell)\, b^{*}_{m}\, c_{m'}\, i^{\ell}\, Y^{m-m'*}_{\ell}(\Theta, \Phi)$$
$$4\pi \int Y^{m*}_{2}\, Y^{m-m'}_{\ell}\, Y^{m'}_{1} \sin\vartheta\, d\vartheta\, d\varphi \int_0^{r_s} j_{\ell}(\bar{k}_{3d} r)\, R^{*}_{3d}\, U'_{4s}\, r^2\, dr. \tag{8.7}$$

The angular integrals of the product of three spherical harmonics are tabulated in Condon and Shortley.[36] Only terms for which $\ell = 1$ or 3 do not vanish.

The last term, B_3, in the scattering amplitude formula, equation (4.30) is proportional to $\vec{q}\cdot \int \nabla U_{4s}(\partial \bar{U}^{*}_{3d}/\partial s)\,d\tau_o$. By partial integration this can be converted to $-\vec{q}\cdot \int \bar{U}^{*}_{3d} \nabla (\partial U_{4s}/\partial s)\,d\tau_o$. The term $\vec{q}\cdot\nabla(\partial U_{4s}/\partial s)$ can be separated into a spherical and a non-spherical part as follows:

$$\vec{q}\,\hat{\varepsilon} : \nabla\nabla U_{4s} = \vec{q}\cdot\hat{\varepsilon}\,(U'_{4s}/r)$$
$$+ \left\{(\vec{q}\cdot\vec{r})(\hat{\varepsilon}\cdot\vec{r})/r\right\}(d/dr)(U'_{4s}/r)$$
$$= \vec{q}\,\hat{\varepsilon} : \left\{(\vec{r}\,\vec{r} - \overline{\overline{I}}\, r^2/3)/r\right\}(d/dr)(U'_{4s}/r)$$
$$+ \vec{q}\cdot\hat{\varepsilon}\, \left\{(U'_{4s}/r) + (r/3)(d/dr)(U'_{4s}/r)\right\}. \tag{8.8}$$

The non-spherical part can be expanded in terms of spherical harmonics of second order, that is

$$\vec{q}\,\hat{\varepsilon} : (\vec{r}\,\vec{r} - \overline{\overline{I}}\, r^2/3)/r^2 = \sum(m)\, d_m\, Y^{m}_{2}(\vartheta, \varphi). \tag{8.9}$$

The integral can now be expanded in the same manner as those above.

$$\vec{q}\cdot \int \nabla U_{4s}\ (\partial \bar{U}^{*}_{3d}/\partial s)\ d\tau_o$$
$$= -q \sum(m, m', \ell)\, d_m\, b^{*}_{m'}\, i^{\ell}\, Y^{m'-m*}_{\ell}(\Theta, \Phi)$$
$$\times \int Y^{m'*}_{2}\, Y^{m}_{2}\, Y^{m'-m}_{\ell} \sin\vartheta\, d\vartheta\, d\varphi\, 4\pi \int_0^{r_s} j_{\ell}(\bar{k}_{3d}\, r)\, R^{*}_{3d}$$
$$\times (d/dr)(U'_{4s}/r)\, r^3\, dr + \vec{q}\cdot\hat{\varepsilon} \sum(m)\, b^{*}_{m}\, Y^{m*}_{2}(\Theta, \Phi)\, 4\pi$$
$$\times \int_0^{r_s} j_2(\bar{k}_{3d}\, r)\, R^{*}_{3d} \left\{(U'_{4s}/r) + r(d/dr)(U'_{4s}/r)/3\right\} r^2\, dr. \tag{8.10}$$

In this case the only non-zero terms are $\ell = 0$, 2, and 4.

In Appendix E the three integrals (8.5), (8.7) and (8.10) are evaluated. C(q), a factor of B_1, is approximately

$$C(q) = (2/3)\,(KE)_F = 1.83\, e^2/2a_o. \tag{8.11}$$

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[36] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, 1935), p. 178.

In integral (8.5) the sum can be reduced by taking the polar axis in expansion (8.1) to be $\overline{k}_{3d}$. Then $\Theta = 0$, and

$$\Sigma(m)\ b_m^* \, Y_2^m(\Theta\,,\Phi) = b_0^* \,(5/4\pi)^{\frac{1}{2}} = 0.63\ b_0^*. \tag{8.12}$$

Using equations (4.30), (E.12), and (E.15), one can evaluate the sum of B_1 and B_3 as follows:

$$\begin{aligned}
&(B_1 + B_3)/(i\ N^{-\frac{1}{2}}\ a_{qj}) \\
&= \left\{(1.83)(0.63)(0.147) - 2(0.0213)\right\}\ b_0^*\ \vec{q}\cdot\ \hat{\varepsilon}_{qj} \\
&+\ 2q\ (0.294\ d_0\ b_0^* + 0.306\ Q_1 + 0.337\ Q_2) \\
&=\ 0.128\ b_0^*\ \vec{q}\ .\ \hat{\varepsilon}_{qj}\ \ e^2/2a_0 \\
&+\ q\ (0.588\ d_0\ b_0^* + 0.612\ Q_1 + 0.674\ Q_2)\ \ e^2/2a_0,
\end{aligned} \tag{8.13}$$

where

$$\begin{aligned}
Q_1 &= d_1\ b_1^* + d_{-1}\ b_{-1}^*. \\
Q_2 &= d_2\ b_2^* + d_{-2}\ b_{-2}^*.
\end{aligned} \tag{8.14}$$

Referring to Figure 3, for 3d states on the Fermi level as calculated by Fletcher[17], one notices that $b_0 \approx 0$. Consequently, the only parts of equation (8.13) that contribute appreciably are those proportional to Q_1 and Q_2. Q_1 and Q_2 are discussed in Appendix F.

It will now be shown that for normal 4s - 3d scattering, B_2 is negligible compared to $B_1 + B_3$. Substituting equation (E.14) into B_2 of equation (4.30), one finds

$$\begin{aligned}
&B_2/iN^{-\frac{1}{2}}\ a_{qj} \\
&= (\hbar^2/2m)(\overline{k}_{3d}^2 - k_{4s}^2)(0.0539\ c_0\ \ b_0^* + 0.0487\ T_1)/a_0,
\end{aligned} \tag{8.15}$$

where

$$T_1 = c_1\ b_1^* + c_{-1}\ b_{-1}^*. \tag{8.16}$$

The energy of the phonon, $E_1 - E_f$, has been neglected. T_1 is discussed in Appendix F.

In order to compare expressions (8.13) and (8.15), the conditions for normal scattering to maximize expression (8.15) and to minimize expression (8.13) will be sought. Equation (8.15) is proportional to the amount of

$|m| = 1$ state, since $b_0 \approx 0$. Referring to Figure 3 it is seen that there are states on axes Δ and Λ that are pure $|m| = 1$. The larger k_{3d} for the Fermi level is on Λ. This $\vec{k}_{3d}$ is about $0.8/a_0$ in length. This choice maximizes $k^2_{3d} - k^2_{4s}$, and thus equation (8.15). Equation (8.13) is proportional to q. The minimum q would be with $\vec{k}_{4s}$ in the same direction as $\vec{k}_{3d}$. For this case $q = 0.8/a_0 - 0.6/a_0 = 0.2/a_0$. The angle α between $\vec{k}_{3d}$ and $\vec{q}$ is zero. Referring to equations (F.16), (F.18), and (F.38), one sees that shear waves cause scattering in both $B_1 + B_3$ and B_2. For this case the values of equations (8.13) and (8.15) are

$$(B_1 + B_3)/iN^{-\frac{1}{2}}\, a_{qj} = (0.2)(0.612)(4\pi/15)^{\frac{1}{2}}$$

$$= 0.118\ e^2/2a_0^2, \tag{8.17}$$

$$B_2/iN^{-\frac{1}{2}}\, a_{qj} = (0.0487)(0.64 - 0.36)(4\pi/3)^{\frac{1}{2}}$$

$$= 0.0278\ e^2/2a_0^2. \tag{8.18}$$

Thus for normal scattering, B_2 at its largest is still only 0.24 times as large as $B_1 + B_3$, and therefore B_2 will be neglected for normal scattering.

Suppose k_{3d} is on the Σ axis. As shown by Figure 3, this state is type $|m| = 2$. From equations (8.13) and (F.26), the normal scattering probability to any 4s state is given by

$$(0.674)^2(4\pi/15)\ N\ a^2_{ql}\ F_2(\alpha,\beta_2)(e^4/4a_0^4), \tag{8.19}$$

where α, β_2 are the polar and azimuthal angles of $\vec{q}$ in a system as described in Appendix F. The amplitude of the longitudinal mode is a_{ql}. $F_2(\alpha,\beta_2)$ is defined in equation (F.26), and is plotted in the lower left hand corner of Figure 8.

Suppose instead $\vec{k}_{3d}$ is on the axis Δ. There are three states, two type $|m| = 1$ and one $|m| = 2$. Scattering from the type $|m| = 2$ state is the same as described above. From equations (8.13) and (F.19) the transition probability from the type $|m| = 1$ state to any 4s state on the Fermi level is given by

$$(0.612)^2(4\pi/15)\ N\ a^2_{ql}\ F_1(\alpha,\beta_1)(e^4/4a_0^4), \tag{8.20}$$

where the angles are similar to those above, and $F_1(\alpha,\beta_1)$ is defined by equation (F.19) and is plotted in the upper right hand corner of Figure 8.

For $\vec{k}_{3d}$ on the axis Λ, as well as at a general position on the Fermi surface, the 3d wave function consists of both $|m| = 1$ and $|m| = 2$ type functions. If one defines b and γ by the relations

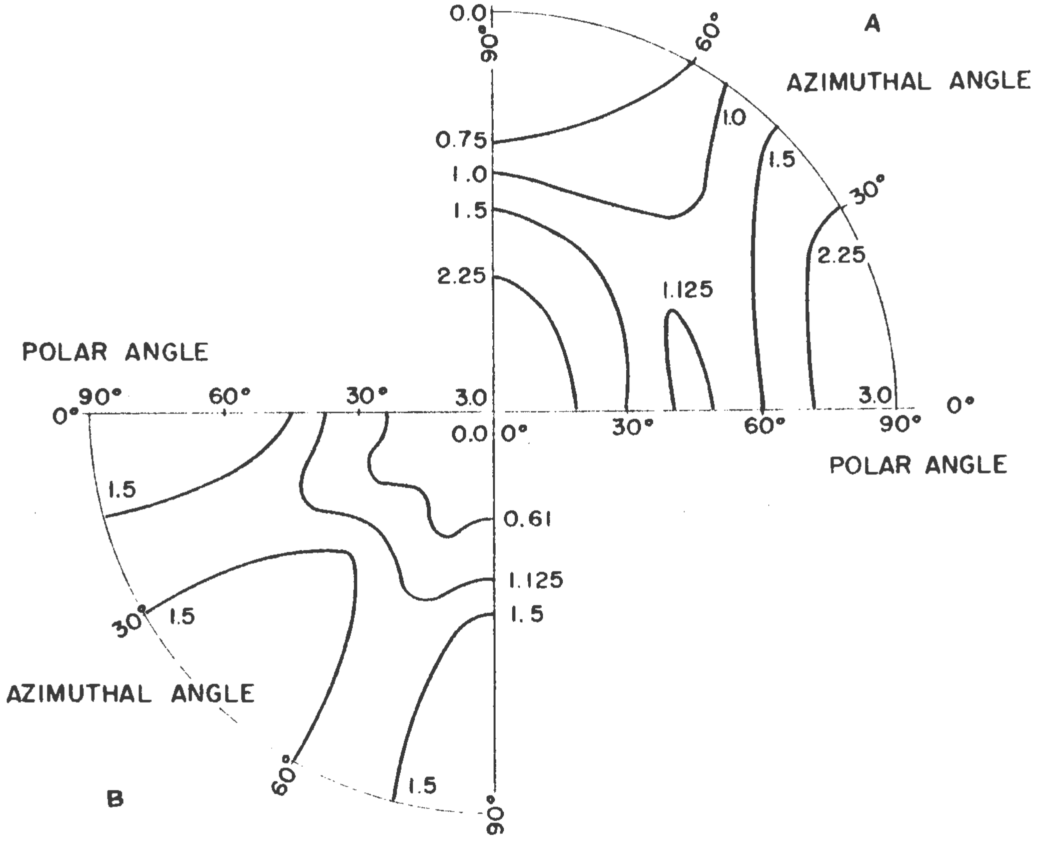

Figure 8. (A) Contours of $F_1(\alpha, \beta_1)$ are plotted as a function of α and β, the polar and azimuthal angles of $\vec{q}$ relative to $\vec{k}_{3d}$ where the azimuthal angle is measured in a special system as discussed in Appendix F. This function is proportional to the transition probability for normal scattering between a pure $|m| = 1$ 3d state and a 4s state. (B) In like manner contours of $F_2(\alpha, \beta_2)$ are plotted. The probability for scattering between an $|m| = 2$ 3d state and a 4s state is proportional to F_2. In each case it is sufficient to plot contours for only one octant, because of symmetry.

$$0.612\, \overline{b}_3^* = b \cos \gamma \ ,$$
$$0.674\, \overline{b}_1^* = b \sin \gamma \ , \tag{8.21}$$

then the transition probability will be given by

$$(4\pi/15)\, N\, a_{q1}{}^2\, b^2 \left\{ \cos^2\gamma \ F_1(\alpha, \beta_1) + \sin^2\gamma\, F_2(\alpha, \beta_2) + \sin 2\gamma \ F_{12}(\alpha, \beta_1, \beta_2) \right\} (e^4/4a_o{}^4) \quad , \tag{8.22}$$

where $F_{12}(\alpha, \beta_1, \beta_2)$ is defined by equation (F.29) and is discussed in Appendix F. Equation (8.22) is obtained by the combination of equations (8.13), (8.21) and (F.29).

For Umklapp process, $\overline{k}_{3d}$ is much larger than k_{4s}, and consequently B_2 is much more important than for normal processes. For $|m| = 1$ type 3d functions, B_2 will contribute most strongly when $\vec{q}$ is on the Brillouin zone boundary. This behavior can be understood in the following way.

Both normal and Umklapp scattering enter when $\vec{q}$ is near a zone boundary. Referring back to the discussion on normal and Umklapp 4s - 4s scattering, one finds that normal scattering is caused by $\vec{q}_1$ and Umklapp scattering is caused by $\vec{q}_2$ when $\vec{q}$ is on the zone boundary. By symmetry requirements, waves with $\vec{q}$'s on the square face and on line LW of the hexagonal face will have polarization vectors such that one, $\hat{\varepsilon}_1$, will be perpendicular to the surface, and the other two, $\hat{\varepsilon}_2$ and $\hat{\varepsilon}_3$, will be parallel to the surface. Now

$$\vec{q}_1 \cdot \hat{\varepsilon}_1 = - \vec{q}_2 \cdot \hat{\varepsilon}_1, \tag{8.23}$$

and so, since for these cases normal and Umklapp scattering are added in equal amounts, contributions from normal and Umklapp processes tend to cancel. Normal and Umklapp scattering will not cancel for the other polarizations, but will add and be proportional to the sine of the angle between $\vec{q}$ and the nearby $\vec{K}$. Contributions of $\hat{\varepsilon}_1$ will cancel completely if the form of the scattering for normal and Umklapp processes is the same, as it nearly is for $B_1 + B_3$. Thus for $\vec{q}$'s on the square face and on lines analogous to LW there will be a part of the scattering from $B_1 + B_3$ due to normal and Umklapp terms, and a part from B_2 proportional to the amount of $|m| = 1$ 3d wave function. The former is proportional to the sine of the angle between $\vec{q}$ and the nearby $\vec{K}$.

4s - 3d scattering is much more complicated in its angular dependence than is 4s - 4s scattering. Axial symmetry, as possessed by 4s - 4s scattering is no longer present in 4s - 3d scattering.

In this work it has been convenient to consider the scattering from some 3d states to relevant 4s states. For conductivity calculations, it would be desirable to know the scattering from any 4s state on the Fermi level to all 3d states satisfying the requirements of energy conservation. This would require a more extensive knowledge of $b_m(\overline{k}_{3d})$ than is available at this time.

IX. DISCUSSION

A. 4s - 4s Scattering

The most reliable work on thermally induced electronic scattering in monovalent metals is that of Bardeen.[6] The results of the present investigation for 4s - 4s scattering are shown in Figure 7. They agree fairly well with those of Bardeen for long wave length elastic waves. For short wave lengths, for example, a $\overline{q}$ on the zone boundary, the large Umklapp scattering averaged with the smaller normal scattering, gives a result of an amplitude about ten times greater than that of Bardeen. The deformable potential would not be expected to be very accurate for short wave length deformations, since if the charge is carried along with the ions, the potential locally is not like that of a homogeneously deformed crystal, deformed to the local strain. This last is one of the fundamental assumptions of the deformable potential as used in this investigation. In brief, the results of this investigation would be expected to be fairly accurate for small $\overline{q}$'s (small angle scattering) but probably not reliable for large $\overline{q}$'s.

This investigation predicts that 4s - 4s scattering falls off faster with scattering angle for small scattering angles, but is larger for large scattering angles than Bardeen's results indicate. This is in agreement with the analysis of the experimental temperature dependence of monovalent metals by Ziman.[14]

Bardeen treated the ionic cores as rigid and the s electrons as weakly bound to them. Upon deforming a crystal, the potential changes in two ways. One, the ionic core potentials are relocated at the new ion sites. Two, there is an additional change in potential due to the conduction electrons redistributing themselves in the new ion core potential. Bardeen computed the latter by a self-consistent field calculation.

In this work a continuous deformation is assumed. Conduction electrons are first considered to move with the ionic cores so that electrical neutrality is maintained. The local potential is assumed to be that of a homogeneously deformed crystal, deformed to the local deformation. The fine detail of the potential in the homogeneously deformed crystal is assumed to be that of a deformable potential, that is, the potential in the deformed lattice at a deformed position is equal to the potential at the original point in the undeformed lattice. A function of strain, independent of position, is added to the potential so that the total electronic energy will be a minimum for the equilibrium lattice spacing. If the conduction electrons are moved along with the ionic cores so that electrical neutrality is preserved, the Fermi energy may fluctuate in the crystal if the deformation is not homogeneous. Thus to the potential of a homogeneously deformed crystal must be added the potential produced by the charge imbalance when conduction electrons redistribute so as to equalize any fluctuation of the Fermi energy throughout the crystal.

B. 4s - 3d Scattering

Mott[7] has given a brief discussion of s to d scattering. He assumed that a 4s electron's wave function is of the form

$$\psi_k^{4s} = A\psi_s + B\psi_p + C\psi_d \qquad (9.1)$$

where $A \gg B \gg C$. Since all functions are normalized, A is approximately one. He used the deformable potential to describe the electron lattice interaction. The transition probability for s to s scattering is proportional to

$$\left| AB\int \psi_s^* \nabla V \psi_p \, d\tau \right|^2 \qquad (9.2)$$

while that for s to d scattering is proportional to

$$\left| B\int \psi_d^* \nabla V \psi_p \, d\tau \right|^2 . \qquad (9.3)$$

Since both probabilities depend on the second power of B, and $A \approx 1$, Mott concluded that the probability of scattering an electron from an s state was roughly independent of whether the final state was s or d. In the deformable potential theory as used by Bethe,[4] this would mean a constant G(u), or so called isotropic scattering.

Wilson[8] carried through a calculation for the electrical conductivity of transition metals using isotropic 4s - 4s and 4s - 3d scattering. For high temperatures his results agree fairly well with experiment. The low temperature resistance depends on the gap in k-space between the s and d parts of the Fermi surface. Since $\vec{k}_i - \vec{k}_f = -\vec{q}$ for regular processes, a phonon with minimum q is required before s to d scattering can take place. At temperatures low compared to the energy of this phonon, the number of modes with q large enough to cause s to d scattering will vary exponentially with temperature. Thus, the contribution to the resistance due to s to d scattering will vary exponentially in this temperature region. Since this effect has never been observed, it seems likely that the d band energy surface fluctuates sufficiently to have the d band Fermi surface intersect the s band Fermi surface.

Mott's work on the probability for scattering is only an order of magnitude calculation, so it is not surprising that the present work shows a moderately strong angular dependence, where he thought the scattering would be mainly isotropic.

C. Umklapp s - s Scattering

Bhatia[13] has discussed the effect of s - s Umklapp scattering on the temperature dependence of resistance of monovalent metals. He finds results at high temperatures that agree well with experiment, but predicts that at temperatures low enough so that few modes with q greater than

$$K - 2k_{4s} \tag{9.4}$$

are excited, Umklapp processes would be impossible and thus shear waves would not contribute to scattering. The consequent lowering of resistance is not observed. The results of the present investigation do not predict this sharp cutoff in resistance since Umklapp processes do not cut off sharply, being averaged with normal scattering with weight factor some function of the magnitude of the propagation vector.

D. Limitations and Approximations

Aside from using the one-electron formalism, the major assumption in this work is that electron lattice interaction can be represented by a deformable potential. Since results on 4s - 4s scattering using the deformable potential are more nearly like those of Bardeen[6] than are Nordheim's[5] results, the deformable potential seems preferable to the rigid core method of Nordheim.

Some error was introduced by the use of wave functions for copper for a calculation on nickel, but it seems unlikely that this would change the major results of the calculations.

Error has also been introduced by neglecting p and d state mixing with the 4s state. The neglect of wave functions located at ion sites other than the origin in equation (8.1) for 3d wave functions introduces small error since the overlap of 3d atomic functions is small.

Uncertainty of interaction integrals for the strong binding calculation for 3d electrons in nickel leaves knowledge of $b_m(\bar{K}_{3d})$ somewhat uncertain. Were different types of 3d states than those predicted by Fletcher on the

Fermi level, the 4s - 3d scattering would be different from that described. Further work of Fletcher's[34] seems to cast doubt on the interaction integrals.

The numerical integration of matrix elements, and the spherical approximation of the unit cell have both introduced errors into the numerical factors of this work, but do not seem likely to have affected the major results.

E. Conclusions

The transition amplitude for 4s - 3d scattering is of comparable size to that of 4s - 4s scattering. That for 4s - 4s scattering has azimuthal symmetry as a function of the final k vector relative to the initial k vector, while that for 4s - 3d scattering has moderate angular dependence both in polar and azimuthal angles of the final k vector relative to the initial k vector.

For 4s - 4s scattering when $\overrightarrow{k_f - k_i}$ is in the first Brillouin zone, normal scattering is caused by the longitudinal part of elastic waves. Umklapp scattering is caused by both the longitudinal and transverse parts of elastic waves. For small $\overrightarrow{k_f - k_i} = \vec{q}$, only normal scattering enters. As $\vec{q}$ approaches the zone boundary, Umklapp scattering must be added to normal scattering, so that when $\vec{q}$ is on the zone boundary, normal and Umklapp scattering amplitudes are averaged with equal weight factors.

For 4s - 4s scattering when $\overrightarrow{k_f - k_i}$ is outside the first Brillouin zone, Umklapp scattering is caused by the longitudinal part of elastic waves alone. Normal scattering is caused by both the longitudinal and transverse parts of elastic waves. When $\overrightarrow{k_f - k_i}$ is on zone boundary, normal and Umklapp scattering enter with equal weight factors. As $\overrightarrow{k_f - k_i}$ increases further, the weight factor for Umklapp scattering increases at the expense of that for normal scattering so that when $\overrightarrow{k_f - k_i} = -\vec{K}$, only Umklapp scattering remains. Thus as $\overrightarrow{k_f - k_i}$ changes from 0 to $-\vec{K}$, scattering changes from completely normal to completely Umklapp.

All modes cause both normal and Umklapp 4s - 3d scattering.

X. APPENDICES

The details of various mathematical derivations in this report are included in the Ph.D. thesis of the same title by John B. Gibson, which is on file at the library of Iowa State College, Ames, Iowa. These derivations are included in Appendices A-F of the thesis.