

systems, and by Compton *et al.*¹⁶ in the Mo-Tc system, correspond to the maximum of γ for Cr-Fe alloys at an electron concentration of about 6.4,¹ Fig. 7. It is, therefore, very likely that γ also has a maximum in the Mo-Re, W-Re, and Mo-Tc systems at approximately the same electron concentration. The data, now available, strongly suggest that the general features of the

shape of the d band, including the separation into subbands, as established by low-temperature specific-heat measurements for the bcc alloys of the first long period,¹ Fig. 7, are reproduced also in the second and third long periods.

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¹⁶ V. B. Compton, E. Corenzwit, J. P. Maita, B. T. Matthias, and F. J. Morin, Phys. Rev. **123**, 1567 (1961).

Multiphonon Processes Occurring in First-Order Perturbation Theory*

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An estimate of the effect of the multiphonon processes in first-order perturbation theory on the electrical conductivity in metals is made, according to a simplified model of the electron-phonon interaction, and a correspondingly simple model of the electron wave functions (plane waves). A method for taking Umklapp processes into account is worked in detail and the calculation is set up in the framework of the variational principle. A sample computation of the effect of double-phonon processes on the conductivity of the alkali metals is performed using a nonisotropic phonon spectrum, the result being a decrease by less than four percent (1% being more characteristic for the lighter elements). The method is not restricted to long-wave phonons, but does not include the effects of higher-order perturbation theory or of interference terms, which may be considerable.

I. INTRODUCTION

IN studying electron transport phenomena, we are concerned with the interactions of a two-component system—the electrons and the phonons. The scattering of electrons by the phonon field gives rise, for example, to electrical resistance. Such a scattering is ordinarily described in terms of the creation and annihilation of single phonons and expressions for electron-phonon collision probabilities are obtained with the aid of first-order, time-dependent perturbation theory. Multiphonon processes, in which two or more phonons are created or annihilated while the electron changes its state, are also possible. We may analyze the types of possible transitions in the following way. It is well known that the electron-lattice perturbation energy may be expanded as an infinite series in the displacements of the atoms. Application of first-order perturbation theory to a given term in the expansion leads to one certain type of process (for example single-phonon processes from the first term, double-phonon processes from the second and so on) in which the electron changes its state, in each case, by a single

transition without recourse to any intermediate states. On the other hand, treatment of even the first term of the perturbation energy expansion in conjunction with perturbation theory of higher order than first leads to double-phonon processes with one intermediate state, triple-phonon processes with two intermediate states, and other similar processes all involving intermediate states which are transitory in nature. The other terms of the perturbation potential lead to additional, more complicated, higher-order effects. Now a consideration of multiphonon processes involving intermediate states presents formidable mathematical difficulties, but those not involving such states may be treated in a systematic manner which is also mathematically tractable if the electronic states are characterized by plane waves. The purpose of this paper is to investigate the latter type of process. In the plane wave approximation the matrix element of the electron-lattice interaction may be separated into two factors. The first is a matrix element of a single ionic potential shielded in some fashion by the conduction electrons, and the second is a matrix element involving the annihilation and creation operators characteristic of multiphonon processes. Such a separation is carried out in Sec. II and explicit expressions are derived for the single-, and double-phonon transition probabilities. Evaluation of the electronic portion of the matrix element is described in Sec. III on the basis of a Fermi-Thomas statistical model.

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Finally, using the variational method of Kohler, we examine the effects of double-phonon processes on electrical conductivity in Sec. IV.

II. DETERMINATION OF THE ELECTRON TRANSITION PROBABILITY

From first-order, time-dependent perturbation theory, the probability per unit time for an electronic transition from a state with wave vector \mathbf{k} to one with wave vector \mathbf{k}' is given by

$$P(\mathbf{k} \rightarrow \mathbf{k}') = \hbar^{-2} \sum_{\eta'} |M_{\mathbf{k}\mathbf{k}'}(\eta, \eta')|^2 \Omega[E(\mathbf{k}') + E(\eta') - E(\mathbf{k}) - E(\eta)], \quad (2.1)$$

where η describes the initial phonon configuration and η' the final. A sum over final states η' and an average over initial states η are taken. $M_{\mathbf{k}\mathbf{k}'}(\eta, \eta')$ is the matrix element of the perturbing potential taken between the initial and final states of the electron-phonon system. The function Ω has the nature of an energy conserving δ function,

$$\Omega(x) = [\sin(xt/2\hbar)/(xt/2\hbar)]^2 t. \quad (2.2)$$

We consider the perturbation as arising only from the thermal motion of the atoms constituting the lattice. The perturbing potential may thus be written

$$\Delta W = -e \sum_l \{v[\mathbf{r} - \mathbf{R}(l) - \mathbf{u}(l)] - v[\mathbf{r} - \mathbf{R}(l)]\}, \quad (2.3)$$

where \mathbf{r} is the position of the electron, $\mathbf{R}(l)$ the equilibrium position of the ion in cell l , and $\mathbf{u}(l)$ the deviation of this ion from the equilibrium position, v is the ionic potential screened in some fashion, to be discussed later, by the other conduction electrons. In the plane wave approximation, after taking into account normalization, the interaction matrix element is

$$M_{\mathbf{k}\mathbf{k}'}(\eta, \eta') = V^{-1} \left(\eta' \left| \int e^{-i\mathbf{k}' \cdot \mathbf{r}} \Delta W e^{i\mathbf{k} \cdot \mathbf{r}} d^3r \right| \eta \right). \quad (2.4)$$

The disturbance of the l th ion may be written,

$$\mathbf{u}(l) = (MN)^{-\frac{1}{2}} \sum_{\sigma j} \zeta_j(\sigma) \{a_j(\sigma) \exp[i\sigma \cdot \mathbf{R}(l)] + a_j^*(\sigma) \exp[-i\sigma \cdot \mathbf{R}(l)]\}. \quad (2.5)$$

$$\begin{aligned} M_{\mathbf{k}\mathbf{k}'}(\eta, \eta') &= M_{\mathbf{k}\mathbf{k}'}^{(e)}(\eta') \left\{ -eV^{-1}N^{\frac{1}{2}}M^{-\frac{1}{2}} \sum_{\sigma j \mathbf{K}_s} [-i\mathbf{K} \cdot \zeta_j(\sigma)] [a_j(\sigma)\delta_- + a_j^*(\sigma)\delta_+] \right. \\ &\quad + e(2VM)^{-1} \sum_{j\sigma j'} \cdots \sum_{\sigma' \mathbf{K}_s} [-i\mathbf{K} \cdot \zeta_j(\sigma)] [-i\mathbf{K} \cdot \zeta_{j'}(\sigma')] [a_j(\sigma)a_{j'}(\sigma')(\delta_- \delta_-') \\ &\quad \left. + a_j^*(\sigma)a_{j'}(\sigma')(\delta_+ \delta_-') + a_j(\sigma)a_{j'}^*(\sigma')(\delta_- \delta_+') + a_j^*(\sigma)a_{j'}^*(\sigma')(\delta_+ \delta_+')] \right\} |\eta\rangle. \end{aligned} \quad (2.8)$$

In writing Eq. (2.8) we have employed the following notation:

$$\delta_{\pm} = \delta(\mathbf{K} \pm \sigma + \mathbf{K}_s, 0), \quad (\delta_{\pm} \delta_{\pm}') = \delta(\mathbf{K} \pm \sigma \pm \sigma' + \mathbf{K}_s, 0). \quad (2.9)$$

Action of the annihilation and creation operators on the phonon field in Eq. (2.8) may be conveniently indicated

Here $\zeta_j(\sigma)$ is a unit vector in the direction of displacement, and the $a_j(\sigma)$ and $a_j^*(\sigma)$ play the role of annihilation and creation operators acting on the phonon field; M is the ionic mass and N the number of ions in the crystal. The sum is taken over all modes where σ and j denote the wave vector and polarization of the mode. Substituting Eq. (2.3) into (2.4) and letting

$$\mathbf{r} - \mathbf{R}(l) - \mathbf{u}(l) = \mathbf{q}' \quad \text{and} \quad \mathbf{r} - \mathbf{R}(l) = \mathbf{q},$$

we obtain, after making a series expansion of the first term in powers of $\mathbf{u}(l)$ and combining terms,

$$\begin{aligned} M_{\mathbf{k}\mathbf{k}'}(\eta, \eta') &= -eV^{-1} \left(\eta' \left| \sum_l \{ [i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{u}(l)] \right. \right. \\ &\quad \left. \left. - \frac{1}{2} [(\mathbf{k} - \mathbf{k}') \cdot \mathbf{u}(l)]^2 + \cdots \right\} \right. \\ &\quad \left. \times \left\{ \int \exp[i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{q}' + \mathbf{R}(l))] v(\mathbf{q}') d^3\rho' \right\} \right| \eta \right). \end{aligned} \quad (2.6)$$

The first term in Eq. (2.6) will lead to electronic transitions involving single-phonon processes whereas the second leads to two-phonon transitions. Successively higher-order terms in the expansion would lead to other multiphonon processes but it will be our objective in the remainder of this paper to investigate a procedure for taking into account only the two-phonon processes. Because of the plane wave approximation, an electronic portion of the matrix element involving the screened ionic potential evaluated between plane wave states may be factored out. Denoting this by $M_{\mathbf{k}\mathbf{k}'}^{(e)}$, we have

$$M_{\mathbf{k}\mathbf{k}'}^{(e)} = \int \exp(-i\mathbf{K} \cdot \mathbf{q}') v(\mathbf{q}') d^3\rho', \quad (2.7)$$

where we have used $\mathbf{K} = \mathbf{k}' - \mathbf{k}$. Using the well-known relation,

$$\sum_l e^{i\mathbf{q} \cdot \mathbf{R}(l)} = N\delta(\mathbf{q}, \mathbf{K}_s),$$

where \mathbf{q} is any vector, \mathbf{K}_s is 2π times a principle vector of the reciprocal lattice, and δ is the Kronecker δ function ($\delta = 1$ if $\mathbf{q} = \mathbf{K}_s$ and $\delta = 0$ if $\mathbf{q} \neq \mathbf{K}_s$), we obtain the following reduction upon substituting Eqs. (2.5) and (2.7) in (2.6):

by an additional δ function notation,

$$\delta_{\pm}^{(n)} = \delta[n_j'(\sigma), n_j(\sigma) \pm 1], \quad (2.10)$$

where $n_j(\sigma)$ is the phonon occupation number of the σ , j mode. A primed δ function has a similar meaning for the σ' , j' mode.

Thus, with $\omega_j(\sigma)$ the circular frequency of the σ , j mode,

$$\begin{aligned} M_{\mathbf{k}\mathbf{k}'}(\eta, \eta') = & M_{\mathbf{k}\mathbf{k}'}^{(e)} \{ eV^{-1} N^{\frac{1}{2}} M^{-\frac{1}{2}} \sum_{\sigma, j, \mathbf{K}_s} [i\mathbf{K} \cdot \boldsymbol{\zeta}_j(\sigma)] [\hbar/2\omega_j(\sigma)]^{\frac{1}{2}} \{ [n_j(\sigma)]^{\frac{1}{2}} \delta_{-}^{(n)} + [n_j(\sigma)+1]^{\frac{1}{2}} \delta_{+}^{(n)} \} \\ & + e(2VM)^{-1} \sum_{\sigma, j, \mathbf{K}_s} \cdots \sum_{j', \mathbf{K}_s} [i\mathbf{K} \cdot \boldsymbol{\zeta}_j(\sigma)] [i\mathbf{K} \cdot \boldsymbol{\zeta}_{j'}(\sigma')] [\hbar/2\omega_j(\sigma)]^{\frac{1}{2}} [\hbar/2\omega_{j'}(\sigma')]^{\frac{1}{2}} \\ & \times \{ [n_j(\sigma)]^{\frac{1}{2}} [n_{j'}(\sigma')]^{\frac{1}{2}} (\delta_{-}^{(n)} \delta_{-}^{(n')} + [n_j(\sigma)+1]^{\frac{1}{2}} [n_{j'}(\sigma')]^{\frac{1}{2}} (\delta_{+}^{(n)} \delta_{+}^{(n')}) \\ & + [n_j(\sigma)]^{\frac{1}{2}} [n_{j'}(\sigma')+1]^{\frac{1}{2}} (\delta_{-}^{(n)} \delta_{+}^{(n')}) + [n_j(\sigma)+1]^{\frac{1}{2}} [n_{j'}(\sigma')+1]^{\frac{1}{2}} (\delta_{+}^{(n)} \delta_{+}^{(n')}) \} \}. \quad (2.11) \end{aligned}$$

The initial configuration η and the final configuration η' in the matrix element $M_{\mathbf{k}\mathbf{k}'}(\eta, \eta')$ will allow at most only one of the $\delta_{\pm}^{(n)} \delta_{\pm}^{(n')}$ combinations not to give zero. Hence upon squaring $M_{\mathbf{k}\mathbf{k}'}(\eta, \eta')$ the cross terms can never be anything but zero. When the thermal average over η is then taken, the $n_j(\sigma)$'s become the equilibrium configuration. Inserting a factor $\frac{1}{2}$ so that the $\sigma\sigma'$ sums do not count the same interaction twice, and performing the sum over η' , we get

$$P(\mathbf{k} \rightarrow \mathbf{k}') = P^{(1)}(\mathbf{k} \rightarrow \mathbf{k}') + P^{(2)}(\mathbf{k} \rightarrow \mathbf{k}'), \quad (2.12)$$

where

$$P^{(1)}(\mathbf{k} \rightarrow \mathbf{k}') = |M_{\mathbf{k}\mathbf{k}'}^{(e)}|^2 \frac{Ne^2}{V^2 \hbar^2 M} \left\{ \sum_{\sigma, j, \mathbf{K}_s} [\mathbf{K} \cdot \boldsymbol{\zeta}_j(\sigma)]^2 \left[\frac{\hbar n_j(\sigma)}{2\omega_j(\sigma)} \delta_{-} \Omega_{-} + \frac{\hbar (n_j(\sigma)+1)}{2\omega_j(\sigma)} \delta_{+} \Omega_{+} \right] \right\}, \quad (2.13a)$$

$$\begin{aligned} P^{(2)}(\mathbf{k} \rightarrow \mathbf{k}') = & |M_{\mathbf{k}\mathbf{k}'}^{(e)}|^2 \frac{e^2}{32M^2 V^2} \sum_{\sigma, j, \mathbf{K}_s} \cdots \sum_{j', \mathbf{K}_s} [\mathbf{K} \cdot \boldsymbol{\zeta}_j(\sigma)]^2 [\mathbf{K} \cdot \boldsymbol{\zeta}_{j'}(\sigma')]^2 [\omega_j(\sigma) \omega_{j'}(\sigma')]^{-1} \\ & \times \{ [n_j(\sigma)+1] [n_{j'}(\sigma')+1] (\Omega_{+} \Omega_{+}') (\delta_{+} \delta_{+}') + n_j(\sigma) n_{j'}(\sigma') (\Omega_{-} \Omega_{-}') (\delta_{-} \delta_{-}') \\ & + n_j(\sigma) [n_{j'}(\sigma')+1] (\Omega_{-} \Omega_{+}') (\delta_{-} \delta_{+}') + [n_j(\sigma)+1] n_{j'}(\sigma') (\Omega_{+} \Omega_{-}') (\delta_{+} \delta_{-}') \}. \quad (2.13b) \end{aligned}$$

In these equations we have used the following abbreviations:

$$\begin{aligned} \delta_{\pm}^{(n)} & \rightarrow \Omega[E' - E \pm \hbar\omega_j(\sigma)] = \Omega_{\pm}, \\ \delta_{\pm}^{(n)} \delta_{\pm}^{(n')} & \rightarrow \Omega[E' - E \pm \hbar\omega_j(\sigma) \pm \hbar\omega_{j'}(\sigma')] \\ & = (\Omega_{\pm} \Omega_{\pm}'). \quad (2.14) \end{aligned}$$

The sum over \mathbf{K}_s in Eqs. (2.13) is over all types of Umklapp processes that can occur. Thus we have expressed the total transition probability in Eq. (2.12) as a term from single-phonon processes, Eq. (2.13a), plus a term from double-phonon processes, Eq. (2.13b). Clearly, triple-phonon processes and so on would contribute in an analogous way.

One of the double-phonon possibilities is illustrated diagrammatically in Fig. 1. The actual first Brillouin zone which is a rhombic dodecahedron for the bcc lattice has been replaced by a sphere of equal volume. It is clear from Fig. 1 that, for double-phonon processes, the transition between given initial and final electron states can occur in a multiplicity of ways. In fact the point where σ meets σ' can wander about anywhere in the volume common to the σ and σ' spheres.

III. THE ELECTRONIC PORTION OF THE MATRIX ELEMENT

Evaluation of $M_{\mathbf{k}\mathbf{k}'}^{(e)}$ is accomplished most easily by the use of a Fermi-Thomas statistical model fol-

lowing Bardeen and Pines,¹ Overhauser,² and others. In this way we obtain

$$M_{\mathbf{k}\mathbf{k}'}^{(e)} = (1/S) \int e^{-\mathbf{K} \cdot \mathbf{r}} v(\text{ion}) d^3r, \quad (3.1)$$

where $(1/S)$ is a shielding factor of the matrix element

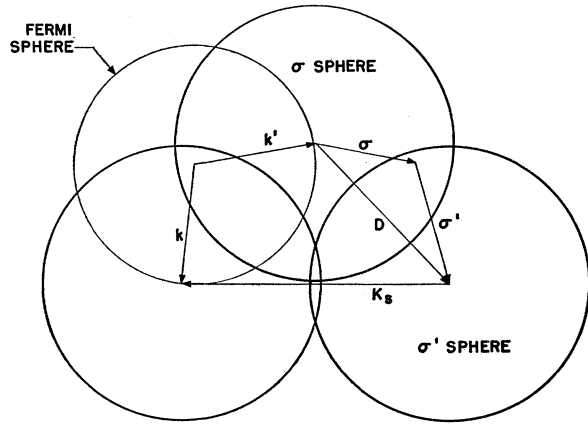


FIG. 1. A double-phonon Umklapp transition in which an electron is scattered from \mathbf{k} to \mathbf{k}' while creating phonons with wave vectors σ and σ' .

¹ J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

² A. Overhauser, Phys. Rev. **89**, 689 (1953).

of the unshielded ionic potential $v(\text{ion})$. Its form is

$$S = 1 + [4e^2(2\zeta)^{1/2}m^{3/2}]/(\pi\hbar^3K^2) = 1 + (\lambda^2/K^2), \quad (3.2)$$

which also defines λ . To evaluate the remainder of the matrix element we assume that $v(\text{ion})$ arises from a uniform distribution of positive charge throughout the atomic sphere of radius r_s . Thus,

$$M_{\mathbf{k}\mathbf{k}'}^{(\epsilon)} = \frac{4\pi e}{K^2 + \lambda^2} \left[\frac{3j_1(Kr_s)}{Kr_s} \right], \quad (3.3)$$

where j_1 denotes the first spherical Bessel function.

This expression is very similar to that obtained by Bardeen³ on the basis of a more accurate though more complicated theory. Where we have used a Fermi-Thomas statistical calculation, Bardeen takes account of shielding of the ionic potential by calculating the change in the self-consistent field of the conduction electrons through a perturbation calculation when the crystal is distorted. The chief difference in the results lies in the fact that λ^2 in Eq. (3.3) is multiplied by a factor which varies from 1.0 for zero-scattering angle to 0.5 for 180° scattering. If included, it would make large-angle scattering (Umklapp processes) somewhat more effective.

We may also note that for single-phonon processes our result is identical with that obtained by Brooks⁴ relative to a "rigid ion jellium model." Briefly stated, the rigid ion jellium model envisages uniform rigid cell blocks of positive charge which are assumed to move according to the ordinary "rigid ion" lattice dynamics without distortion.

IV. APPLICATION OF THE VARIATIONAL PROCEDURE

In order to examine the effects of double-phonon processes on electrical conductivity, we use a solution to the Boltzmann equation based on a variational principle first suggested by Kohler.^{5,6} The first term in an expansion of the electrical conductivity is given by

$$\sigma = \alpha_0^2/d_{00}, \quad (4.1)$$

where

$$\alpha_0 = e\hbar m^{-1} \int k_x^2 \frac{\partial f_0}{\partial E} \frac{d^3k}{4\pi^3}, \quad (4.2)$$

and

$$d_{00} = -V(8\pi^3)^{-2}(\kappa T)^{-1} \int \int P(\mathbf{k} \rightarrow \mathbf{k}') f_0(1-f_0') \times k_x(k_x' - k_x) d^3k d^3k'. \quad (4.3)$$

We have assumed the electric field to be in the x direction; f_0 is the Fermi function with ζ the Fermi energy:

$$f_0 = (e^{\epsilon} + 1)^{-1}, \\ \epsilon = [E(\mathbf{k}) - \zeta]/\kappa T.$$

The evaluation of α_0 proceeds very readily, with the result

$$\alpha_0 = -e(2m\zeta)^{3/2}/(3\pi^2\hbar^4) = -e/(\hbar\Delta_0), \quad (4.4)$$

where Δ_0 is the atomic volume. The six-dimensional element of integration in Eq. (4.3) may be written

$$d^3k d^3k' \approx (4m^4/k^2\hbar^8) E^2 dE dE' (\sin\theta' d\theta') d(\Psi),$$

where $d(\Psi) = \sin\theta d\theta d\phi d\phi'$. θ' and ϕ' are the polar and azimuthal angles of \mathbf{k}' about the polar axis taken to be in the \mathbf{k} direction. θ and ϕ are then the polar and azimuthal angles of \mathbf{k} relative to a polar axis in the direction of the electric field.⁷ The integration over E' then converts the Ω functions to true δ functions. The integration over E may be accomplished following Wilson⁸ leaving, then, only the integration over angles. In Eqs. (2.13), the factors $[\mathbf{K} \cdot \boldsymbol{\zeta}_j(\boldsymbol{\sigma})]^2$ appear. These are of the form $K^2 \cos^2\alpha$, where α is the angle between \mathbf{K} and $\boldsymbol{\zeta}_j(\boldsymbol{\sigma})$. In the case of single-phonon, non-Umklapp processes the summation over j has only one non-zero term; that corresponding to the longitudinal modes where $\alpha=0$. In all other cases we take, for simplicity, an independent average for $\cos^2\alpha$. This procedure, which should not upset order of magnitude results, yields, $\langle \cos^2\alpha \rangle_{\text{av}} = \frac{1}{3}$. The independent average over (Ψ) has been shown rigorously⁷ to be equivalent to an average over the directions of the difference vector \mathbf{K} . Thus, letting

$$u = \sin(\theta'/2), \quad \gamma = \hbar\omega_j(\boldsymbol{\sigma})/\kappa T, \quad \xi = \zeta/\kappa T,$$

we obtain for the single-phonon contribution to d_{00} ,

$$d_{00}^{(1)} = \frac{2e^2(2m)^5(\kappa T)^2\xi^3}{9\pi^3\hbar^8\Delta_0 M} \int \sum_{\boldsymbol{\sigma}; \mathbf{K}_s} |M_{\mathbf{k}\mathbf{k}'}^{(\epsilon)}|^2 \left\langle \frac{\delta_+ + \delta_-}{(e^\gamma - 1)|1 - e^{-\gamma}|} \right\rangle_{\text{av}(\Psi)} u^5 du. \quad (4.5)$$

³ J. Bardeen, Phys. Rev. **52**, 688 (1937); and Can. J. Phys. **34**, 1171 (1956).

⁴ H. Brooks, in an unpublished communication to M. Bailyn.

⁵ M. Kohler, Z. Physik. **124**, 772 (1948); **125**, 679 (1949); **126**, 495 (1949).

⁶ M. Bailyn, Phys. Rev. **112**, 1587 (1958). Bailyn's Eq. (32) should be multiplied by a factor $\frac{1}{2}$ since the electron cannot flip its spin in the transition.

⁷ M. Bailyn, Phys. Rev. **121**, 1336 (1961).

⁸ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1954), pp. 335-336.

An expression for $d_{00}^{(2)}$ may be developed in a similar manner, with the following result:

$$d_{00}^{(2)} = \frac{8e^2 m^6 (\kappa T)^2 \xi^4}{27 \pi^5 \hbar^9 \Delta_0 M^2 N} \int \sum_{\sigma; \sigma'} \cdots \sum_{j' \mathbf{K}_s} |M_{\mathbf{k}\mathbf{k}'}^{(e)}|^2 u^7 \left\langle \frac{(\gamma + \gamma')}{\gamma \gamma'} \frac{[(\delta_+ \delta_+') + (\delta_- \delta_-')]}{|e^{\gamma'} - 1| (1 - e^{-\gamma - \gamma'}) (e^\gamma - 1)} + \frac{(\gamma - \gamma')}{\gamma \gamma'} \frac{[(\delta_+ \delta_-') + (\delta_- \delta_+')]}{|e^{\gamma'} - 1| (e^{-\gamma' + \gamma} - 1) (1 - e^{-\gamma})} \right\rangle_{\text{av } (\Psi)} du. \quad (4.6)$$

This is the basic expression at all temperatures for the contribution of double-phonon processes to the d_{00} integral in the conductivity expression, Eq. (4.1). To go further and obtain numerical results, we shall make a high temperature approximation, treating γ and γ' as small quantities. Retaining only first terms in the expansion and denoting the factors which appear before the integral signs in Eqs. (4.5) and (4.6) by $D^{(1)}$ and $D^{(2)}$, respectively, we obtain

$$d_{00}^{(1)} = D^{(1)} \int \sum_{\sigma; \mathbf{K}_s} |M_{\mathbf{k}\mathbf{k}'}^{(e)}|^2 \langle (\delta_+ + \delta_-) \gamma^{-2} \rangle_{\text{av } (\Psi)} u^5 du, \quad (4.7)$$

$$d_{00}^{(2)} = D^{(2)} \int \sum_{\sigma; \sigma'} \cdots \sum_{j' \mathbf{K}_s} |M_{\mathbf{k}\mathbf{k}'}^{(e)}|^2 \langle [(\delta_+ \delta_+') + (\delta_- \delta_-') + (\delta_+ \delta_-') + (\delta_- \delta_+')] (\gamma \gamma')^{-2} \rangle_{\text{av } (\Psi)} u^7 du. \quad (4.8)$$

That the expansion is really quite good for $\gamma < 1$ can be seen from the fact that next higher-order terms cancel out in both the single-, and double-phonon contributions to d_{00} .

The calculation of the electrical conductivity may now proceed directly upon substitution of Eqs. (4.4), (4.7), (4.8) and the electronic portion of the matrix element, Eq. (3.3), all in Eq. (4.1). Several ancillary comments concerning the calculation are in order. (1) The vibrational spectrum is approximated by a Debye spectrum such that $\hbar \omega_j(\sigma) = \kappa \theta_j \sigma / \sigma_{\max}$, where θ_j is the Debye temperature associated with the vibrational mode having polarization index j and σ_{\max} is the radius of the first Brillouin zone in the spherical approximation. (2) Debye temperatures are averaged over crystalline directions independently of other factors. (3) In the non-Umklapp contribution to $d_{00}^{(1)}$ only the longitudinal modes are effective in scattering. The upper limit of the integration over scattering angles, u_0 , is determined by, $\sigma_{\max} = 2k_f u_0$, where k_f is the radius of the Fermi sphere. (4) In the Umklapp contribution to $d_{00}^{(1)}$ the averaging of $|\sigma|^{-2} = |\mathbf{K} + \mathbf{K}_s|^{-2}$ over (Ψ) actually corresponds to an averaging over all angles between \mathbf{K} and \mathbf{K}_s .⁷ Denoting this angle by Ψ , the integration is carried out between 0 and π but the δ condition makes the contribution from the domain $\Psi > \Psi_0$ equal to zero where Ψ_0 is determined by $\sigma_{\max}^2 = |\mathbf{K}|^2 + |\mathbf{K}_s|^2 - 2|\mathbf{K}||\mathbf{K}_s| \cos \Psi_0$. This averaging technique is similar to that originally used by Ziman⁹ and independently by Bailyn.¹⁰ A variation of Ziman's method is also given by Jones.¹¹ (5) In the non-Umklapp

as well as the Umklapp contribution to $d_{00}^{(2)}$ the sum over wave vectors is converted to a sum over a single variable, α ($= \mathbf{D}/2\sigma_{\max}$, where \mathbf{D} is the separation of σ and σ' spheres; see Fig. 1). The function summed is expressible in terms of Spence integrals as shown in the Appendix. u_0 is 1 since double-phonon processes can produce scattering through all angles even in non-Umklapp processes. (6) The (Ψ) averaging is more difficult to perform in the double-phonon case, but it can be shown that

$$\langle \mathfrak{S}(|\alpha|) \delta[\mathbf{K} + 2\sigma_{\max} \alpha + \mathbf{K}_s, 0] \rangle_{\text{av } (\Psi)} = \frac{\sigma_{\max} u_0}{2|\mathbf{K}_s| u} \int_{\frac{1}{2} |(\mathbf{u}/u_0) - (|\mathbf{K}_s|/\sigma_{\max})|}^{\alpha'} \mathfrak{S}(|\alpha|) \alpha d\alpha,$$

where

$$\alpha' = \frac{1}{2} [(u/u_0) + (|\mathbf{K}_s|/\sigma_{\max})] \quad \text{if } u \leq u_0 [2 - (|\mathbf{K}_s|/\sigma_{\max})] \\ = 1 \quad \text{if } u \geq u_0 [2 - (|\mathbf{K}_s|/\sigma_{\max})],$$

and \mathfrak{S} is defined in the Appendix.

The result of the conductivity calculation may be put into the form,

$$\sigma = 1/(AT + BT^2), \quad (\text{electrostatic units}) \quad (4.6)$$

where values of A and B for the alkali metals are given in Table I.

V. SUMMARY AND DISCUSSION

In this paper, an approximate method for dealing with the multiphonon processes in first-order perturbation theory has been shown. The resulting double-phonon transition probability has been applied, together with the complementary single-phonon one, to the calculation of the electrical conductivity of the alkali metals. Our results may be discussed under three headings. (1) The single-phonon processes: These

⁹ J. M. Ziman, Proc. Roy. Soc. (London) **A226**, 436 (1954).

¹⁰ M. Bailyn, thesis, Harvard University, 1956 (unpublished); see also M. Bailyn and H. Brooks, Bull. Am. Phys. Soc. **1**, 300 (1956). Bailyn incorporated the anisotropy of the phonons in his averaging and hence his average did not reduce to a simple integral such as Ziman found and we use here, essentially following Ziman.

¹¹ H. Jones, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 248.

TABLE I. Values of the constants appearing in Eq. (4.6) together with experimental and theoretical values of the electrical conductivity (esu) for the alkali metals.

	A	B	$\sigma_{\text{exp}}(0^\circ\text{C})$	$\sigma_1(0^\circ\text{C})^a$	$\sigma_{1+2}(0^\circ\text{C})^b$	$\%_{\text{red.}}(0^\circ\text{C})^c$
Na	0.996×10^{-20}	1.105×10^{-24}	20.9×10^{-16}	36.76×10^{-16}	35.67×10^{-16}	3.0
K	1.889×10^{-20}	2.834×10^{-24}	14.7×10^{-16}	19.38×10^{-16}	18.62×10^{-16}	3.9
Rb	2.196×10^{-20}	3.535×10^{-24}	7.8×10^{-16}	16.67×10^{-16}	15.97×10^{-16}	4.2
Cs	2.658×10^{-20}	4.075×10^{-24}	4.9×10^{-16}	13.77×10^{-16}	13.22×10^{-16}	4.0

^a Conductivity calculated on the basis of single-phonon processes only.^b Conductivity calculated on the basis of both single-, and double-phonon processes.^c Percent reduction in the single-phonon conductivity caused by double-phonon scattering.

by themselves provide a resistivity which can be compared with experiment, the comparison being useful in that we can see what are the effects of the restrictions on our model necessitated by our calculating multiphonon processes in a systematic way. (2) The multiphonon processes: On the basis of the theory, we can determine the magnitude of the double-phonon effect in electrical conductivity *relative* to the single-phonon effect. We may also speculate on other higher-order contributions indicated by the theory. (3) Experimental detection of multiphonon effects: We may inquire what the likelihood is of the multiphonon processes having a measureable effect.

Regarding the first point we have raised, a comparison of experimental values with the calculated values of electrical conductivity is made in Table I. In each case the theoretical value is too high with the closest agreement occurring in the case of K. For the heavier elements, Rb and Cs, the theoretical value is more than twice what it should be. In analyzing these differences, two observations should be made. We indicated in Sec. III that the scattering matrix element we obtained from our crude model was essentially equivalent to that obtained by Bardeen, on the basis of a more rigorous model, except for a difference in the shielding factor. Bardeen's factor made shielding of the ion somewhat less effective for large-angle scattering (Umklapp processes). If we had employed this correction, the importance of Umklapp scattering would be increased and our theoretical values of conductivity would all be reduced bringing them into better agreement with experiment. The second observation concerns the use of a free-electron model. For Na and K this is reasonably acceptable¹² but for the heavier elements it is an unsatisfactory representation and the poor agreement between theory and experiment in the case of Rb and Cs may be due, in large measure, to this cause.

Concerning the second point in our summary, the effect of multiphonon processes on electrical conductivity, we again refer to Table I. The double-phonon processes not involving intermediate states produce about a 4% reduction in the calculated conductivity

at 0°C. The effect increases slightly with the weight of the element except for some anomalous behavior on the part of Cs where it decreases. This may be due to an error in the elastic constants which were used in the calculation of the Debye temperatures. In the numerical calculation we have considered only the shortest set of \mathbf{K}_s but an additional calculation for the next shortest set indicates that such Umklapp processes have a completely negligible effect on the conductivity. From the contributions to d_{00} we may estimate that the effect of n -phonon processes not involving intermediate states goes down as $[(m/M)(\xi/\kappa T)]^n$ at least as far as an order of magnitude approximation is concerned.¹³ We have not calculated the effects of double-phonon transitions involving a single intermediate state, though they are likely to be significant, particularly as regards interference effects.¹⁴ The difficulties which such a calculation entails are considerable, and any work on this would be best based on a thorough investigation of second-order processes in the density matrix formulation of the transport problem.

Finally, as regards experimental detection of multiphonon effects, the last point in our summary, we observe that any manifestation of double-phonon processes would occur as a nonlinearity in resistance as a function of temperature [See Eq. (4.6)]. There is indeed a nonlinearity exhibited at high temperatures in the experimental curve, but it is considerably more than can be accounted for by double-phonon processes alone (about seven times more in the case of Na near the melting temperature). Generation of lattice defects prior to melting, as suggested by MacDonald,¹⁵ is therefore more likely to be the cause of the observed nonlinearity.

¹³ H. D. Vasileff, Bull. Am. Phys. Soc. 4, 36 (1959). Vasileff has made calculations of double-, and triple-phonon transition probabilities, but the details of his work seem to be unpublished.

¹⁴ This has been shown to be the case in semiconductors. See for example T. Holstein, Phys. Rev. 113, 479 (1959); and C. Herring, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961), pp. 60-67.

¹⁵ D. K. C. MacDonald, J. Chem. Phys. 21, 177 (1953); 21, 2097 (1953) and *Report of Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 383.

¹² E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).

APPENDIX: REDUCTION OF THE DOUBLE-PHONON SUMMATION

With the assumptions made in Sec. IV (temperatures above the Debye temperature; elasticity of collisions), determination of the electronic transition probability through two-phonon interaction rests on the calculation of

$$\sum_{\sigma\sigma'} (\sigma_{\max}/\sigma)^2 (\sigma_{\max}/\sigma')^2 [(\delta_+\delta_+'') + (\delta_-\delta_-'') + (\delta_+\delta_-'') + (\delta_-\delta_+'')].$$

Only the absolute values of the wave vectors enter into this expression and, because of elastic collisions, all of the electronic wave vectors terminate on the Fermi sphere so the summation is identical for each of the four terms. The geometry pertinent to the first term, which we designate as I , is indicated in Fig. 1. The summation in σ, σ' may be readily converted as follows:

$$\sum_{\sigma\sigma'} \cdots \rightarrow \sum_{\mathbf{D}} N\Delta_0 (2\pi)^{-3} \int \cdots d^3\sigma'.$$

Using cylindrical coordinates with the origin at the midpoint of \mathbf{D} and the z axis directed along \mathbf{D} axial symmetry exists. Further, the radial integration may be easily performed with the result,

$$I = \sum_{\mathbf{D}} 4\pi N\Delta_0 \sigma_{\max}^4 (2\pi)^{-3} \int_0^{\sigma_{\max}-D/2} \left\{ \ln \left(1 - \frac{2Dz}{\sigma_{\max}^2} \right) + \ln \left(\frac{D+2z}{D-2z} \right)^2 \right\} \frac{dz}{4Dz}. \quad (\text{A1})$$

With the substitutions,

$$y = z/(\sigma_{\max} - \frac{1}{2}D), \quad \alpha = D/2\sigma_{\max},$$

Eq. (A1) may be written

$$I = (\pi/2) N\Delta_0 \sigma_{\max}^3 (2\pi)^{-3} \sum_{\alpha} [I_1 + I_2 - I_3], \quad (\text{A2})$$

where

$$I_1 = \int_0^1 \ln[1 - 4\alpha y(1-\alpha)] (\alpha y)^{-1} dy, \quad (\text{A3a})$$

$$I_2 = \int_0^1 \ln[1 + (1-\alpha)y/\alpha]^2 (\alpha y)^{-1} dy, \quad (\text{A3b})$$

$$I_3 = \int_0^1 \ln[1 - (1-\alpha)y/\alpha]^2 (\alpha y)^{-1} dy. \quad (\text{A3c})$$

If we now substitute ξ for each of the arguments of the logarithm and adjust the integration limits accordingly, Eqs. (A3a, b, and c) are seen to be forms of the Spence integral,¹⁶

$$\text{Rl}(x) = \int_1^x (\xi-1)^{-1} \ln \xi d\xi. \quad (\text{A4})$$

Powell¹⁷ has tabulated $\text{Rl}(x)$ for the following values of the parameter x :

$$\begin{aligned} 0 \leq x \leq 2 & \text{ in steps of } 0.01, \\ 2 \leq x \leq 6 & \text{ in steps of } 0.02. \end{aligned}$$

For values of x not covered by Powell's table the following relation is of use and rather easily verified;

$$\text{Rl}(x) + \text{Rl}(1/x) = (\ln x)^2/2.$$

Because of absolute values a different form is obtained for I_3 when $\alpha \leq 0.5$ and we finally have the result,

$$I_1 = (1/\alpha) \text{Rl}[1 - 4\alpha(1-\alpha)], \quad 0 \leq \alpha \leq 1 \quad (\text{A5a})$$

$$I_2 = (2/\alpha) \text{Rl}[1/\alpha], \quad 0 \leq \alpha \leq 1 \quad (\text{A5b})$$

$$I_3 = (2/\alpha) \{ \text{Rl}(0) + \ln[(1-2\alpha)/\alpha] \ln[(1-\alpha)/\alpha] - \text{Rl}[(1-\alpha)/\alpha] \}, \quad 0 \leq \alpha \leq 0.5 \quad (\text{A5c})$$

$$I_3 = (2/\alpha) \text{Rl}[(2\alpha-1)/\alpha], \quad 0.5 \leq \alpha \leq 1. \quad (\text{A5d})$$

The original double-phonon summation has thus been reduced to

$$\begin{aligned} \sum_{\sigma\sigma'} (\sigma_{\max}/\sigma)^2 (\sigma_{\max}/\sigma')^2 [(\delta_+\delta_+'') + (\delta_-\delta_-'') + (\delta_+\delta_-'') + (\delta_-\delta_+'')] \\ = 4N\Delta_0 \sigma_{\max}^3 (2\pi)^{-3} \sum_{\alpha} \mathfrak{S}(|\alpha|) \\ \times \delta[\mathbf{K} + 2\sigma_{\max}\alpha + \mathbf{K}_s, 0], \quad (\text{A6}) \end{aligned}$$

where

$$\mathfrak{S}(|\alpha|) = (I_1 + I_2 - I_3)\pi/2. \quad (\text{A7})$$

¹⁶ A. Fletcher, J. C. P. Miller, and L. Rosenhead, *An Index of Mathematical Tables* (Scientific Computing Service Limited, London, 1946), pp. 343-344.

¹⁷ E. O. Powell, *Phil. Mag.* **34**, 600 (1943).