

416 (1966).

¹⁰Here “ N dimensional” means N dimensions greater than $\xi_C(T > T_C) \approx 0.85(l\xi_0)^{0.5}/(t-1)^{0.5}$.

¹¹The terms “paraconductivity” and “magnetoparaconductivity” were suggested, respectively, by R. A. Ferrell, Batsheva Lecture Notes, 1968 (unpublished), and S. J. Williamson.

¹²In experimentally convenient units of $\sigma_n(\text{ohm}^{-1} \text{cm}^{-1})$ and $\gamma(\text{erg cm}^{-3} \text{K}^{-2})$, Eqs. (1a) and (1b) become $\Delta\sigma_{F3}/\sigma_n = 8.9 \times 10^{-6}/[\sigma_n(l\xi_0)^{1/2}(\ln t)^{1/2}] \approx 8.9(\gamma T_C)^{1/2}/[\sigma_n^{3/2}(\ln t)^{1/2}]$; and Eq. (2) becomes $(\xi_0 l)^{1/2} = 10^{-6}(\sigma_n/\gamma T_C)^{1/2}$.

¹³See e.g., P. G. de Gennes, Superconductivity of Metals and Alloys (W. A. Benjamin, Inc., New York, 1966), p. 225.

¹⁴R. E. Glover, Phys. Letters **25A**, 542 (1967), obtains agreement with the more usual form of Eq. (3), with $\ln t$ replaced by $\tau=t-1$, but the two forms differ by <5% at $t \leq 1.1$ and <16% at $t \leq 1.4$.

¹⁵L. J. Barnes and R. R. Hake, Phys. Rev. **153**, 435 (1967); see also Ref. 3.

¹⁶This conjecture can eventually be checked by the application of large H above 4.2°K.

¹⁷A. K. Sinha, J. Phys. Chem. Solids **29**, 749 (1968).

¹⁸A. Calverly and A. C. Rose-Innes, Proc. Roy. Soc. (London), Ser. A **255**, 267 (1960); R. R. Hake, Phys.

Rev. **123**, 1986 (1961); J. F. Cochran, Ann. Phys. (N.Y.) **19**, 186 (1962); B. B. Goodman, J. Phys. Radium **23**, 704 (1962).

¹⁹Here H_{C2} is defined as the field at which the steep linear portion of $V(J=3 \text{ A/cm}^2, J\parallel H)/V_S$ extrapolates to zero; and H_S is defined to be about 5% higher than the field at which $[V(H)-V_S]$ at $(J=3 \text{ A/cm}^2, J\parallel H)$ bends sharply towards the H axis (this sharp bend is “off scale” in Fig. 2).

²⁰Heating at the current contacts may occur at $J=300 \text{ A/cm}^2$ but since ρ is constant to within $\approx 8\%$ for $10 < T < 300^\circ\text{K}$ such heating should, according to Kohler’s rule, have little effect on the ordinary normal-state magnetoresistance.

²¹A merely suggestive application of Kohler’s rule to previous data on pure polycrystalline Ti by R. R. Hake, T. G. Berlincourt, and D. H. Leslie, Phys. Rev. **127**, 170 (1962), yields an ordinary normal-state magnetoresistance of $\Delta\rho(H=50 \text{ kG})/\rho(H=0) \approx 10^{-6}$ for a hypothetical “pure” Ti with $\rho_n = 10^{-4} \Omega \text{ cm}$ as for $\text{Ti}_{84}\text{Mo}_{16}$.

²²A comparison of our data with recent theories of high- H paraconductivity by K. Maki, Progr. Theoret. Phys. (Kyoto) **39**, 897 (1968), and to be published; L. W. Gruenberg, Bull. Am. Phys. Soc. **14**, 420 (1969), and to be published; K. D. Usadel, to be published; and H. J. Mikeska and H. Schmidt, to be published.

NEW EFFECT IN THE ELECTRON-PHONON RESISTIVITY OF DILUTE METAL ALLOYS

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(Received 24 July 1969)

The electron-phonon contribution to the resistivity of a dilute metal alloy at low temperatures is drastically different from that of the ideally pure host metal if the conduction-electron cross section for impurity scattering varies with energy on a scale comparable with or less than the Debye energy of the host metal. Experimentally the effect should be of particular importance for magnetic or nearly magnetic transitional impurities in appropriate nontransitional hosts.

Consider an ideally pure metal A in which is dissolved a small concentration c of a dissimilar metal B . Denote by $\rho_{\text{ep}}^0(T)$ the electron-phonon (el-ph) resistivity of the pure metal A at temperature T and by $\tau_0(\epsilon_{\vec{k}}) = \tau_0(\epsilon_{\vec{k}}; c, T)$ the conduction-electron relaxation time for elastic scattering from the B impurities in the dilute binary alloy. The conduction-electron energy associated with the momentum state $\hbar\vec{k}$ is $\epsilon_{\vec{k}}$. In this Letter we point out that the resistivity which results from el-ph scattering in the alloy, $\rho_{\text{ep}}(T, c)$, is appreciably different from $\rho_{\text{ep}}^0(T)$, i.e.,

$$[\rho_{\text{ep}}(T, c) - \rho_{\text{ep}}^0(T)] / \rho_{\text{ep}}^0(T) > 1,$$

if, in the region of the Fermi energy ϵ_F , $\tau_0(\epsilon_{\vec{k}})$ varies with $\epsilon_{\vec{k}}$ on a scale comparable with or less than the Debye energy $\hbar\omega_D$ of the host metal.

In the latter situation the difference $\rho_{\text{ep}}(T, c) - \rho_{\text{ep}}^0(T)$ is a direct consequence of the inelasticity of the el-ph scattering event. For spherical energy bands coupled to an isotropic acoustic-phonon field we obtain the simple result

$$\rho_{\text{ep}}(T, c) = \rho_{\text{ep}}^0(T) [1 + a^2] \quad (1)$$

for temperatures sufficiently low that $\rho_0 \gg \rho_{\text{ep}}^0(T)$, that is, $T \ll T_0(c)$, where $\rho_{\text{ep}}^0(T_0) \equiv \rho_0$. Here ρ_0 denotes the impurity resistivity $m/ne^2\tau_0(\epsilon_F)$, and

$$a = \hbar\omega_F [\partial \ln \tau_0(\epsilon_k) / \partial \epsilon_k]_{\epsilon_k = \epsilon_F}, \quad (2)$$

where $\omega_F = sk_F$, s denotes the isotropic sound velocity, k_F the Fermi wave vector, and m , n , and e the electronic mass, number density, and charge, respectively. The quantities a and ρ_0

can depend on c and T through their dependence on τ_0 .

The main impact of our result is that the temperature-dependent component of the resistivity of a dilute alloy at low temperatures is not even approximately given by the pure host resistivity $\rho_{\text{ep}}^0(T)$ (Matthiessen's rule) when the electron-impurity scattering is significantly energy dependent. Experimentally the effect will be of particular importance ($a \geq 1$) for dilute alloy systems in which the impurity is either magnetic or nearly magnetic, i.e., transitional impurities in appropriate nontransitional hosts. It would also be of importance in degenerate semiconductors ($a \sim \hbar\omega_F/\epsilon_F$) where, in the absence of many-body effects, a can be of the order of unity.

The modified el-ph resistivity described by (1), and by an extension of (1) (given below) to the higher temperature regime $T > T_0$, is probably the key to the understanding of the remarkable resistive anomalies observed in a large number of alloy systems over a wide range of temperatures.¹ For "Kondo systems," Eq. (1) clearly accounts for the curious observation that when the known host el-ph resistivity $\rho_{\text{ep}}^0(T)$ is subtracted from the total alloy resistivity, $\rho_A(T, c)$, a marked resistance minimum is still observed in the so obtained $\rho_A(T, c) - \rho_{\text{ep}}^0(T)$ data.² Equation (1) relates the anomalous el-ph contribution to the electron-diffusive thermoelectric power.

Our discussion of the alloy resistivity starts from the Ziman³-type formula,

$$\rho_A(T, c) = \frac{1}{2k_B T} \sum_{\vec{k}, \vec{k}'} [V_0(\vec{k}, \vec{k}') + V_{\text{ep}}^{(0)}(\vec{k}, \vec{k}')] \times (\varphi_{\vec{k}'}^* - \varphi_{\vec{k}}^*)^2 \left| \frac{e}{\Omega} \sum_{\vec{k}} \vec{v}_{\vec{k}} \varphi_{\vec{k}} \frac{\partial f_{\vec{k}}^0}{\partial \epsilon_{\vec{k}}} \right|^{-2}, \quad (3)$$

where $\varphi_{\vec{k}}^* (\partial f_{\vec{k}}^0 / \partial \epsilon_{\vec{k}})$ defines the departure of the conduction-electron distribution function $f_{\vec{k}}$ from its equilibrium value $f_{\vec{k}}^0$, k_B denotes Boltzmann's constant, Ω the volume, $\vec{v}_{\vec{k}}$ the electronic group velocity, and V_0 and $V_{\text{ep}}^{(0)}$ the linearized transition rates³ for electron-impurity and el-ph scattering, respectively, the latter being appropriate for the ideally pure host. Equation (3) follows from the linearized Boltzmann equation for $\varphi_{\vec{k}}^*$ for combined electron-impurity, el-ph scattering. We have suppressed spin and band indices and have considered the phonon system to be at equilibrium. In order to indicate the origin of the new terms in the el-ph contribution to $\rho_A(T, c)$ it will be sufficient to consider a spher-

ical energy band $\epsilon_{\vec{k}} = \epsilon_k$ coupled to an isotropic acoustic-phonon field $\hbar\omega_{\lambda}(\vec{q}) = \hbar s q$. In the more general situation in which these assumptions are relaxed the results will not differ qualitatively from those obtained here.

We first note that in the low-temperature regime, $T \ll T_0(c)$, the function φ_k is negligibly different from that given by the solution of the Boltzmann equation for impurity scattering alone,³

$$\varphi_{\vec{k}} = -e \vec{E} \cdot \vec{v}_{\vec{k}} \tau_0(\epsilon_k), \quad T \ll T_0(c). \quad (4)$$

\vec{E} denotes the electric field. It is this function which must be used in (3) to evaluate the el-ph contribution to $\rho_A(T, c)$ at low temperatures.

When (4) is substituted into (3) the term proportional to V_0 reduces to a familiar expression for the impurity resistivity,⁴

$$\rho_{\text{imp}}(T, c) = \frac{\rho_0}{\int_0^\infty d\epsilon_k [\tau_0(\epsilon_k) / \tau_0(\epsilon_F)] (\partial f_k^0 / \partial \epsilon_k)}, \quad (5)$$

where, in the integrand, an energy dependence of the electronic group velocity has been neglected relative to the energy dependence of $\tau_0(\epsilon_k)$.

The term proportional to V_{ep}^0 , i.e., the el-ph contribution to $\rho_A(T, c)$, may be evaluated on the lines of the standard calculation of this quantity.⁵ The new feature is that in computing the difference, $\delta\varphi(\vec{k}, \vec{k}')^2 = (\varphi_{\vec{k}'}^* - \varphi_{\vec{k}}^*)^2$, for the inelastic el-ph scattering event, there will be a contribution arising from the increment in $\tau_0(\epsilon_k)$ as well as from the change in the electronic group velocity $\vec{v}_{\vec{k}}$. Denote the latter contribution by $\delta\varphi_0(\vec{k}, \vec{k}')^2$. Let us assume that $\tau_0(\epsilon)$ is analytic in the region of ϵ_F so that we may expand $\tau(\epsilon_k)$ in a Taylor's series about ϵ_F . Retaining only the zeroth- and first-order terms in this expansion the quantity $\delta\varphi^2$ is⁶

$$\delta\varphi(\vec{k}, \vec{k}')^2 = \delta\varphi_0(\vec{k}, \vec{k}')^2 (1 + a^2), \quad (6)$$

$$\delta\varphi_0(\vec{k}, \vec{k}')^2 = \frac{1}{3} [eE q \hbar \tau_0(\epsilon_k) / m]^2 (\vec{q} = \vec{k} - \vec{k}'), \quad (7)$$

where a is given by (2) and we have neglected terms of relative magnitude $\hbar\omega_D/\epsilon_F$ and $k_B T/\epsilon_F$. A term linear in a , contributing to $\delta\varphi^2$, is canceled by an equal term of opposite sign on accounting for both processes of emission and absorption of a phonon quanta. In what follows we shall replace $\tau_0(\epsilon_k)$ by $\tau_0(\epsilon_F)$ in the above expression for $\delta\varphi_0^2$. This means that we shall be disregarding terms of relative order $k_B T a / \hbar\omega_s$. The neglect of these terms, which will be retained in a detailed account⁶ of the present work, avoids the explicit presentation of some cumbersome algebraic expressions in the extension of

the result (1) to higher temperatures. (In the illustrative calculation to be presented at the end of the present communication these terms would contribute superfluously.) With $\tau(\epsilon_k) = \tau(\epsilon_F)$, Eq. (7) for $\delta\varphi_0^2$ is the expression for $\delta\varphi^2$ which ordinarily determines the host resistivity, $\rho_{ep}^0(T)$.⁵ The denominator of (3) is proportional to the square of the integral in Eq. (5). Thus from (3) and (5)-(7) the low-temperature el-ph contribution is simply

$$\rho_{ep}(T, c) = \rho_{ep}^0(T)(1 + a^2)(\rho_{imp}/\rho_0)^2, \quad (8)$$

$$T \ll T_0(c),$$

which reduces to (1) on neglecting the difference between ρ_0 and ρ_{imp} at low T . We note that the derivation of (8) is independent of the details of the el-ph coupling constant. If τ_0 is proportional to c and independent of T , a is a constant. Thus for "simple" host metals for which $\rho_{ep}^0 \sim T^5$ ($T \ll \theta_D$), the coefficient of the T^5 term observed for the impure metal is $1 + a^2$ times larger than that of the ideally pure metal. Note also that $T_0 \rightarrow 0$ as $c \rightarrow 0$, so that the anomalous term in (8) is absent in the limit $c \rightarrow 0$.

At higher temperatures, $T \gtrsim T_0(c)$, φ_k is no longer given by (4). We may get a qualitatively correct expression for $\rho_{ep}(T, c)$ in this regime by using (4) with $\tau_0(\epsilon)$ replaced by $\tau(\epsilon)$, where

$$\tau(\epsilon) = [\tau_0(\epsilon)^{-1} + \tau_{ep}^0{}^{-1}]^{-1} \approx \tau_0(\epsilon)\rho_0/[\rho_0 + \rho_{ep}^0(T)]. \quad (9)$$

In (9), τ_{ep}^0 denotes an energy-independent relaxation time⁷ for el-ph scattering in the pure host metal. Equation (9) expresses the approximation that at a temperature T only a fraction $\rho_0/[\rho_0 + \rho_{ep}^0(T)]$ of electrons are distributed according to the impurity distribution (4). It follows from (9) that in place of (8) we have the formula

$$\rho_{ep}(T, c) = \rho_{ep}^0(T) \left\{ 1 + \frac{a^2}{[1 + \rho_{ep}^0(T)/\rho_0]^2} \right\} \quad (10)$$

for high⁸ and low temperatures, where again we have neglected the difference between $\rho_{imp}(T, c)$ and ρ_0 . Clearly, as the magnitude of $\rho_{ep}^0(T)$ exceeds ρ_0 with increasing T the anomalous contribution to $\rho_{ep}(T, c)$ diminishes, as it should. A more general calculation of the anomalous contribution to $\rho_{ep}(T, c)$ will be presented elsewhere.⁶

We define a "subtracted" resistivity $\Delta(T, c) \equiv \rho_A(T, c) - \rho_{ep}^0(T)$. The anomalous contribution to $\Delta(T, c)$ is $\Delta_2(T, c) \equiv \rho_{ep}(T, c) - \rho_{ep}^0(T)$. As an illustrative calculation Eq. (10) has been used to

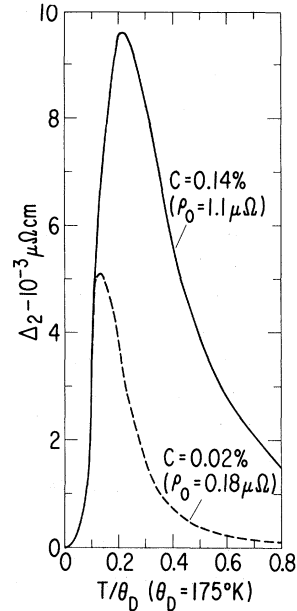


FIG. 1. $\Delta_2(T, c) = \rho_{ep}(T, c) - \rho_{ep}^0(T)$ versus temperature for two dilute Au:Fe alloys, estimated from Eq. (10) as explained in the text. The residual resistivity of each alloy is indicated. The value of $\rho_{ep}^0(T)$ for pure Au was obtained from Ref. 11.

estimate $\Delta_2(T, c)$ for two dilute Au:Fe alloys, $c = 0.02$ and 0.14 at. % Fe. The results are shown in Fig. 1 as a function of temperature. In the absence of a suitable theoretical expression for $\tau_0(\epsilon_k)$, for these alloy systems the key parameter, a , was obtained empirically from the observed low-temperature thermoelectric power $S(T, c)$ of the alloys⁹:

$$a(T, c) = (\hbar\omega_s/\epsilon_F)[S(T, c)/S_0] \quad [T \ll T_0(c)], \quad (11)$$

where S_0 denotes the "free-electron" value ($\pi^2 k_B^2 T / 3e\epsilon_F$). In identifying the right-hand side of (11) with a we have assumed that the usual $\partial \ln \tau(\epsilon) / \partial \epsilon$ formula for $S(T, c)$ is valid for scattering from magnetic impurities.¹⁰ The resulting $\Delta_2(T, c)$ correlates both qualitatively and quantitatively with measurements of $\Delta(T, c)$ taken on Au:Fe¹¹ and other^{11, 12} dilute magnetic impurity systems. We expect similar results for nonmagnetic transitional impurities (virtual bound states) and a study of these¹³ and other⁶ systems is to be published.

We thank C. B. Duke, A. J. Bennett, and I. Giaever of this laboratory and W. A. Harrison and J. R. Schrieffer for lively discussions of this work.

¹These anomalies are usually presented in the context of deviations from Matthiessen's rule, e.g., J. O.

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²Grüneisen, Ref. 1; Gerritsen and Linde, Ref. 1; W. B. Pearson, *Phil. Mag.* **46**, 911 (1955) (footnote, p. 915); Domenicali and Christenson, Ref. 1.

³J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), Chap. VII.

⁴N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936).

⁵See, for example, Ref. 3, pp. 357-360.

⁶M. J. Rice, to be published. It is shown that the retention of only the first derivative in the expansion of τ_0 is valid in the limit of small concentrations.

⁷For metals, $(\partial \ln \tau_{ep} / \partial \epsilon)_{\epsilon = \epsilon_F} \sim \epsilon_F^{-1}$.

⁸I.e., high compared with $T_0(c)$ but small compared with $T_s = (\hbar \omega_s / k_B a)$ (since we have neglected terms of relative size T/T_s).

⁹D. K. C. MacDonald, W. B. Pearson and I. M. Templeton, *Proc. Roy. Soc. (London), Ser. A* **266**, 161

(1962). The dilute Au:Fe thermoelectric data can be represented at low temperatures by the formula $S = A(k_B/e)T/(T+T_0')$ [A. M. Guenault, quoted by J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **34**, 372 (1965)]. We took $A = 0.2$, $T_0' = 1^\circ\text{K}$ for both of the alloys quoted in the text. This gives $a \sim 1$ at $T \sim 10^\circ\text{K}$, and $a \sim 12$ in the low-temperature limit.

¹⁰We have checked this assumption by explicitly differentiating the theoretical formula for $\tau_0(\epsilon)$ obtained within the s - d exchange model. [See, for example, Y. Nagaoka, *Progr. Theoret. Phys. (Kyoto)* **39**, 533 (1968).] The $\partial \ln \tau_0 / \partial \epsilon$ formula differs from that rigorously obtained by evaluating the appropriate Onsager coefficients [K. Maki, *Progr. Theoret. Phys. (Kyoto)* **41**, 586 (1969)] only by a numerical constant of the order of unity. We thank D. R. Hamann for a discussion of this point.

¹¹Domenicali and Christenson, Ref. 1.

¹²Gerritsen and Linde, Ref. 1.

¹³M. J. Rice and O. Bunce, to be published. Similar effects will occur in the el-ph contribution to the thermal resistivity. More generally, we note that a strongly energy-dependent electron-impurity cross section will modify any "ideal" resistivity that results from inelastic electron scattering at low temperatures. Thus we expect corrections, similar to those found here for the el-ph resistivity, to result for the resistivities arising from electron-electron and electron-magnon scattering.

FAR-INFRARED RECOMBINATION RADIATION FROM IMPACT-IONIZED SHALLOW DONORS IN GaAs †

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(Received 24 September 1969)

Radiation corresponding to transitions from excited shallow donor states and from conduction-band states to the donor ground state has been observed in impact-ionized GaAs at temperatures near 4.2°K. Spectral measurements show a main peak at a wavelength of 282 μ (4.4 meV), corresponding to a $2p \rightarrow 1s$ transition, and a broader continuum extending to higher photon energies. A total radiated power of 10^{-7} W has been measured corresponding to an external quantum efficiency of about 10^{-6} .

The far-infrared photoconductivity spectra of shallow donor states in high-purity epitaxial GaAs have been studied recently at temperatures near 4.2°K, and the Zeeman splitting of the donor levels has been measured in magnetic fields up to 50 kG.¹⁻³ In this Letter we report the observation of recombination radiation involving such states, as well as measurements of the emission spectra and of output power. To our knowledge the only previous evidence of recombination radiation associated with shallow impurity states was observed for impact-ionized germanium⁴ at 4.2°K; however, the detected power was quite

low (3×10^{-12} W) and no spectral measurements were reported.

The high-purity epitaxially grown GaAs samples used in the present work were similar to those studied in the photoconductivity experiments.^{3,5} Most of the measurements were made on a 0.4-mm-thick epitaxial layer grown on a semi-insulating substrate. For this sample a shallow-donor concentration of $N_D = 2.5 \times 10^{14}$ cm⁻³ and a total acceptor concentration of $N_A = 1.6 \times 10^{14}$ cm⁻³ were determined from an analysis of the temperature dependence of the Hall constant using the usual single-donor statistics.