In conclusion we emphasize that it is essential to include this impurity-induced term in any analysis of the temperature dependence of the resistivity for even the purest metal samples, and, a fortiori, for alloys.

We would like to thank D. L. Mills for several illuminating discussions of this problem, and G. Böbel and D. Sherrington for their comments on and interest in this work.

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*Work in collaboration supported jointly by the Science Research Council and the Consiglio Nazionale delle Ricerche.

†Research Unit of the Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche.

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Temperature Dependence of the Contribution to the Transport Properties from Electron-Phonon Scattering in Dilute Alloys

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(Received 29 October 1970)

A mechanism is suggested to explain the temperature dependence and magnitude of a contribution to the electrical resistivity observed in a number of alloys.

The temperature dependence of the electrical resistivity ρ of pure, nonmagnetic metals should be accurately described by the Bloch-Grüneisen theory.[1] This theory predicts that $\Delta\rho = \rho(T) - \rho(0)$ should vary with temperature like T^5 when $T \ll \Theta_D$, the Debye temperature.

Recently, Caplin and Rizzuto[2] have completed a careful study of $\Delta\rho$ for a number of dilute alloys of Al with nonmagnetic transition-metal impurities. They find a contribution $\Delta(T)$ to ρ with the following properties:

(a) At low temperatures, $\Delta(T) = BT^3$.

(b) The magnitude of B seems independent of the type of impurity present in the alloy. However, B was observed to have a very weak dependence on the residual resistivity ρ_0 of the sample. This dependence is slight; as ρ_0 varies over four orders of magnitude, B changes by less than one order of magnitude. Caplin and Rizzuto suggest that in Al, B is proportional to $\ln\rho_0$.

(c) As ρ_0 is decreased, the range of temperatures over which the T^3 behavior is observed tends to become smaller. As the temperature increases, $\Delta(T)$ appears to become independent of T, but scatter in the data makes this conclusion tentative.

(d) Campbell, Caplin, and Rizzuto[3] have presented a heuristic argument based on the breakdown of wave-vector conservation which leads to an empirical formula that relates B to the high-temperature value of ρ in a number of alloys. They propose that

$$\Delta(T)|_{\text{low } T} = \frac{K}{\Theta_D^2}\left(\frac{d\rho}{dT}\right)_\infty T^3 \qquad (1)$$

with $K = 4.8$ accounts for the magnitude of B for

alloys of Al, Be, Cd, Cu, Ga, Au, Ag, Mn, Sn, In, and Zn. With $K = 4.8$, the magnitude of the temperature-dependent portion of the electrical resistivity at low temperatures for the above systems may be accounted for with a factor of 2. In Eq. (1), $(d\rho/dT)_\infty$ is the temperature coefficient of the resistivity when $T > \Theta_D$.

Since a term $\Delta(T)$ in the low-temperature resistivity of alloys with the properties described in statements (a)-(d) has apparently been observed in a large number of systems (although a complete analysis of the data has been carried out only for the Al-based alloys[2]), we expect that the phenomenon is a general one. The purpose of this paper is to present a simple theory which offers an explanation of the principal features of the data. The breakdown of wave-vector conservation, as suggested in Ref. 3, is an important element in our theory.

Consider a single, parabolic band of electrons, and suppose that they are coupled to a single branch of phonons with a Debye spectrum. An electron of wave vector $\vec{k}$ has energy $E(k) = k^2/2m$, and we use units with $\hbar = 1$.

We take the electron-phonon interaction to have the form

$$H_{ep} = (ig/N^{1/2})\sum_{\vec{q}} q^{1/2} c_{\vec{k}+\vec{q}}^{\dagger} c_{\vec{k}} (a_{\vec{q}} - a_{-\vec{q}}^{\dagger}). \qquad (2)$$

We also include in the Hamiltonian a term that

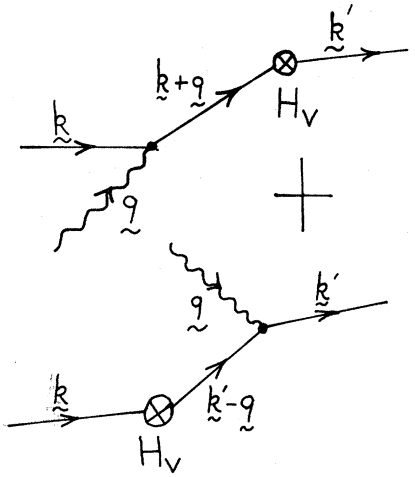

FIG. 1. The process that gives rise to the T^3 term in the low-temperature electrical resistivity of alloys.

describes scattering of the electron by a set of local potentials, randomly distributed in low concentration throughout the host matrix:

$$H_V = \frac{V_0}{N}\sum_{\vec{k}\vec{k}'}\sum_i \exp[i\vec{x}_i\cdot(\vec{k}-\vec{k}')] c_{\vec{k}'}^{\dagger} c_{\vec{k}}, \qquad (3)$$

where $\vec{x}_i$ is the position of the ith impurity.

From standard treatments of the Boltzmann equation, one finds that the transport relaxation rate τ^{-1} appropriate to the electrical resistivity may be written[1]

$$\frac{1}{\tau} = \frac{m}{\xi N k_B T}\sum_{\vec{k}\vec{k}'} \hat{x}\cdot\vec{v}_{\vec{k}}[\hat{x}\cdot(\vec{v}_{\vec{k}}-\vec{v}_{\vec{k}'})] f_0(\vec{k})[1-f_0(\vec{k}')] W(\vec{k},\vec{k}'), \qquad (4)$$

where $W(\vec{k},\vec{k}')$ is the transition rate for scattering from $\vec{k}$ to $\vec{k}'$, $\vec{v}_{\vec{k}} = \vec{k}/m$, $\hat{x}$ is the direction of current flow, ξ is the number of conduction electrons per unit cell, and N the number of unit cells in the crystal.

Consider the contribution to W from the process described graphically in Fig. 1. Only the contribution to τ^{-1} from phonon absorption will be considered explicitly. In the present treatment, the contribution from phonon emission equals that from absorption. From Fig. 1 we have, if v_s is the sound velocity,

$$W(\vec{k},\vec{k}') = 2\pi\sum_{\vec{q}} |M_{\vec{q}}(\vec{k},\vec{k}')|^2 \delta(E(\vec{k}')-E(\vec{k})-v_s q), \qquad (5)$$

where

$$M_{\vec{q}}(\vec{k},\vec{k}') = (igV_0/N^{3/2}) q^{1/2} n_q^{1/2} \sum_i \exp[i\vec{x}_i\cdot(\vec{k}+\vec{q}-\vec{k}')] \{[E(\vec{k}+\vec{q})-E(\vec{k})-v_s q]^{-1} + [E(\vec{k}'-\vec{q})-E(\vec{k})]^{-1}\}. \qquad (6)$$

The crucial feature of the process of Fig. 1 may be appreciated from the first diagram. At low temperatures, only phonons with wave vector q small compared to the Fermi wave vector k_F enter the scattering. Since k is close to k_F in magnitude, the difference $E(\vec{k}+\vec{q})-E(\vec{k})$ will be very small. Indeed, when Eq. (6) is inserted into Eq. (5), both energy denominators diverge as one sums over q, and $W(\vec{k},\vec{k}')$ is singular. Therefore, it is necessary to include the effect of lifetime broadening of the intermediate state in the calculation. We do this by inserting a factor of $i\Gamma$ into the denominators of Eq. (6), where Γ is the inverse lifetime of an electron at the Fermi surface. After this is done, the modified Eq. (6) is inserted into Eq. (5), and then an average over impurity positions is taken. Upon utiliz-

ing the energy-conservation condition, and noting that $v_s \ll v_F$, we have

$$W(\vec{k},\vec{k}') = \frac{2\pi c g^2 V_0^2}{N^2}\sum_{\vec{q}} q n_q \left|\frac{1}{v_F\hat{k}\cdot\vec{q}+E(\vec{q})+i\Gamma}+\frac{1}{-v_F\hat{k}\cdot\vec{q}+E(\vec{q})+i\Gamma}\right|^2 \delta(E(\vec{k}')-E(\vec{k})-v_s q), \tag{7}$$

where c is the impurity concentration. We assume that both $\vec{k}$ and $\vec{k}'$ lie close to k_F. [Note that upon summing the graphs that describe multiple scattering of the incoming or outgoing electron from the same impurity, the factor V_0^2 in Eq. (7) may be replaced by $|\mathcal{T}|^2$ where $\mathcal{T}$ is the t matrix for scattering of an electron at the Fermi surface from a single impurity.]

At low temperatures, the factors of $E(\vec{q})$ in the denominators of Eq. (7) may be ignored. In all circumstances of experimental interest, one will have $v_F q \gg \Gamma$, since the electron mean free path is longer than the thermal phonon wavelength in the dilute alloy at all temperatures. In this limit, one has

$$\int d\Omega(\hat{q})\left|\frac{1}{v_F\hat{k}\cdot\vec{q}+i\Gamma}+\frac{1}{-v_F\hat{k}'\cdot\vec{q}+i\Gamma}\right|^2 = \frac{4\pi^2}{v_F q\Gamma}+O\left(\frac{1}{v_F^2 q^2}\right).$$

The integration is over the direction of the wave vector $\vec{q}$. We then find

$$W(\vec{k},\vec{k}') = \frac{c g^2 V_c V_0^2}{v_s^3 v_F \Gamma N}|E'-E|^2 n(E'-E),$$

where V_c is the volume of the unit cell, $n(x) = [\exp(x/k_B T)-1]^{-1}$, and E and E' are the energies of the states with wave vectors $\vec{k}$ and $\vec{k}'$, respectively. Upon inserting this result into Eq. (4), one has

$$\frac{1}{\tau} = \frac{3\zeta(3)}{\pi^2}\frac{c V_0^2 g^2 V_c^2 m^2}{v_s^3\Gamma}(k_B T)^3. \tag{8}$$

We now discuss the principal features of Eq. (8).

(i) At low temperatures, the electron lifetime is limited by impurity scattering. Then, for our model, $\Gamma = \Gamma_0 = 2\pi c V_0^2 \rho(E_F)$ where $\rho(E_F)$ is the density of states per spin direction at the Fermi level. (Again, by the appropriate graphical summation, V_0^2 may be replaced by the single-impurity t matrix, evaluated at the Fermi energy.) Thus, at low temperatures, the process of Fig. 1 gives a contribution to $\Delta\rho$ that varies with temperature as T^3. Furthermore, since the product cV_0^2 drops out of the right-hand side of Eq. (8), this contribution is independent of both the concentration and type of impurity present in the metal. Thus, we identify the process of Fig. 1 as responsible for the anomalous contribution $\Delta(T)$ to the resistivity discussed in the first portion of the paper. In the present approximation, the very slow variation of $\Delta(T)$ with ρ_0 observed[2] in Al is not produced.

(ii) As the temperature increases, the phonons will contribute to the relaxation rate Γ. We write $\Gamma = \Gamma_0 + \Delta\Gamma(T)$. Since $\Delta\Gamma$ increases with T, the right-hand side of Eq. (8) should exhibit a slower variation with T than the T^3 behavior appropriate to the lowest temperatures. In the pure matrix, one expects[4] $\Delta\Gamma(T) \sim T^3$ for $T \ll \Theta_D$. If this temperature dependence is correct also for the alloy, then $\Delta(T)$ should become temperature independent when $\Delta\Gamma \gg \Gamma_0$. Caplin and Rizzuto[2] indeed find that in Al, $\Delta(T)$ flattens out and becomes independent of temperature as T increases. Furthermore, if $\Delta\Gamma(T)$ can be approximated by the value appropriate to the host matrix, then Eq. (8) suggests that the T^3 term should begin to level off when the lattice resistivity is comparable with the residual resistivity. This criterion appears in fair accord with the data on Al-based alloys. In the more concentrated alloys of Al, the ratio Δ/ρ_0 is not independent of ρ_0 in the regime where $\Delta(T)$ is temperature independent. This suggests that in these systems, the strength of the T^3 term in $\Delta\Gamma(T)$ is affected by the presence of impurities.

The above discussion suggests that the process in Fig. 1 leads to a contribution $\Delta(T)$ to the resistivity that can account for the principal features of the data discussed in the beginning of the paper. The question of the order of magnitude of $\Delta(T)$ remains. For this, one needs an expression for the high-temperature limit of $\Delta\rho$.

At high temperatures, the temperature-dependent portion of ρ is dominated by the first-order scattering produced by H_{ep} alone. The high-temperature form of τ^{-1} is readily computed for our model. For this temperature-dependent portion, we find

$$\frac{1}{\tau}_{\infty} = \frac{m g^2 V_c k_B T}{\pi v_s}. \tag{9}$$

Upon comparing Eq. (9) with the low-temperature form of Eq. (8), a relation of the form proposed by Campbell, Caplin, and Rizzuto [Eq. (1)] linking the magnitude of the high-temperature resistivity with the low-temperature behavior is ob-

tained. For the constant K in Eq. (1) we have

$$K = 3\zeta(3)(q_D/k_F)^2, \tag{10}$$

where $k_F = (3\pi^2\xi)^{1/3}/V_c$ is the Fermi wave vector, and $q_D = (6\pi^2)^{1/3}/V_c$ is the Debye wave vector. Clearly, the value of K obtained from the model falls in the range required to fit the data. We see that K should vary somewhat from host to host, since the parameter ξ appears in the ratio q_D/k_F. In a complete theory, one would expect the precise value of K to depend on properties of the host matrix such as the Fermi-surface geometry, the phonon spectrum, and the details of the electron-phonon coupling at large wave vectors. However, it is clear that we find a contribution to $\Delta\rho$ of very close to the correct magnitude from the process of Fig. 1.

Since the theory presented above does not invoke any special property of the Fermi surface, the phonon spectrum, or the impurity potential, one should expect to observe the contribution $\Delta(T)$ in a wide class of alloy systems. Indeed, this seems to be the case.[3]

As remarked above, Campbell, Caplin, and Rizzuto[3] have suggested that the T^3 behavior of $\Delta\rho$ at low temperatures has its origin in the breakdown of wave-vector conservation in electron-phonon collisions in the disordered crystal. The mechanism of Fig. 1 includes as an essential feature the breakdown of wave-vector conservation, since $k' \neq k+q$ in Fig. 1. However, the small energy difference between the initial and intermediate states is a second crucial feature of this process. If the energy denominators were well behaved, then the contribution from such a second-order process to $\Delta\rho$ would be proportional to the impurity concentration c.

Let us also recall that in the present theory, $\Delta(T)$ appears as an additional contribution to the total resistivity. This contribution appears superimposed on a background which consists of the residual resistivity, and the Bloch-Grüneisen contribution. The heuristic argument of Ref. 3 produces a modification of the Bloch-Grüneisen portion of the electrical resistivity.

We have also calculated the contribution to the temperature-dependent portion ΔW of the thermal resistivity from the process of Fig. 1. We find a term in ΔW proportional to T^2 from the impurity-induced scattering at low temperatures, where $\Gamma \cong \Gamma_0$. In the low-temperature region, this portion of ΔW is independent of the product cV_0^2, just as is the electrical resistivity. Note that the contribution to ΔW from the process in Fig. 1 displays the same temperature dependence as that from the wave-vector–conserving process obtained by treating H_{ep} only in lowest order. The impurity-induced contribution to ΔW is roughly four times larger than the first-order scattering characteristic of the pure matrix. The Lorenz number $L = \Delta\rho/T\Delta W$ formed from the temperature-dependent parts of the electrical and thermal resistivity should thus be independent of temperature at low temperatures, where $\Delta\rho$ varies as T^3. In this region, from our model we estimate that $L = 0.07L_S$, where L_S is the classical Sommerfeld value of the Lorenz number. Detailed experimental studies of the behavior of L at low temperatures will provide a most important test of the theory.

The present discussion indicates that in all real metals, Matthiessen's rule should always break down, provided one examines the behavior of $\Delta\rho$ at temperatures low enough for the impurity-induced T^3 term to dominate the Bloch-Grüneisen T^5 term characteristic of the pure crystal. A similar situation exists in ferromagnetic alloys, where an impurity-induced $T^{3/2}$ term from electron-magnon scattering should dominate $\Delta\rho$ at low temperatures.[5]

It is a pleasure to thank Dr. I. A. Campbell and Dr. A. D. Caplin for a number of stimulating conversations, and for their comments on an early version of this manuscript.

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†On leave from the University of California at Irvine, Fall Quarter 1970.

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