

of the elastic constants is larger for BaF₂ than in the case of CaF₂, indicating that anharmonicity effects are more pronounced in the case of BaF₂.

As can be seen, c_{11} and c_{12} vary by about 10% over the temperature range 4.2–300°K, while c_{44} hardly changes at all. A similar behavior is also observed for the alkali halides.¹² The reason for this being that the variation of c_{44} with temperature is caused only by the thermal expansion of the lattice. On the other hand, in the case of c_{11} and c_{12} the shift in the vibrational frequencies of the lattice with temperature also contributes to the temperature dependence¹³ in addition to the contribution of the thermal expansion.

From the values of the elastic constants extrapolated to 0°K, the Debye temperature at 0°K can be com-

puted. Using the procedure of Marcus and Kennedy,¹⁴ a value of 282°K for the Debye temperature at 0°K is determined. Since very-low-temperature specific-heat data for BaF₂ are not available, no direct comparison between the Debye temperatures determined from specific-heat and elastic data can be made. The Debye temperature determined from the lowest temperature (13.79°K) specific-heat data available⁶ is 169°K. The discrepancy may be due to a rapid rise of the Debye temperature in the range 14–0°K.

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to R. T. Smith for the x-ray orientation of the crystal, R. J. Paff for the thermal expansion measurements, and to C. Horak, Sr. and his staff in the grinding shop for the cutting and grinding of the crystal.

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Changes in Electrical Resistance Caused by Incoherent Electron-Phonon Scattering

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(Received 13 March 1964)

A small proportion of the events in which a conduction electron is scattered by an impurity atom involve the emission or absorption of a phonon. An investigation is made of the suggestion that such incoherent electron-phonon interactions may lead to appreciable deviations from Matthiessen's rule. The effect of such processes on the electrical resistivity is found to be too small to be observable.

I. INTRODUCTION

ACCORDING to Matthiessen's rule, the electrical resistance of a dilute alloy is separable into a temperature-dependent part, which is characteristic of the pure metal, and a residual part due to impurities.¹ The deviations that have been observed^{2–4} from this rule have not yet received a satisfactory explanation, for although a number of mechanisms that might cause such deviations have been suggested, none appears to give a numerical value that is sufficiently large.

One of the first such calculations was due to Sondheimer,⁵ who took account of the fact that electron-phonon scattering is inelastic. His solution of the Boltzmann transport equation showed a deviation from Matthiessen's rule too small to agree with experi-

ment. The anisotropy of relaxation time of the conduction electrons in the noble metals has also been calculated,⁶ but was found too small to explain the observed results.

An interesting suggestion was made by Koshino,⁷ who proposed that the scattering of electrons by the thermal motion of the impurities could lead to a significant additional resistance. His result was later criticized on the grounds that in an expansion of the lattice displacements, he had omitted a set of terms which give a contribution almost exactly cancelling the rest of the series. A rigorous demonstration was given⁸ that when the change in electron energy is neglected, the scattering of a single free electron by an impurity atom is quite independent of its thermal motion. No attempt was made to solve the Boltzmann equation using this revised expression for the scattering, and only an intuitive argument was given that the presence of other electrons

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⁸ P. L. Taylor, *Proc. Phys. Soc. (London)* **80**, 755 (1962).

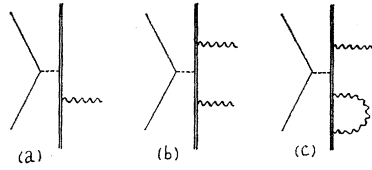


FIG. 1. Inelastic scattering processes.

would not modify the scattering enough to cause any appreciable change in resistance. However, the recent appearance in the literature of some articles⁹⁻¹¹ that question this view indicates that a more careful derivation of this result is necessary.

To this end we shall derive an explicit expression for the scattering probability, avoiding the transformed correlation functions of the earlier paper,⁸ and then show that the solution of the Boltzmann equation leads only to a negligible change in the resistivity.

II. THE SCATTERING PROBABILITY

We consider the scattering of a free electron between states having wave numbers \mathbf{k} and \mathbf{k}' by a potential situated at \mathbf{X} . The dependence of the scattering matrix for this process on the position of the scatterer is given⁸ by

$$T(\mathbf{k}, \mathbf{k}', \mathbf{X}) = \exp(i\mathbf{K} \cdot \mathbf{X}) T(\mathbf{k}, \mathbf{k}'),$$

where \mathbf{K} is $\mathbf{k}' - \mathbf{k}$, and $T(\mathbf{k}, \mathbf{k}')$ is the scattering matrix when the potential is at the origin. The probability of a scattering process occurring in which the lattice containing the impurity atom at \mathbf{X} changes its state from $|X_i\rangle$ to $|X_f\rangle$ is then given by

$$Q(\mathbf{k}, \mathbf{k}') = (2\pi/\hbar) |\langle X_i | T(\mathbf{k}, \mathbf{k}') \exp(i\mathbf{K} \cdot \mathbf{X}) | X_f \rangle|^2 \times \delta(\mathcal{E}_{k'} - \mathcal{E}_k + \mathcal{E}_{if}).$$

Here \mathcal{E}_k is the energy of the electron and \mathcal{E}_{if} the change in energy of the lattice. Because $T(\mathbf{k}, \mathbf{k}')$ does not contain the lattice coordinates it may be removed from the brackets. We next expand the exponential in powers of \mathbf{X} . This is justifiable since the component of $\mathbf{K} \cdot \mathbf{X}$ due to any one crystal mode is always small. If we assume the impurity to have an atomic mass M close to that of the solvent, we may write \mathbf{X} as a sum of creation and annihilation operators¹² for the phonon modes \mathbf{q} . There will be two kinds of term in the expansion—those that change the lattice state and those that do not. These are represented symbolically in Figs. 1 and 2, respectively. We shall consider only first-order processes in inelastic scattering [Fig. 1(a)] and zeroth- and second-order processes in elastic scattering [Figs. 2(a) and 2(b)]. We then find that

$$Q(\mathbf{k}, \mathbf{k}') = (2\pi/\hbar) |T(\mathbf{k}, \mathbf{k}')|^2 \left\{ [1 - \sum_{\mathbf{q}} D_{\mathbf{q}}^2 (2n_{\mathbf{q}} + 1)] \times \delta(\mathcal{E}_{k'} - \mathcal{E}_k) + \sum_{\mathbf{q}} D_{\mathbf{q}}^2 \bar{n}_{\mathbf{q}} \delta(\mathcal{E}_{k'} - \mathcal{E}_k \pm \hbar\omega_{\mathbf{q}}) \right\}.$$

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Here $n_{\mathbf{q}}$ is the average number of phonons of energy $\hbar\omega_{\mathbf{q}}$ present in the crystal, $\bar{n}_{\mathbf{q}}$ is $n_{\mathbf{q}} + 1$ or $n_{\mathbf{q}}$ corresponding to the \pm sign, and

$$D_{\mathbf{q}}^2 = \hbar K^2 / 2MV\omega_{\mathbf{q}},$$

where V is the crystal volume. For simplicity we have assumed the phonon spectrum to be isotropic, and have summed over polarization directions.

Finally, we must take account of the fact that transitions can only occur from occupied to unoccupied electron states. We write

$$P(\mathbf{k}, \mathbf{k}') = f_k (1 - f_{k'}) Q(\mathbf{k}, \mathbf{k}'),$$

where f_k is the probability that the state \mathbf{k} is occupied. This will tend to inhibit the inelastic scattering at low temperatures. At the absolute zero all that remains of the term in braces is

$$(1 - \sum_{\mathbf{q}} D_{\mathbf{q}}^2) \delta(\mathcal{E}_{k'} - \mathcal{E}_k),$$

which represents the reduction of the simple scattering by the zero-point motion of the impurity. One recognizes in this the first two terms of the expansion of $1 - \gamma_0$, the zero-temperature Debye-Waller factor for the crystal.

III. SOLUTION OF THE BOLTZMANN EQUATION

The conductivity tensor, σ , is given¹³ by

$$\sigma = -e^2 \sum_{\mathbf{k}} \mathbf{v}_k \Lambda_{\mathbf{k}} (\partial f_{\mathbf{k}} / \partial \mathcal{E}_{\mathbf{k}}),$$

where \mathbf{v}_k is the electron velocity and $\Lambda_{\mathbf{k}}$ is the vector mean free path, which is found from the Boltzmann transport equation

$$\mathbf{v}_k f_{\mathbf{k}} (1 - f_{\mathbf{k}}) = \sum_{\mathbf{k}'} P(\mathbf{k}, \mathbf{k}') (\Lambda_{\mathbf{k}} - \Lambda_{\mathbf{k}'}).$$

If we assume the first term, $P^{(0)}(\mathbf{k}, \mathbf{k}')$, in the expression for $P(\mathbf{k}, \mathbf{k}')$, representing elastic scattering, to be much greater than all the subsequent terms, we may expand the mean free path and derive an expression for the change in conductivity. Writing

$$P = P^{(0)} + P^{(a)}, \quad \Lambda = \Lambda^{(0)} + \Lambda^{(a)},$$

we have, to first order,

$$\begin{aligned} \mathbf{v}_k f_{\mathbf{k}} (1 - f_{\mathbf{k}}) &= \sum_{\mathbf{k}'} P^{(0)}(\mathbf{k}, \mathbf{k}') (\Lambda_{\mathbf{k}}^{(0)} - \Lambda_{\mathbf{k}'}^{(0)}); \\ \sum_{\mathbf{k}'} P^{(0)}(\mathbf{k}, \mathbf{k}') (\Lambda_{\mathbf{k}}^{(a)} - \Lambda_{\mathbf{k}'}^{(a)}) &= - \sum_{\mathbf{k}'} P^{(a)}(\mathbf{k}, \mathbf{k}') (\Lambda_{\mathbf{k}}^{(0)} - \Lambda_{\mathbf{k}'}^{(0)}). \end{aligned}$$

We assume $T(\mathbf{k}, \mathbf{k}')$ to be a smoothly varying function,

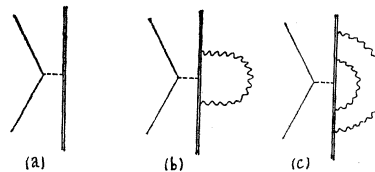


FIG. 2. Elastic scattering processes.

¹³ P. L. Taylor, Proc. Roy. Soc. (London) **A275**, 200 (1963).

so that when the summation over \mathbf{k}' is split into a summation over surfaces of constant energy, $T(\mathbf{k}, \mathbf{k}')$ may be taken to be independent of the energy of the state \mathbf{k}' . This is a good approximation because the scattering probability is only appreciable within the thickness of the Fermi surface, owing to the presence of the factor $f_k(1-f_{k'})$. We now make the substitutions

$$\eta = (\mathcal{E}_k - \zeta)/kT; \quad f_k = (e^\eta + 1)^{-1}$$

$$\rho = \hbar\omega_q/kT; \quad n_q = (e^\rho - 1)^{-1},$$

according to the rules of Fermi and Bose statistics. Here ζ is the chemical potential and kT the Boltzmann energy. We can now also replace K^2 by its average value, K_{av}^2 . After some manipulations one finds that σ is given in terms of $\sigma^{(0)}$, the conductivity calculated for a stationary scatterer, by

$$\sigma = \sigma^{(0)} \left\{ 1 + \sum_q D_q^2 \left[(2n_q + 1) - \int_{-\infty}^{\infty} d\eta \int_0^{\infty} d\mathcal{E}_{k'} \right. \right.$$

$$\left. \left. \times f_k(1-f_{k'}) \tilde{n}_q \delta(\mathcal{E}_{k'} - \mathcal{E}_k \pm \hbar\omega_q) \right] \right\}.$$

We have made use of the fact that

$$\int_{-\infty}^{\infty} f_k(1-f_k) d\eta = 1.$$

Since the summand depends only on the phonon energy, the summation over \mathbf{q} may be replaced by integration over the density of phonon states, $g(\omega)$. A little more algebra reveals that

$$\sigma = \sigma^{(0)}(1 + \alpha),$$

where

$$\alpha = \int_{-\infty}^{\infty} f_k(1-f_k) d\eta \int_0^{\infty} D_\omega^2 g(\omega) \left[\frac{\sinh \rho}{\cosh \rho + \cosh \eta} \right] d\omega.$$

The integral over ω may be interpreted as giving the variation of relaxation time as a function of the electron energy η .

We may examine the form of this expression in the limits of high and low temperatures. Remembering that $\hbar\omega = \rho kT$ we see that α vanishes in the limit of large T , since the density of states has fallen to zero long before the term in brackets has become appreciable.

At zero temperature the term in brackets tends to unity giving, as we expect,

$$\alpha = \int_0^{\infty} D_\omega^2 g(\omega) d\omega = \gamma_0,$$

where $1 - \gamma_0$ is the Debye-Waller factor for zero temperature. The correction term involves only phonons of

small wave number, and so we make the Debye approximation, in terms of which

$$D_\omega^2 g(\omega) = (3\hbar^4 K_{av}^2 T / MV k^2 \Theta^3) \rho,$$

Θ being the Debye temperature and k Boltzmann's constant. Upon substitution and integration over η and ρ we find

$$\sigma \approx \sigma^{(0)} [1 - 2\gamma_0 + \gamma(T)],$$

where

$$\gamma(T) = \frac{3\hbar^2 K_{av}^2}{4 M k \Theta} \left[1 + \frac{2\pi^2}{3} \left(\frac{T}{\Theta} \right)^2 + \dots \right].$$

We note that no assumptions about the isotropy of the electron system have been made in deriving this result.

IV. CONCLUSIONS

The form that we have derived for the variation with temperature of the impurity resistance is shown schematically in Fig. 3. The total resistance is composed of

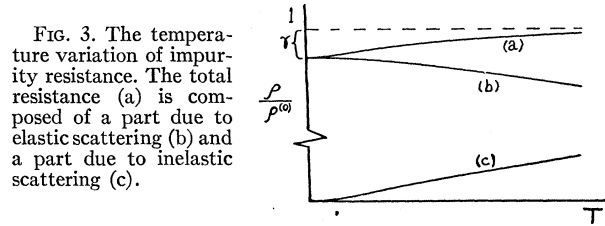


FIG. 3. The temperature variation of impurity resistance. The total resistance (a) is composed of a part due to elastic scattering (b) and a part due to inelastic scattering (c).

two parts, one due to elastic scattering processes, the other to inelastic ones. At the zero of temperature the resistance is entirely due to elastic scattering, and is smaller by an amount γ_0 than the resistance that would be found if the impurity atom were infinitely massive. The factor γ_0 is typically of the order of 10^{-2} .

As the temperature is raised the amount of inelastic scattering increases, while the amount of elastic scattering decreases. However, as this happens the ordinary lattice resistance, which varies as T^5 , starts to become appreciable. Let us consider a highly impure specimen for which the lattice resistance at room temperature, ρ_Θ , is equal to the residual resistance, ρ_0 . Then at low temperatures the total resistance is composed of three parts,

$$\rho \approx 10^{-2} \left(\frac{T}{\Theta} \right)^2 \rho_0 + 500 \left(\frac{T}{\Theta} \right)^5 \rho_\Theta + \rho_0,$$

the first term arising from incoherent scattering and the second from coherent scattering, according to the usual Bloch-Grüneisen theory. We see from this expression that the T^2 term would be hidden by the lattice resistance except at temperatures below $\Theta/40$. This represents a resistance change of less than $10^{-5} \rho_0$, and would not generally be observable.