[41] S. J. Gregg, in *Chemisorption*, edited by W. E. Garner (Butterworths, London, 1957), pp. 68–75.

[42] Although H_2O was not studied, this is a reasonable conclusion from the results with O_2 and CO_2 obtained by D. Brennan, D. O. Hayward, and B. M. W. Trapnell, Proc. Phys. Soc. (London) A256, 81 (1960); D. Brennan and F. H. Hayes, Phil. Trans. Roy. Soc. London A258, 347 (1965).

[43] J. A. Appelbaum and W. F. Brinkman, Phys. Rev. B 2, 907 (1970).

[44] L. N. Lieberman, D. R. Fredkin, and H. B. Shore, Phys. Rev. Letters 22, 539 (1969).

[45] C. A. Neugebauer, in *Structure and Properties of Thin Films*, edited by C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea (Wiley, New York, 1959), pp. 358–369.

[46] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1956), 2nd ed., Chap. 9, p. 219.

[47] D. C. Tsui, Solid State Commun. 7, 91 (1969).

[48] J. A. Appelbaum, J. C. Phillips, and G. Tzouras, Phys. Rev. 160, 554 (1967).

[49] U. Gradmann and J. Müller, Phys. Status Solidi 27, 313 (1968).

[50] E. Grünbaum and R. Schwartz, J. Appl. Phys. 40, 3364 (1969).

[51] V. M. Kosevich, L. S. Palatnik, and L. E. Chernyakova, Fiz. Metal. i Metalloved. 25, 568 (1968) [Phys. Metals Metallog. 25, 205 (1968)].

[52] C. A. Neugebauer, in *Physics of Thin Films II*, edited by George Hass and Rudolf E. Thun (Academic, New York, 1964), pp. 1–59; L. Holland, *Vacuum Deposition of Thin Films* (Chapman and Hall, London, 1963), pp. 205–208.

PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Anomalous Electron-Phonon Transport Properties of Impure Metals. I. The Electrical Resistivity

M. J. Rice
General Electric Research and Development Center, Schenectady, New York 12301

and

O. Bunce
Parkhurst Institute, Isle of Wight, England

(Received 2 January 1970)

The electron-phonon contribution $\rho_{ep}(T, c)$ to the resistivity of an impure metal, or dilute metal alloy, can be drastically different from that of the ideally pure metal, $\rho^0_{ep}(T)$, if, in the region of the Fermi energy, the conduction-electron relaxation time $\tau_0(\epsilon)$ for impurity scattering varies with energy ϵ on a scale comparable to or less than the Debye energy $\hbar\omega_D$ of the metal. This effect is a consequence of the sensitivity of the (inelastic) electron-phonon resistivity to any energy-dependent component in the nonequilibrium electron-distribution function. We present a working formula for the effect and indicate several important consequences for nontransitional metals containing magnetic or nonmagnetic transitional impurities. In the limit of small impurity concentrations c, the alloy and host electron-phonon resistivities are connected to the electron-diffusion thermopower $S(T, c)$ of the alloy via the simple relation $\rho_{ep}(T, c) \simeq \rho^0_{ep}(T)\, \{1 + (\hbar\omega_D/\epsilon_F)^2\, [S(T, c)/S_0(T)]^2\}$, where S_0 denotes the "free-electron" thermopower. More generally, $\rho_{ep}(T, c)$, and also $\rho_{imp}(T, c)$, the resistivity resulting from impurity scattering, are expressed in terms of the first and second derivatives of τ_0 at the Fermi energy ϵ_F. The anomalous electron-phonon resistivity will cause sharp peaks to appear in the atomic-resistivity temperature curves of very dilute magnetic-impurity systems (e.g., *Cu*Fe, *Au*Fe, *Au*Mn). Experimentally, measurements of deviations from Matthiessen's rule should furnish useful information on the energy dependence of the electron-impurity scattering.

I. INTRODUCTION AND SUMMARY

This paper is the first of a series of papers which deals with the influence of a very energy-dependent electron-impurity scattering cross section on the electron-phonon contributions to the electronic transport properties of an impure metal or dilute metal alloy. It is devoted to a discussion of the electrical resistivity.

Suppose a small concentration c of metallic impurity atoms is dissolved in a pure metal. Let $\rho^0_{ep}(T)$ denote the electron-phonon resistivity of the pure metal at temperature T and

$$\tau_0(\epsilon_{\vec{k}};\, c,\, T) = \tau_0(\epsilon_{\vec{k}}) \ ,$$

the conduction-electron relaxation time which ensues for elastic scattering from the impurity atoms. We assume the presence of a single paramagnetic conduction band in which the energy of an electron in the Bloch momentum state $\hbar\vec{k}$ is $\epsilon_{\vec{k}}$. The essential new finding[1] of our work is that the electrical resistivity which results from electron-phonon (ep) scattering *in the alloy*, $\rho_{ep}(T, c)$, is appreciably different from $\rho^0_{ep}(T)$ if, in the region of the Fermi energy ϵ_F, the relaxation time $\tau_0(\epsilon)$ varies with energy ϵ on a scale comparable to or less than the Debye energy $\hbar\omega_D$ of the pure metal. For spherical energy bands coupled to an isotropic acoustic-phonon field, we will obtain the simple result

$$\rho_{ep}(T, c)=\rho^0_{ep}(T)\,[1+a_0(T, c)^2] \tag{1.1}$$

for temperatures sufficiently low that $\rho_0 \gg \rho^0_{ep}(T)$, that is, $T \ll T_0(c)$, where $\rho_0(T_0, c)=\rho^0_{ep}(T_0)$. Here $\rho_0(T, c)$ denotes the impurity resistivity $[m/ne^2 \times \tau_0(\epsilon_F\,; T, c)]$ and

$$a_0(T, c)=\hbar\omega_F\left(\frac{\partial \ln\tau_0(\epsilon_k;\, T, c)}{\partial\epsilon_k}\right)_{\epsilon_k=\epsilon_f}, \tag{1.2}$$

where $\omega_f = sk_f$; s denotes the isotropic sound velocity; k_f the Fermi wave vector; and m, e, and n the electronic mass, charge, and number density, respectively. As will be seen in the subsequent text, the modification of the alloy ep resistivity relative to the pure-metal value is a consequence of the sensitivity of the inelastic ep resistivity to any energy-dependent component in the nonequilibrium electronic distribution function. For small concentrations, Eq. (1.1) is approximately generalized to higher temperatures, $T > T_0$, by the result

$$\rho_{ep}(T, c)=\rho^0_{ep}(T)\left(1+\frac{a_0^2}{[1+\rho^0_{ep}(T)/\rho_0]^2}\right), \tag{1.3}$$

where, for breivty, we have dropped the arguments of a_0 and ρ_0. Formulas more general than (1.3) will be derived. Equations (1.1) and (1.3) serve amply to illustrate in this introductory section the new effects with which this paper is concerned.

The important consequence of (1.3) is that the temperature-dependent component of the resistivity of a dilute alloy or impure metal at low temperatures ($T \lesssim T_0$) is not even approximately given by the pure-host resistivity $\rho^0_{ep}(T)$ (*Matthiessen's Rule*) when the electron-impurity scattering is significantly energy dependent. Experimentally, this effect will be of particular importance ($a_0 \gtrsim 1$) for dilute-alloy systems in which the impurity is either magnetic or nearly magnetic, i.e., transitional impurities in appropriate nontransitional hosts. Perhaps the most significant indication of a strongly energy-dependent electron-impurity scattering in these alloy systems is the experimental observation of the anomalously large thermoelectric powers of these alloys.[2] If the celebrated $\partial \ln\tau_0/\partial\epsilon$ formula[3] is used to connect the absolute thermopower S to the first energy derivative of τ_0 at ϵ_F, then the key parameter a_0 entering (1.3) is obtained from the observed thermopower by the formula

$$a_0(T, c)\simeq(\hbar\omega_F/\epsilon_F)\,[S(T, c)/S_0(T)] \quad (T<T_0), \tag{1.4}$$

where S_0 denotes the free-electron value $S_0 = (\pi^2k_B^2T/3e\epsilon_F)$. For typical noble-metal magnetic-impurity systems, such as is formed by a few hundred ppm of Fe or Mn in Cu or Au, Eq. (1.4) yields magnitudes of a_0 in excess of unity for temperatures at and below roughly $\Theta_D/10$.[4]

Presumably, the effect described by (1.3) is also important for degenerate semiconductors ($a_0 \sim \hbar\omega_D/\epsilon_F$) where, in the absence of many-body effects, a_0 can be found to be of the order of unity.

The modification of the ep resistivity by the energy dependence of the impurity scattering has consequences relevant to the following particular situations: (a) the empirical determination of $\rho^0_{ep}(T)$ for noble, and possibly other metals from specimens containing small traces of transitional impurities; (b) the presentation and interpretation of resistivity data on dilute local-moment alloys based on the validity of Matthiessen's Rule; (c) the understanding of remarkable deviations from Matthiessen's Rule observed[5] in a large number of dilute-alloy systems at temperatures low and intermediate relative to Θ_D; (d) the measurement of $[\rho_{ep}(T, c) - \rho^0_{ep}(T)]$ as a probe of the energy dependence of τ_0.

Our discussion of the electrical resistivity starts from a Ziman type of formula[6] in which the deviation of the electron-distribution function from its equilibrium value is taken to be of a simple but plausible superposition of the solutions of the linearized Boltzmann equations for impurity scattering and ep scattering alone. With this ansatz, both the impurity and ep contributions to the alloy resistivity are evaluated for a spherical band of electrons. An isotropic acoustic-phonon field is assumed. The results are expressed in terms of the pure-metal resistivity $\rho^0_{ep}(T)$, ρ_0, and parameters (like a_0) related to the first and second energy derivatives of τ_0 evaluated at ϵ_F. In the limit of low concentrations, the results for ρ_{ep} reduce to (1.3). Explicit calculations of the magnitude of the new terms are performed for several well-known dilute local-moment alloy systems like *Au*Fe and *Cu*Fe. The theory is also discussed for the case of nonmagnetic transitional alloys, and calculations are presented for the nearly-local-moment alloys[7] *Al*Cr and *Al*Mn. The modification of the impurity resistivity by the energy dependence of $\tau_0(\epsilon_{\vec{k}})$ is necessarily also considered. The results of the theoretical study and of the explicit computations are discussed in the light of the points (a)–(d) listed in the previous paragraph.

II. MODEL AND GENERAL CONSIDERATION

Our derivation of the electrical resistivity of a dilute alloy starts from the linearized Boltzmann equation for combined electron-impurity electron-phonon scattering:

$$-e\vec{\mathrm{E}}\cdot\vec{\mathrm{v}}_{\vec{\mathrm{k}}}\frac{\partial f^0_{\vec{\mathrm{k}}}}{\partial\epsilon_{\vec{\mathrm{k}}}}=\left(\varphi_{\vec{\mathrm{k}}}\frac{\partial f^0_{\vec{\mathrm{k}}}}{\partial\epsilon_{\vec{\mathrm{k}}}}\middle/\tau_0(\epsilon_{\vec{\mathrm{k}}};\;T,c)\right)+P^0_{\mathrm{ep}}\varphi_{\vec{\mathrm{k}}}\,, \tag{2.1}$$

where $\vec{\mathrm{E}}$ denotes the electric field, $\vec{\mathrm{v}}_{\vec{\mathrm{k}}}=\partial\epsilon_{\vec{\mathrm{k}}}/\partial\vec{\mathrm{k}}\hbar$ the electronic group velocity, and the function $\varphi_{\vec{\mathrm{k}}}$ is the usual function[6] that specifies the deviation of the conduction-electron distribution function from its Fermi-Dirac equilibrium distribution $f^0_{\vec{\mathrm{k}}}$,

$$f_{\vec{\mathrm{k}}}-f^0_{\vec{\mathrm{k}}}=-\varphi_{\vec{\mathrm{k}}}\frac{\partial f^0_{\vec{\mathrm{k}}}}{\partial\epsilon_{\vec{\mathrm{k}}}}\,. \tag{2.2}$$

The first term of the right-hand side of (2.1) is the effect of the elastic impurity scattering, characterized by the energy-dependent relaxation time $\tau_0(\epsilon_{\vec{\mathrm{k}}};c,T)$. The latter quantity may depend on both the absolute temperature T and the concentration of impurities c. For brevity, we will exhibit the possible dependence of τ_0 on T and c only when we wish to stress this possibility; otherwise, we shall merely write $\tau_0(\epsilon_{\vec{\mathrm{k}}})$. The second term on the right-hand side of (2.1) denotes the linearized ep collision integral[8] appropriate for the pure metal,

$$P^0_{\mathrm{ep}}\varphi_{\vec{\mathrm{k}}}\equiv\frac{2\pi}{\hbar}\sum_{\vec{\mathrm{q}}}\frac{V^0_{\mathrm{ep}}(\vec{\mathrm{k}},\vec{\mathrm{k}}+\vec{\mathrm{q}})(\varphi_{\vec{\mathrm{k}}+\vec{\mathrm{q}}}-\varphi_{\vec{\mathrm{k}}})}{k_BT}\quad, \tag{2.3}$$

where

$$\begin{aligned}V^0(\vec{\mathrm{k}},\vec{\mathrm{k}}+\vec{\mathrm{q}})&=(2\pi/\hbar)\,|\lambda(q)|^2n^0(\hbar\omega_q)\\&\times[f^0_{\vec{\mathrm{k}}}(1-f^0_{\vec{\mathrm{k}}+\vec{\mathrm{q}}})\,\delta(\epsilon_{\vec{\mathrm{k}}+\vec{\mathrm{q}}}-\epsilon_{\vec{\mathrm{k}}}-\hbar\omega_q)+f^0_{\vec{\mathrm{k}}+\vec{\mathrm{q}}}(1-f^0_{\vec{\mathrm{k}}})\\&\times\delta(\epsilon_{\vec{\mathrm{k}}+\vec{\mathrm{q}}}-\epsilon_{\vec{\mathrm{k}}}+\hbar\omega_q)]\,.\end{aligned} \tag{2.4}$$

The expression (2.4) for the linearized ep transition rate considers a spherical band of electrons coupled to an isotropic acoustic-phonon field $\hbar\omega_q=\hbar sq$ via a coupling constant $\lambda(\vec{\mathrm{q}})$. When an explicit knowledge of the q dependence of $\lambda(q)$ is required, we shall assume that $|\lambda(q)|^2\propto q$ for small $q/2k_F$. However, in the limit of small concentrations, it will turn out that we will not require the explicit q dependence of $\lambda(q)$. $n^0(\hbar\omega_q)$ denotes the equilibrium Bose-Einstein distribution function. We have assumed that the phonon field is at equilibrium.

If we multiply the left-hand side of (2.1) by $\varphi_{\vec{\mathrm{k}}}/\Omega$ and sum over all states $\hbar\vec{\mathrm{k}}$ (Ω denotes the volume of the system), the resulting expression is seen to be the vector product of the electric current $\vec{\mathrm{i}}$ and the field $\vec{\mathrm{E}}$. On eliminating the field $\vec{\mathrm{E}}$ by the transport relation $\vec{\mathrm{i}}=\vec{\mathrm{E}}/\rho$, we obtain the following positive definite form[9] for the alloy resistivity:

$$\begin{aligned}\rho_A(T,c)=&\left(\frac{1}{\Omega}\sum_{\vec{\mathrm{k}}}\varphi^2_{\vec{\mathrm{k}}}[\tau_0(\epsilon_k)]^{-1}\frac{\partial f^0_k}{\partial\epsilon_k}\right.\\&\left.+\frac{1}{2k_BT\Omega}\sum_{\vec{\mathrm{k}}}\sum_{\vec{\mathrm{q}}}V^0_{\mathrm{ep}}(\vec{\mathrm{k}},\vec{\mathrm{k}}+\vec{\mathrm{q}})\,(\varphi_{\vec{\mathrm{k}}+\vec{\mathrm{q}}}-\varphi_{\vec{\mathrm{k}}})^2\right)\Bigg/\\&\left(\frac{e}{\Omega}\sum_{\vec{\mathrm{k}}}v_k\varphi_k\frac{\partial f^0_k}{\partial\epsilon_k}\right)^2\end{aligned} \tag{2.5}$$

$$\equiv\rho_{\mathrm{imp}}(T,c)+\rho_{\mathrm{ep}}(T,c)\,. \tag{2.6}$$

The first term in (2.6) denotes the "impurity resistivity" and is defined as the term in (2.5) proportional to τ_0^{-1}. The second term of (2.6) is the "electron-phonon resistivity of the alloy" and is defined as the term in (2.5) proportional to $V^0_{\mathrm{ep}}(\vec{\mathrm{k}},\vec{\mathrm{k}}\,')$. The terms $\rho_{\mathrm{imp}}(T,c)$ and $\rho_{\mathrm{ep}}(T,c)$ are, of course, not independent as they are both to be determined by a common solution of Eq. (2.1) for $\varphi_{\vec{\mathrm{k}}}$.

At this stage, we wish to make a few general remarks concerning the evaluation of (2.5) and (2.6). The general solution of (2.1) will be of the form[8]

$$\varphi_{\vec{\mathrm{k}}}=-e\vec{\mathrm{E}}\cdot\vec{\mathrm{v}}_{\vec{\mathrm{k}}}\tau(\epsilon_k)\,, \tag{2.7}$$

where τ has dimensions of time and, for our isotropic model, depends only on the modulus of $\vec{\mathrm{k}}$. In the limit of low temperatures, the ep term in (2.1) vanishes[8] so that at the lowest temperatures

$$\varphi_{\vec{\mathrm{k}}}=-e\vec{\mathrm{E}}\cdot\vec{\mathrm{v}}_{\vec{\mathrm{k}}}\tau_0(\epsilon_k;\;T,c)\quad(T\ll T_0)\,. \tag{2.8}$$

Provided that τ_0 does not vary appreciably over an energy range comparable to k_BT, the resulting resistivity will be given by the usual expression $\rho_0^{-1}=ne^2\tau_0(\epsilon_F)/m$. We recall that T_0 is the temperature at which $\rho^0_{\mathrm{ep}}(T)=\rho_0(T,c)$. In the limit of high temperatures ($T\gg T_0$), the ep term dominates the right-hand side of the Boltzmann equation and, consequently,

$$\varphi_{\vec{\mathrm{k}}}=-e\vec{\mathrm{E}}\cdot\vec{\mathrm{v}}_{\vec{\mathrm{k}}}\tau^0_{\mathrm{ep}}(\epsilon_k)\quad(T\gg T_0)\,, \tag{2.9}$$

where $\tau^0_{\mathrm{ep}}(\epsilon_k)$ is obtained from the solution of the linearized Boltzmann equation for ep scattering alone. It can be deduced that, in the region of ϵ_F, τ^0_{ep} varies with energy on the scale of ϵ_F.[10] Consequently, since we shall only be interested in contributions to $\tau(\epsilon)$ that vary on an energy scale comparable to $\hbar\omega_D$ or less, we shall take

$$\tau^0_{\mathrm{ep}}(\epsilon_k)=\tau^0_{\mathrm{ep}}(\epsilon_F)=\tau^0_{\mathrm{ep}}\,.$$

This quantity is obtainable from experiment via

$$\rho^0_{\mathrm{ep}}(T)=(ne^2\tau^0_{\mathrm{ep}}/m)^{-1}\,, \tag{2.10}$$

where $\rho^0_{\mathrm{ep}}(T)$ denotes the ep resistivity of the pure metal.

We note that the ep contribution to the resistivity $\rho_{\mathrm{ep}}(T,c)$ is proportional to a sum over terms involving the square of fluctuations of $\varphi_{\vec{\mathrm{k}}}$:

$$\delta\varphi^2_{\vec{k},\vec{q}} = (\varphi_{\vec{k}+\vec{q}} - \varphi_{\vec{k}})^2 \ . \tag{2.11}$$

The appearance of these terms is not peculiar to the ep scattering mechanism, but is a general occurrence for any scattering mechanism, a fact that is clearly related to the dissipation-fluctuation theorem.[11] However, a key feature that distinguishes the ep mechanism from that of the present impurity-scattering mechanism is that the former is *inelastic*. This has the consequence that in (2.11) $\varphi_{\vec{k}}$ will change not only with variations in the electronic group velocity $\vec{v}_{\vec{k}}$ but also with changes in the relaxation time τ:

$$\delta\varphi = -e\vec{E}(\delta\vec{v}\tau + \vec{v}\delta\tau) \ . \tag{2.12}$$

The first term in (2.12) is the fluctuation in $\varphi_{\vec{k}}$ that is ordinarily considered in the calculation of ρ^0_{ep}. Denote this by $\delta\varphi^0_{\vec{k},\vec{q}}$. The second term of (2.12) is usually tacitly ignored as it is considered to make a contribution of relative order $\hbar\omega_D/\epsilon_F$. For ϵ_k and $\epsilon_{\vec{k}+\vec{q}}$ close to ϵ_F, and with $\delta\vec{v} \sim \hbar\vec{q}/m$ and

$$\delta\tau \sim \pm\left(\frac{\partial\tau}{\partial\epsilon}\right)_{\epsilon=\epsilon_F} \hbar\omega_q \ ,$$

as is appropriate for the ep scattering event,[12] we have

$$\delta\varphi_{\vec{k},\vec{q}} = \delta\varphi^0_{\vec{k},\vec{q}}\left(1 \pm \frac{a\hat{k}\cdot\vec{E}}{\hat{q}\cdot\vec{E}}\right) , \tag{2.13}$$

where a is defined by

$$a = \hbar\omega_s \left.\frac{\partial \ln\tau(\epsilon)}{\partial\epsilon}\right|_{\epsilon=\epsilon_F} \tag{2.14}$$

and $\hat{k}$ and $\hat{q}$ denote unit vectors specifying the directions of $\vec{k}$ and $\vec{q}$. Clearly, if τ is taken to be τ^0_{ep}, then

$$a \sim \hbar\omega_D/\epsilon_F \sim 10^{-2}\text{–}10^{-3} \ ,$$

implying the neglect of the second term in (2.12) or (2.13). However, for the dilute alloy or impure metal at temperatures low compared to T_0, we have $\tau(\epsilon) \simeq \tau_0(\epsilon)$, and if in the region of ϵ_F, τ_0 varies with ϵ_k on a scale comparable to or less than $\hbar\omega_s$, then the parameter $a \gtrsim 1$. In this case, the second term in (2.11) or (2.12) is at least as great as the first term and cannot be ignored. This is the origin of the effect with which this paper is concerned.

At temperatures exceeding T_0, $\tau(\epsilon)$ must approach τ^0_{ep} so that a becomes negligible and the effect described above vanishes, i.e., the electron-phonon component of the resistivity of the dilute alloy becomes the same as that of the pure host metal. In order to obtain this high-temperature limit in the present calculation, we will assume that $\tau(\epsilon)$ is generally given by

$$\tau(\epsilon)^{-1} = \tau_0(\epsilon)^{-1} + (\tau^0_{ep})^{-1} \ . \tag{2.15}$$

This form of $\tau(\epsilon)$ is correct in the two limits $T \ll T_0$ and $T \gg T_0$, but is probably in error in the transitional regime $T \sim T_0$. However, we believe (2.15) to be capable of giving at least semiquantitatively correct results for temperatures of the order T_0. The basis for this remark is that our subsequent results for the modification of $\rho_{ep}(T, c)$ from $\rho^0_{ep}(T)$ will be generally expressed in terms of the first and second derivatives of the exact $\tau(\epsilon)$ at $\epsilon = \epsilon_F$, and it is only in the explicit calculation of these energy derivatives that the assumption (2.15) is made.

A major assumption that we shall make in our evaluation of the resistivity is that of expanding $\tau(\epsilon)$ in a Taylor series:

$$\tau(\epsilon) = \tau(\epsilon_F) + \left(\frac{\dot{\tau}}{\tau}\right)_{\epsilon=\epsilon_F}(\epsilon - \epsilon_F) + \frac{1}{2!}\left(\frac{\ddot{\tau}}{\tau}\right)_{\epsilon=\epsilon_F}(\epsilon - \epsilon_F)^2 \ , \tag{2.16}$$

retaining only those terms of order $(\epsilon - \epsilon_F)^2$ or less. We may rewrite (2.16) in the form

$$\frac{\delta\tau}{\tau} \equiv \frac{\tau(\epsilon) - \tau(\epsilon_F)}{\tau(\epsilon_F)} = a\left(\frac{T}{\Theta'_D}\right)\xi + \frac{b}{2}\left(\frac{T}{\Theta'_D}\right)^2\eta^2 \ , \tag{2.17}$$

where $\eta = (\epsilon - \epsilon_F)/k_BT$, $k_B\Theta'_D = \hbar\omega_s$, and the parameter b measures the strength of the second derivitive of τ,

$$b = \left(\frac{\hbar^2\omega_F^2}{\tau}\frac{\partial^2\tau}{\partial\epsilon^2}\right)_{\epsilon=\epsilon_F} \ . \tag{2.18}$$

Now, in the evaluation of the resistivity, from formula (2.5) for example, the important values of η are those less than approximately unity – corresponding to the measure of electrons in the thermal layer k_BT at the top of the Fermi sea. The expansion (2.16) will be valid for $\delta\tau/\tau \ll 1$, which implies that the coefficients of η and of η^2 in (2.17) be $\ll 1$. These conditions demand that

$$a(T, c) \ll (\Theta'_D/T) \ , \tag{2.19}$$

$$b(T, c) \ll 2(\Theta'_D/T)^2, \tag{2.20}$$

at any temperature T and concentration c. The significance of (2.19) and (2.20) is that while the characteristic energy of variation of τ should be comparable to or less than $\hbar\omega_D$ for our effect to be important, the use of the Taylor-series expansion for τ requires that the characteristic energy be nevertheless much greater than k_BT. The usual $\partial\ln\tau/\partial\epsilon$ formula for the low-temperature electronic thermopower follows from the use of (2.16) and is[3]

$$S(T, c) = \frac{\pi^2}{3}\frac{k_B^2 T}{e}\left.\frac{\partial \ln\tau(\epsilon; T, c)}{\partial\epsilon}\right|_{\epsilon=\epsilon_F} , \tag{2.21}$$

where functions varying with energy on the scale of ϵ_F have been neglected. Expressing a in terms of S, we evidently require

$$1 \lesssim \left(\frac{\hbar\omega_F}{\epsilon_F}\right)\frac{S(T,\,c)}{S_0(T)} \ll \left(\frac{\Theta_D'}{T}\right). \tag{2.22}$$

As mentioned in Sec. I, the inequality on the left-hand side of (2.22) is satisfied for magnetic transitional impurities for temperatures $\lesssim \frac{1}{10}\Theta_D$. This temperature range clearly satisfies the right-hand side of (2.22).[13] We stress that the satisfaction of the inequality on the right-hand side of (2.22) is consistent with the use of (2.21) for the electronic thermopower.

Some comments on the possible experimental determination of the parameter b will be discussed at a latter stage of this paper. We now consider the explicit evaluation of $\rho_{\text{imp}}(T,\,c)$ and $\rho_{\text{ep}}(T,\,c)$ from Eq. (2.5).

III. EVALUATION OF RESISTIVITIES

The evaluation of $\rho_{\text{imp}}(T,\,c)$ and $\rho_{\text{ep}}(T,\,c)$ as defined by Eqs. (2.5) and (2.6) for the model ep transition rate (2.4) and relaxation-time ansatz, (2.7) and (2.15), is straightforward, although algebraically tedious. In particular, the evaluation of $\rho_{\text{ep}}(T,\,c)$ follows closely that of the standard derivation[14] of this quantity for the pure metal. For these reasons, we will only give the salient features of the calculation.

First, sums over $\vec{k}$ in (2.5) are replaced by integrals according to[15]

$$(1/\Omega)\textstyle\sum_{\vec{k}} \to [2/(2\pi)^3]\int d^3k\ . \tag{3.1}$$

The impurity resistivity is then readily deduced from (2.5) to be of the form

$$\rho_{\text{imp}}(T,\,c) = \left(-\rho_0(T,\,c)\int_0^\infty d\epsilon\,\frac{\partial f_0}{\partial\epsilon}\,\frac{\tau(\epsilon)^2}{\tau_0(\epsilon)\tau_0(\epsilon_F)}\right)\Bigg/\left(\int_0^\infty d\epsilon\,\frac{\partial f_0}{\partial\epsilon}\,\frac{\tau(\epsilon)}{\tau_0(\epsilon_F)}\right)^2\ , \tag{3.2}$$

where

$$\rho_0(T,\,c) \equiv [ne^2\tau_0(\epsilon_F;\ T,\,c)/m]^{-1} \tag{3.3}$$

and, in the region of $\epsilon = \epsilon_F$, we have neglected the energy dependence of the electronic group velocity $\vec{v}_{\vec{k}}$ relative to that of $\tau(\epsilon)$. We note that providing that the conditions (2.19) and (2.20) are satisfied, we may use the Sommerfeld expansion,

$$-\int_0^\infty d\epsilon\,\frac{\partial f_0}{\partial\epsilon}\,\tau(\epsilon) = \tau(\epsilon_F) + (k_BT)^2\,\frac{\pi^2}{6}\left(\frac{\partial^2\tau}{\partial\epsilon^2}\right)_{\epsilon=\epsilon_F} + \cdots \tag{3.4}$$

for the evaluation of the integrals in (3.2). In expanding (3.2), we shall require the first and second derivatives of

$$\tau(\epsilon)^{-1} = [\tau_0(\epsilon)]^{-1} + (\tau^0_{\text{ep}})^{-1}\ \text{at}\ \epsilon = \epsilon_F\ .$$

It will be convenient to work in terms of the dimensionless parameters a and b. Carrying through the differentiation of $\tau(\epsilon)$, these are

$$a = \hbar\omega_s\left(\frac{\partial\ln\tau}{\partial\epsilon}\right)_{\epsilon=\epsilon_F} = \frac{a_0}{1+\tau_0(\epsilon_F)/\tau^0_{\text{ep}}}$$

$$= \frac{a_0}{1+\rho^0_{\text{ep}}(T)/\rho_0}\ , \tag{3.5}$$

while

$$b \equiv \frac{(\hbar\omega_F)^2}{\tau}\left(\frac{\partial^2\tau}{\partial\epsilon^2}\right)_{\epsilon=\epsilon_F}$$

$$= \left(1+\frac{\rho^0_{\text{ep}}(T)}{\rho_0}\right)^{-1}\left(b_0 - \frac{2a_0^2}{1+\rho_0/\rho^0_{\text{ep}}(T)}\right), \tag{3.6}$$

where

$$a_0 = \hbar\omega_F\left(\frac{\partial\ln\tau_0}{\partial\epsilon}\right)_{\epsilon=\epsilon_F}\ ,\qquad b_0 = \frac{(\hbar\omega_F)^2}{\tau_0(\epsilon_F)}\left(\frac{\partial^2\tau_0}{\partial\epsilon^2}\right)_{\epsilon=\epsilon_F}.$$

The "weight" factors involving the ratio $\rho^0_{\text{ep}}(T)/\rho_0$ appear in (3.5) and (3.6) on identifying this ratio with $\tau_0(\epsilon_F)/\tau^0_{\text{ep}}$. Note that as $(T/T_0)\to\infty$, both a and $b\to 0$. The result of applying (3.4) to evaluate (3.2) for ρ_{imp} can now be expressed in terms of a, a_0, b, and b_0:

$$\rho_{\text{imp}}(T,\,c) = \rho_0(T,\,c)\left[1+\frac{\pi^2}{6}\left(\frac{T}{\Theta_D'}\right)^2 \times\frac{2a^2-4aa_0+2a_0^2+2b-b_0}{[1+\rho^0_{\text{ep}}(T)/\rho_0]^2}\right]\Bigg/D(T,\,c)^2\ , \tag{3.7}$$

where

$$D(T,\,c) = 1+\frac{\pi^2}{6}\left(\frac{T}{\Theta_D'}\right)^2\frac{b}{1+\rho^0_{\text{ep}}(T)/\rho_0}\ . \tag{3.8}$$

Equations (3.5)–(3.8) describe the effect which the energy dependence of $\tau(\epsilon)$ has on the impurity contribution to the resistivity. The effect has been considered previously in connection with transitional impurities by Friedel,[16] Korringa and Gerritsen,[17] and Domenicali.[18]

The electron-phonon contribution to the alloy resistivity is given by

$$\rho_{\text{ep}}(T,\,c) = \frac{\Omega}{k_BT}\int\frac{d^3k}{(2\pi)^3}\int\frac{d^3q}{(2\pi)^3} \times V^0_{\text{ep}}(\vec{k},\,\vec{k}+\vec{q})\,\delta\phi^2_{\vec{k},\,\vec{k}+\vec{q}}\Bigg/\left|2e\int\frac{d^3k}{(2\pi)^3}\,\vec{v}_{\vec{k}}\,\phi_{\vec{k}}\,\frac{\partial f^0_{\vec{k}}}{\partial\epsilon_{\vec{k}}}\right|^2. \tag{3.9}$$

The denominator of (3.9) reduces to the consideration of the denominator of (3.2) for $\rho_{\text{imp}}(T,\,c)$, so we are left with the evaluation of the numerator of (3.9). Now, for our isotropic model,

$$\delta\phi^2_{\vec{k},\,\vec{k}+\vec{q}} = \left(\frac{\hbar e\vec{E}}{m}\cdot[(\vec{k}+\vec{q})\tau(\epsilon_{\vec{k}+\vec{q}}) - \vec{k}\tau(\epsilon_{\vec{k}})]\right)^2$$

$$=\frac{1}{3}\left(\frac{\hbar eE}{m}\right)^2[(\vec{k}+\vec{q})\tau(\epsilon_{\vec{k}+\vec{q}})-\vec{k}\tau(\epsilon_{\vec{k}})]^2$$

$$=\frac{1}{3}\left(\frac{\hbar eE}{m}\right)^2[k^2\delta\tau^2+q^2\tau^2(\epsilon_{\vec{k}+\vec{q}})$$

$$-2\vec{k}\cdot\vec{q}\tau(\epsilon)\tau(\epsilon_{\vec{k}+\vec{q}})]$$

$$=\frac{1}{3}\left(\frac{\hbar eE}{m}\right)^2[q^2\tau(\epsilon_{\vec{k}})\tau(\epsilon_{\vec{k}+\vec{q}})+k^2\delta\tau^2], \tag{3.10}$$

where

$$\delta\tau\equiv\tau(\epsilon_{\vec{k}+\vec{q}})-\tau(\epsilon_{\vec{k}}),$$

and we have anticipated the condition[14]

$$-2\vec{k}\cdot\vec{q}=q^2\pm(\hbar\omega_D/\epsilon_F)$$

demanded by the conversation of energy,

$$\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}\pm\hbar\omega_q=0, \tag{3.11}$$

in the ep scattering event. We may now insert into (3.10) the Taylor-series expansion (2.16) for $\tau(\epsilon)$, noting that in view of (3.11), $\epsilon_{\vec{k}+\vec{q}}$ may be replaced by $\epsilon_k\pm\hbar\omega_q$, where the plus and minus signs denote the absorption or emission of a phonon by the scattered electron. The plus sign is to be used when the first term of (2.4) for V^0_{ep} is encountered in evaluating (3.9), while the minus sign is to be used in conjunction with the second term of (2.4). The quantity $\delta\phi^2_{\vec{k},\vec{k}+\vec{q}}$ may be expressed in the form

$$\delta\phi^2_{\vec{k},\vec{k}+\vec{q}}$$

$$=(\delta\phi^0_{\vec{k},\vec{k}+\vec{q}})^2\left[1+\sum_{n,m}a_{nm}\eta^n\left(\pm\frac{\hbar\omega_q}{k_BT}\right)^m\left(\frac{T}{\Theta'_D}\right)^{n+m}\right], \tag{3.12}$$

where

$$(\delta\phi^0_{\vec{k},\vec{k}+\vec{q}})^2=\tfrac{1}{3}[(\hbar/m)eE\tau(\epsilon_F)]^2$$

is the expression for $\delta\phi^2_{\vec{k},\vec{k}+\vec{q}}$ that ordinarily determines the ep resistivity of a pure metal,[14] and the coefficients a_{nm} are related to the first and second derivatives of $\tau(\epsilon)$ evaluated at ϵ_F.

We note at this stage a general result for $T/\Theta'_D\ll 1$. As $(T/\Theta'_D)\to 0$, we have from (3.12)

$$\delta\phi^2_{\vec{k},\vec{k}+\vec{q}}=(\delta\phi^0_{\vec{k},\vec{k}+\vec{q}})^2(1+a_{00}),$$

where, as may be verified by using (3.10) and (2.16), a_{00} is just the square of the parameter a. Since a^2 is independent of the integration variables in the numerator of (3.9), the factor $(1+a^2)$ may be factorized out of this numerator. If the denominator of (3.9) is evaluated at $T=0$, then the resulting expression for $\rho_{\mathrm{ep}}(T,c)/(1+a^2)$ is just the conventional expression for $\rho^0_{\mathrm{ep}}(T)$,[14] i.e., at low temperatures $(T\ll\Theta'_D)$, we have the result

$$\rho_{\mathrm{ep}}(T,c)=\rho^0_{\mathrm{ep}}(T)[1+a(T,c)^2]\quad(T\ll\Theta'_D). \tag{3.13}$$

This result is independent of the form assumed for the isotropic ep coupling constant $\lambda(q)$.

More generally, we have to insert (3.12) into the numerator of (3.9) and perform the appropriate integrations. The method of evaluating these integrals over forms of $\delta\phi^2_{\vec{k},\vec{k}+\vec{q}}$ such as given by (3.12) is discussed in detail in standard treatises.[3,14] Such evaluations lead to the following result for $\rho_{\mathrm{ep}}(T,c)$:

$$\rho_{\mathrm{ep}}(T,c)$$

$$=\rho^0_{\mathrm{ep}}(T)\left\{1+a^2+\left(\frac{T}{\Theta'_D}\right)^2\left[J_{7,5}\left(\frac{\Theta_D}{T}\right)\frac{(2b^2+b-a^2)}{6}\right.\right.$$

$$\left.\left.+\frac{\pi^2}{3}\left(a^2+b^2+\frac{b}{2}\right)\right]\right\}\Big/D(T,c)^2, \tag{3.14}$$

where

$$J_{\mu q}(x)=J_\mu(x)/J_q(x)$$

and

$$J_\mu(x)=\int_0^x\frac{dy\,y^\mu}{(e^y-1)(1-e^{-y})} \tag{3.15}$$

denote Bloch-Grüneisen integrals. The appearance of the factor $(T/\Theta'_D)^2$ as the greatest power of (T/Θ'_D) in the bracketed quantity multiplying ρ^0_{ep} in (3.14) indicates that our Taylor-series expansion (2.16) was terminated after the second-order term. Even powers of (T/Θ'_D) do not appear in (3.14) since contributions to such terms cancel on taking account of both processes of phonon emission and absorption. The square of the quantity $D(T,c)$, defined by (3.8), appears in (3.14) as a result of evaluating the denominator of (3.9). Finally, we mention that the explicit form of the coefficient of $(T/\Theta'_D)^2$ in (3.16) depends on the assumption that $|\lambda(q)|^2\propto q$, for small q. Equations (3.7) and (3.14) are the main results of this section.

Before considering the application of these results to particular situations, we shall check that (3.7) and (3.14) reduce to certain expected results in appropriate limits. We first note that, as they stand, *our results* (3.7) *and* (3.14) *are independent of the ansatz* (2.15) *for the form of* $\tau(\epsilon)$. We assume the ansatz (2.15) when the particular expressions (3.5) and (3.6) are used for a and b, respectively. If (2.15) were in fact rigorous, the total electrical resistivity would simply be

$$\rho_{\mathrm{alloy}}(T,c)=-\left(\frac{ne^2\tau(\epsilon_F)}{m}\right)^{-1}\int_0^\infty d\epsilon\,\frac{\partial f_0}{\partial\epsilon}\,\frac{\tau(\epsilon)}{\tau(\epsilon_F)}$$

$$=[\rho_0+\rho^0_{\mathrm{ep}}(T)][1-\tfrac{1}{6}\pi^2(T/\Theta'_D)^2b], \tag{3.16}$$

where in writing (3.16) the inequalities (2.19) and (2.20) have been assumed. Since $\tau(\epsilon)$ is assumed given by (2.15), b is given by (3.6). Thus, for $T \ll T_0$, we have

$$\rho_{\text{alloy}}(T, c) = \rho_0[1 - \tfrac{1}{6}\pi^2(T/\Theta_D')^2 b_0] , \qquad (3.17)$$

where we have neglected terms of relative order ρ_{ep}/ρ_0 or less. For $T \gg T_0$, (3.6) and (3.16) give

$$\rho_{\text{alloy}}(T, c) = \rho_{\text{ep}}^0(T)\{1 + (\rho_0/\rho_{\text{ep}}^0) \times [1 - \tfrac{1}{6}\pi^2(T/\Theta_D')^2(b_0 - 2a_0^2)]\} . \qquad (3.18)$$

Since the ansatz (2.15) is correct for $T \ll T_0$ and $T \gg T_0$, then our results (3.7) and (3.14) for $\rho_{\text{imp}}(T, c)$ and $\rho_{\text{ep}}(T, c)$ should combine to predict (3.17) and (3.18) in the appropriate limits of temperature. That this is so may be verified by the explicit inspection of formulas (3.7), (3.8), and (3.14), together with the use of (3.5) and (3.6) for a and b. We now consider in Secs. IV–VI some specific applications of the results obtained in this section.

IV. LOW-CONCENTRATION LIMIT AND ATOMIC RESISTIVITY

For very small concentrations, the temperature $T_0(c)$, at which $\rho_0 = \rho_{\text{ep}}^0$, becomes small and can satisfy the inequality $(T_0/\Theta_D) \ll 1$. Consequently, the weight factors

$$R(T, c) = [1 + \rho_{\text{ep}}^0(T)/\rho_0]^{-1} \qquad (4.1)$$

contained in the explicit definitions (3.5) and (3.6) of the key parameters a and b cause these parameters to diminish rapidly for $T \gtrsim T_0$, i.e., the influence of the energy dependence of the electron-impurity scattering is rapidly washed out as the ep mechanism becomes dominant. It follows that for such small concentrations the terms in (3.14) of relative order $(T/\Theta_D')^2$, $(\Theta_D' \sim \Theta_D)$ may be neglected, giving for the ep resistivity

$$\rho_{\text{ep}}(T, c) = \rho_{\text{ep}}^0(T)[1 + a_0(T, c)^2 R(T, c)^2] , \qquad (4.2)$$

which is the result (1.3) of Sec. I. As mentioned in Sec. III, the result (4.2) is independent of the explicit form of the q dependence of the isotropic ep coupling constant. In the present calculation, the factor $\rho_{\text{ep}}^0(T)$ in (4.2) is to be identified with the observed ep resistivity of the pure metal. It need not necessarily be assumed that $\rho_{\text{ep}}^0 \propto T^5 (T \ll \Theta_D)$, which follows from the assumption that $|\lambda(q)|^2 \propto q$ for small q.

Suppose in the low-concentration limit that $\tau(\epsilon)_0^{-1} \propto c$. Then a_0 is independent of c. Thus, *providing* $T \ll T_0(c)$, so that $R(T, c) = 1$, the modification of the alloy resistivity by the energy dependence of the electron-impurity scattering is c independent. Clearly, however, as $c \to 0$, so also does $T_0(c)$, so that the effect we are considering vanishes.

As already discussed in Sec. I, the most important application of (4.2) is to be the case of magnetic transitional impurities where a_0 can be of the order of unity or more at low temperatures. Before considering some explicit calculations of the consequences of (4.2) for some typical dilute magnetic-impurity systems, we shall consider the question of the importance of the modification of the ep resistivity relative to that of the impurity resistivity $\rho_{\text{imp}}(T, c)$.

The total resistance of the alloy may be written as

$$\rho_{\text{alloy}}(T, c) = \rho_0(T=0, c) + \rho_{\text{ep}}^0(T) + \Delta_1(T, c) + \Delta_2(T, c) , \qquad (4.3)$$

where we have defined

$$\Delta_1(T, c) \equiv \rho_{\text{imp}}(T, c) - \rho_0(T=0, c) \qquad (4.4)$$

and

$$\Delta_2(T, c) \equiv \rho_{\text{ep}}(T, c) - \rho_{\text{ep}}^0(T) \qquad (4.5)$$

$$= \rho_{\text{ep}}^0(T)\, a_0^2(T, c)\, R(T, c)^2 \quad (c \to 0) \qquad (4.6)$$

Note that, from (3.7) ,

$$\rho_0(T=0, c) = \rho_{\text{imp}}(T=0, c) ,$$

and that we have taken care to consider the possibility of an intrinsic T dependence of ρ_0, i.e.,

$$\rho_0(T, c)^{-1} = ne^2\tau_0(\epsilon_F;\ T, c)/m .$$

At $T=0$, $\rho_{\text{alloy}} = \rho_0(T=0, c)$ and, in principle, is obtainable from experiment. $\rho_{\text{ep}}^0(T)$ is also obtainable experimentally from measurements on the ideally pure metal. Thus, by observing $\rho_{\text{alloy}}(T, c)$, it will be possible to deduce the sum of $\Delta_1(T, c)$ and $\Delta_2(T, c)$. The question we wish to consider is: "How big is (Δ_2/Δ_1) when $\Delta_1(T, c)$ has its largest value as a function of temperature?" If $\Delta_1(T, c)$ is to be singularly observable, then we require $\Delta_2/(\Delta_1)_{\max} \ll 1$. The maximum value of Δ_1 occurs in the vicinity of $T = T_0 (R \sim \frac{1}{2})$ giving[19]

$$\frac{\Delta_1(T_0, c)}{\rho_0(T=0, c)} \sim \frac{a_0^2(T_0, c)}{4} \, \frac{\rho_0(T_0, c)}{\rho_0(T=0, c)} . \qquad (4.7)$$

Since we have $T_0(c) \ll \Theta_D$, the terms of order $(T/\Theta_D')^2$ in (3.7) and (3.8) may be expanded out to give

$$\frac{\Delta_1(T_0, c)}{\rho_0(T=0, c)} = \frac{\rho_0(T, c) - \rho_0(T=0, c)}{\rho_0(T=0, c)} - \alpha \, \frac{\rho_0(T, c)}{\rho_0(T=0, c)} \left(\frac{T}{\Theta_D'}\right)^2 , \qquad (4.8)$$

where

$$\alpha = \tfrac{1}{6}\pi^2[\tfrac{1}{2} b_0(T_0, c) - \tfrac{1}{8} 3a_0(T_0, c)^2] . \qquad (4.9)$$

We may now compare (4.8) and (4.7), assuming that for magnetic transitional impurities the parameters a_0 and α are of the order unity (or more) at $T \lesssim T_0$. Typical dilute magnetic-impurity systems, e.g., *Cu*Fe or *Au*Fe, indicate that the first term of (4.8), which arises from the intrinsic T dependence of τ_0, is of the order of *minus* 10–15%.[20] This is very much greater than what could ever be expected from the second term of (4.8) $[\sim(T/\Theta_D)^2]$, which we shall therefore neglect. For $a_0 \gtrsim 1$, the magnitude of (4.7) is *positive* and at least ~ 25%. Thus, experimentally, we should expect $\Delta_2(T, c)$ to be distinguishable from $\Delta_1(T, c)$ in the region of the maximum value of Δ_2, i.e., $T \sim T_0$.

Since Δ_1 diminishes while Δ_2 increases (for $T \lesssim T_0$) with increasing T, the observed value of

$$\Delta(T, c) = \Delta_1(T, c) + \Delta_2(T, c)$$

should initially decrease with increasing T and then increase with T after passing through a minimum. This prediction is in general accord with experiment and is a natural explanation of the rather curious observation[21] that when in "Kondo systems" the host $\rho^0_{\text{ep}}(T)$ is subtracted from $\rho_{\text{alloy}}(T, c)$, a resistance minimum *remains* in the "subtracted" $(\rho_{\text{alloy}} - \rho^0_{\text{ep}})$ data. As $T > T_0$, $\Delta_2(T, c)$ decays rapidly to zero, so that after passing through a temperature minimum, the quantity $\Delta(T, c)$ passes through a sharp maximum in the region of $T \sim T_0$. Thus, the qualitative shape of the $\Delta(T, c \to 0)$-versus-T curve is that of a minimum followed by a maximum. This behavior also seems to be in agreement with experimental studies of $\Delta(T, c)$.[22]

Before considering some explicit calculations of $\Delta_1(T, c)$, let us briefly estimate T_0. If we assume $\rho^0_{\text{ep}}(T) = aT^5$ and $\rho_0(T, c) = c\hat{\rho}_0$, where $\hat{\rho}_0$ is a constant of the order of several $\mu\,\Omega$cm/at.%, then

$$T_0(c) = (c\hat{\rho}_0/a)^{1/5} . \tag{4.10}$$

For Fe in pure Cu, we have

$$a \simeq 2.6 \times 10^{-10}\ \mu\,\Omega\text{cm}\ {}^\circ\text{K}^{-5}$$

and $\hat{\rho}_0 = 11\ \mu\,\Omega$cm/at.%, giving

$$T_0(c)/\Theta_D \sim 0.4c^{1/5} ,$$

where we have assumed $\Theta_D \simeq 330$ °K for Cu and c is in at.%. Thus, if $c = 0.01$, $T_0 \sim \Theta_D/16$.

We define the "atomic resistivity" as

$$\Delta\rho(T, c)/c \equiv [\rho_{\text{alloy}}(T, c) - \rho^0_{\text{ep}}(T)]/c . \tag{4.11}$$

If Δ_1 can be neglected relative to Δ_2, i.e., if we consider $\rho_0(T, c) = \rho_0 = T$ independent, we have from (4.3)–(4.6)

$$\frac{\Delta\rho(T, c)}{c} = \frac{\rho_0}{c} + \frac{\rho^0_{\text{ep}}}{c}(T)a_0^2(T, c)R^2(T, c) . \tag{4.12}$$

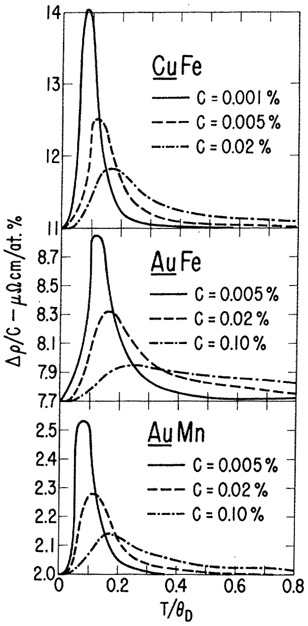

FIG. 1. Atomic resistivities of some dilute magnetic-impurity systems as calculated from Eq. (4.11) of the text. The Debye temperature Θ_D was taken to be 330 °K for Cu and 200 °K for Au.

We shall use this formula to predict the atomic resistivities of dilute *Cu*Fe, *Au*Fe, and *Au*Mn alloys. Formula (1.4) is used to obtain the parameter a_0 from the observed low-temperature thermopower $S(T, c)$ of the alloys. The observed values of S have the form[4,13]

$$S(T, c) = -\frac{A(k_B/e)T}{T + T_s} , \tag{4.13}$$

where A is a constant ranging from about 0.2 to 0.4, and $T_s \sim 1$ °K for concentrations less than ~ 0.1 at.%. From (4.11) and (4.12), we have

$$a_0 = \frac{(3/\pi^2)A\hbar\omega_s}{k_B(T + T_s)}$$

$$\sim 0.3A\Theta_D/(T + T_s) .$$

Although a_0 is very large for $T \ll T_s$,[23] the contribution of the second (anomalous) term of (4.11) is very small in this temperature range, and we shall only require values of a_0 for $T > T_s$. In this temperature range, we have, typically, $a_0 \sim (\frac{1}{10}\Theta_D)T^{-1}$. We shall use this average estimate of a_0 for *all* the alloys we consider. We wish here to predict only the general order of magnitude of the effect on $\Delta\rho/c$. With a_0 fixed in this way, we need only determine the values of Θ_D, ρ_0 (the $T = 0$ atomic resistivity), and $\rho^0_{\text{ep}}(T)$, all of which are easily found in the literature. The results of our calculations are shown in Fig. 1, where concentrations ranging from $c = 0.001$ to $c = 0.1$ at.% have been studied.

As we anticipated earlier in this section, the effect of the anomalous term in the ep resistivity of the alloy is to give rise to a sharp peak in the atomic resistivity as a function of temperature. The effect is particularly strong for *Cu*Fe where Fig. 1 shows that a Fe concentration of only 10 ppm will increase $\Delta\rho/c \sim 40\%$ over its $T = 0$ value. The qualitative observation of sharp peaks (increasing with decreasing c) in the atomic resistivity-versus-T curves of dilute solutions of transitional atoms in certain noble metals was noted some years ago by Gerritsen and Linde.[22] The form of the published data, together with the absence of measurements of the thermopower on the same specimens, does not, in our opinion, allow a numerically detailed comparison between theory and experiment. However, we hope that this paper will inspire subsequent experimental work which will enable a quantitative comparison of theory and experiment to be made.

We now go on to consider briefly the question of more concentrated alloy systems.

V. HIGHER CONCENTRATIONS AND MATTHIESSEN'S RULE

At higher concentrations where T_0/Θ_D is no longer so small as was considered the case in Sec. IV, we must retain the terms in (3.7), (3.8), and (3.14) of relative order $(T/\Theta_D')^2$. Retention of these terms brings in the importance of the parameter b, defined by (3.6), which measures the strength of the second derivative of $\tau(\epsilon)$.

The quantity

$$\begin{aligned}\Delta(T, c) &= \rho_{\text{alloy}}(T, c) - \rho_{\text{ep}}^0(T) - \rho_0(T = 0, c)\\ &= \Delta_1(T, c) + \Delta_2(T, c)\ , \qquad (5.1)\end{aligned}$$

where Δ_1 and Δ_2 are defined by (4.4) and (4.5), may be termed the "deviation from Matthiessen's Rule," and is deducible from the observed total alloy resistivity when ρ_{ep}^0 and $\rho_{\text{alloy}}(T = 0, c)$ are known. As discussed in Sec. IV, the effect of the energy dependence of τ_0 is to produce a positive peak in $\Delta_2(T, c)$ as a function of T. The deviation $\Delta_1(T, c)$, which is negative, is proportional to $\rho_0(T, c)$ which increases with increasing concentration. Thus, as c is increased, $\Delta_1(T, c)$ tends to cancel the positive contribution from $\Delta_2(T, c)$ which varies much slower with c than Δ_1. Thus, the positive contribution to $\Delta(T, c)$ is eliminated after some value of c has been reached (see Fig. 3, Sec. VI). We also note from (3.18) that in the limit $T \gg T_0$, $\Delta_2(T, c)$ becomes negative anyhow if $b_0 > 2a_0^2$.

We see from (4.4) and (4.5) and from (3.7), (3.8), and (3.14), which may be used to obtain explicit expressions from Δ_1 and Δ_2, that $\Delta(T, c)$ is determined by the first- and second-derivative parameters a, b, and a_0 and b_0. Since the former two parameters can be expressed by means of (3.5) and (3.6) in terms of the latter two when ρ_0 and ρ_{ep}^0 are known, then $\Delta(T, c)$ is determined entirely by a_0 and b_0. Now a_0 is, in principle, obtainable from the electronic diffuse thermopower so that measurements of both $\Delta(T, c)$ and $S(T, c)$, together with the use of the theoretical formula $\Delta(T, c)$, could be used to determine the second-derivative parameter $b_0(T, c)$. If, on the other hand, a reliable theoretical expression is available for $\tau_0(\epsilon;\ T, c)$ for ϵ close to ϵ_F, then $\Delta(T, c)$ may be predicted completely theoretically.[24]

A particularly simple situation occurs when $1/\tau_0$ is independent of T and proportional to c, since then the two key parameters a_0 and b_0 are just constants independent of T and c. Thus, providing the inequalities (2.19) and (2.20) are satisfied, $\Delta(T, c)$ is completely determined by the latter two constants. We now consider this situation for the case of nonmagnetic transitional impurities.

VI. APPLICATION TO NONMAGNETIC TRANSITIONAL IMPURITIES

If a_0 and b_0 are constants, the low-temperature thermopower is linear in T while the limiting low-temperature form of the alloy resistivity is, from (3.7), (3.8), and (3.9),

$$\rho_{\text{alloy}}(T, c) = \rho_0[1 - \tfrac{1}{6}\pi^2(T/\Theta_D')^2 b_0] \quad (T \ll T_0)\ . \qquad (6.1)$$

Thus, a_0 and b_0 can be determined experimentally from the low-temperature thermopower and the initial T^2 decrease of the electrical resistivity. We also note that in the limit $T \gg T_0$, we have from (3.18)

$$\rho_{\text{alloy}}(T, c) - \rho_{\text{ep}}^0(T) = \rho_0[1 - \tfrac{1}{6}\pi^2(T/\Theta_D')^2(b_0 - 2a_0^2)] \quad (T \gg T_0)\ . \qquad (6.2)$$

Thus, the coefficient of the negative T^2 deviation from Matthiessen's rule changes by a factor of $(b_0 - 2a_0^2)/b_0$ in going from $T \ll T_0$ to $T \gg T_0$.

A situation corresponding approximately to constant a_0 and b_0 is that of nonmagnetic transitional

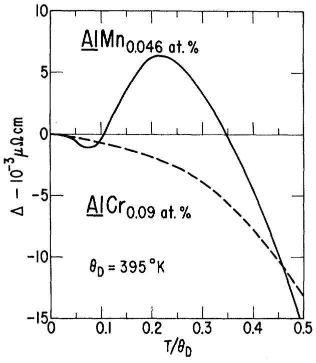

FIG. 2. Theoretically predicted deviations from Matthiessen's rule, Δ, for two nearly-local-moment Al alloys.

impurities in nontransitional hosts, where following the work of Friedel,[16] one can consider the resonant scattering of conduction electrons from virtual d levels, or "virtual bound states" (VBS), in the vicinity of the Fermi energy:

$$\tau_0(\epsilon)^{-1} = \Gamma_0 \Gamma^2/[\Gamma^2 + (\epsilon - \epsilon_0)^2] . \qquad (6.3)$$

Here Γ denotes the half-width of a Lorentzian VBS, and ϵ_0 and Γ_0 denote constants. Γ is related to the conduction-electron phase shift ($l = 2$) by the relation

$$\tan\delta_l = \Gamma/(\epsilon - \epsilon_0) . \qquad (6.4)$$

Equations (6.3) and (6.4) give

$$a_0 = (\hbar\omega_s/\Gamma)\sin(2\delta_l) , \qquad (6.5)$$

$$b_0 = 2(\hbar\omega_s/\Gamma)^2(\sin\delta_l)^2 . \qquad (6.6)$$

If the $l = 2$ phase shift is the dominant phase shift, then by Friedel's sum rule the magnitude of δ_l is fixed by

$$\delta_l = (\pi/2)[z/(2l+1)] , \qquad (6.7)$$

where z denotes the effective valency difference between the transitional impurity atom and host-metal atom.

For typical nonmagnetic transitional impurities in noble metals, we have $(\hbar\omega_s/\Gamma) \sim 0.1$. We require the square of this quantity to be comparable to unity for a sizable modification of $\rho_{ep}(T, c)$. Thus, typically, we do not expect a large effect in $\rho_{ep}(T, c)$ due to nonmagnetic transitional impurities. However, for the particular alloy systems *Al*Mn and *Al*Cr, Caplan and Rizzuto[25] have put forward the interesting idea that the width of the VBS in these alloys is extremely narrow and, in fact, is not much greater than $\hbar\omega_D$. This anomalously small value of Γ is correlated with the close proximity of the impurity state to a state carrying a local (magnetic) moment. If this interpretation of the Al alloys is correct, then these alloy systems would be ideal systems for studying experimentally the present ep effect. Moreover, since measurements of both the low-temperature linear thermopower[26] and of the initial negative T^2 resistance deviation[25] (6.1) have already appeared in the literature, thus providing values of a_0 and b_0, we may use the general results of Sec. III to acutally predict $\Delta(T, c)$ for dilute *Al*Mn and *Al*Cr alloys. For *Al*Mn, we find $a_0 = 0.25$ and $b_0 = 0.45$, while for *Al*Cr we obtain the somewhat lower estimates $a_0 = 0.036$, $b_0 = 0.1$. The result of the theoretical calculation for $\Delta(T, c)$ is shown in Fig. 2 for 0.046-at.% Mn and 0.09-at.% Cr, these being the actual concentrations used in Ref. 25. In the case of *Al*Mn, the energy dependence of τ_0 is sufficiently strong that $\Delta_2(T, c)$ dominates $\Delta_1(T, c)$ over a finite temperature interval, whereas Δ_1 dominates Δ_2 for the case of *Al*Cr for which the energy dependence of τ_0 is considerably weaker. In Fig. 3, we show our theoretical calculations of $\Delta(T, c)$ versus T for *Al*Mn for various values of c. As c is increased from zero, the importance of the denominator $D(T, c)^2$ in (3.7) and (3.14) increases to the extent of causing $\Delta(T, c)$ to be negative for all T and c. However, the presence of the strong positive peak in Δ_2 is evident in the total deviation Δ for all the concentrations studied in Fig. 3.

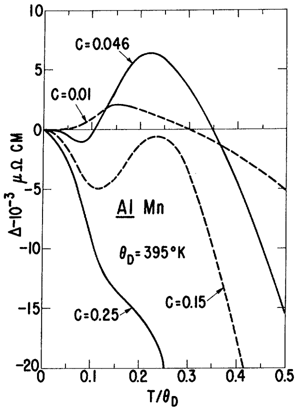

FIG. 3. Theoretically predicted deviations from Matthiessen's rule, Δ, for several dilute *Al*Mn alloys.

Presumably there exist other nearly-local-moment dilute-alloy systems where Γ is beginning to approach $\hbar\omega_D$, and such alloys, together with the Al alloys discussed above, would be particularly suitable for use in an experimental investigation of the effects found theoretically in this paper.

ACKNOWLEDGMENTS

We thank A. J. Bennett, C. B. Duke, I. Giaever, L. M. Roth, and S. D. Silverstein of this laboratory for useful discussions of various aspects of this work. We would also like to thank D. R. Hamann of Bell Telephone Laboratories for an informative discussion and correspondence.

---

[1] The basic effect discussed in this paper was outlined in a recent note, M. J. Rice, Phys. Rev. Letters 23, 1108 (1969). See also M. J. Rice and O. Bunce, J. Appl. Phys. 41, 1009 (1970).

[2] See, for example, A. Ň. Gerritsen [Physica 25, 489 (1959)], who gives a table of references summarizing the electrical and magnetic properties of dilute noble-metal alloys.

[3] A. H. Wilson, *The Theory of Metals* (Cambridge U. P., London, 1953), Chap. 8.

[4] For example, for 0.01-at.% Fe in Cu, we have $S \sim -15\,\mu$V/°K at $T = 15$°K [W. B. Pearson, Phil. Mag. 46, 911 (1955)], giving $S/S_0 \simeq 3\times10^2$ while $\hbar\omega_F/\epsilon_F \simeq 6\times10^{-3}$, so that $a \simeq 1.8$. Θ_D for Cu is of the order 300 °K.

[5] J. O. Linde, Ann. Physik 15, 219 (1932); G. Borelius, Metallwirtschaft 12, 173 (1933); E. Grüneisen, Ann. Phys. (Leipzig) 16, 530 (1933); G. J. van den Berg, *De Electrische Weerstand Van Zuivere Metalen Bij Lage En Zeer Lage Temperaturen* (Amsterdam, 1938); A. N. Gerritsen and J. O. Linde, Physica 18, 877 (1952); E. I. Salkovitz, A. I. Schindler, and E. W. Kammer, Phys. Rev. 98, 543 (1955); 105, 887 (1953); 107, 1549 (1957); D. K. C. MacDonald and W. B. Pearson , Acta Met. 3, 392 (1955); A. T. Robinson and J. E. Dorn, J. Metals Trans. Met. Soc. AIME 3, 457 (1951); P. Alley and B. Serin, Phys. Rev. 116, 334 (1959); C. A. Domenicali and E. L. Christenson, J. Appl. Phys. 32, 2450 (1961); F. T. Hedgecock and W. B. Muir, Phys. Rev. 136, 561 (1964); J. S. Dugdale and Z. S. Basinski, *ibid.* 157, 552 (1967); J. T. Schriempf, in Proceedings of the Seventh Conference on Thermal Conductivity, 1967 (unpublished); Mme. Dreyfus and F. Gautier (unpublished); A. D. Caplin and C. Rizzuto (unpublished).

[6] J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, England, 1960), Chap. 7.

[7] A. D. Caplin and C. Rizzuto, Phys. Rev. Letters 21, 746 (1968).

[8] F. Bloch, Z. Physik 59, 208 (1930); A. H. Wilson, see Ref. 3, Chap. 9.

[9] See Ref. 6.

[10] For example, from the detailed variational calculations of E. H. Sondheimer, Proc. Roy. Soc. (London) A203, 75 (1950).

[11] H. B. Callen and T. A. Welton, Phys. Rev. 83, 34 (1951); R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[12] The plus or minus sign here refers to the emission or absorption of a phonon quantum in the scattering event.

[13] The largest "experimental value" of a appears to occur for dilute *Au*Fe [D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) A266, 161 (1962)], where $a \sim 10$ for T of the order of a few °K. Even here the right-hand side of (2.21) is well satisfied.

[14] See Ref. 6, Chap. 9.

[15] Note that $(1/\Omega)\sum_{\vec{q}} \to [1/(2\pi)^3]\int d^3q$. There is no factor of 2 as in (3.1) for the $\vec{k}$ sums since $\vec{q}$ denotes the momentum transfer which does not carry a spin subscript.

[16] J. Friedel, Can. J. Phys. 34, 1190 (1956).

[17] J. Korringa and A. N. Gerritsen, Physica 19, 457 (1953).

[18] C. A. Domenicali, Phys. Rev. 117, 984 (1960).

[19] From a practical standpoint, it is convenient to compare resistive increments, such as Δ_1 and Δ_2, with the $(T=0)$ residual resistivity.

[20] For example, M. D. Daybell and W. A. Steyert, Phys. Rev. 167, 540 (1968).

[21] E. Grüneisen, Ann. Phys. (Leipzig) 16, 530 (1932); A. N. Gerritsen and J. O. Linde, Physica 18, 877 (1952); W. B. Pearson, Phil. Mag. 46, 911 (1955) (footnote, p. 915); C. A. Domenicali and E. L. Christenson, J. Appl. Phys. 32, 2450 (1961). This effect may also be seen in the recent data of Ref. 20.

[22] See, in particular, A. N. Gerritsen and J. O. Linde, Ref. 5.; C. A. Domenicali and E. L. Christenson, Ref. 5.

[23] a_0 is large but satisfies the inequality (2.19).

[24] For the case of scattering from magnetic impurities, a fully explicit expression for $\tau_0(\epsilon; c, T)$ has been derived; for example, by Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) 39, 533 (1968), and discussed recently by K. Maki, *ibid.* 41, 586 (1969).

[25] A. D. Caplin and C. Rizzuto, Phys. Rev. Letters 21, 746 (1968).

[26] G. Boato and J. Vig, Solid State Commun. 5, 649 (1967).

PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Anisotropy of the Temperature-Dependent Resistivity of Tin between 8 and 300 °K*

S. K. Case and J. E. Gueths
Physics and Astronomy Department, Wisconsin State University, Oshkosh, Wisconsin 54901

(Received 4 June 1970)

Electrical-resistivity measurements have been performed on five single crystals of pure tin in the temperature interval 8–300 °K. From these measurements, the temperature-dependent anisotropy $(a=\rho_\parallel/\rho_\perp)$ of the electrical resistivity has been determined. A striking maximum in the a-versus-T curve is noted at $T\approx 20$ °K. The features of this curve at high, intermediate, and low temperatures are interpreted in terms of a simplified model for an anisotropic metal. The model predicts that the a-versus-T curve for all electrically anisotropic metals with anisotropy a_∞ as $T\to\infty$ will exhibit a maximum $a_{\max}=a_\infty^2$ at intermediate or low temperatures.

INTRODUCTION

This paper reports the results of an experimental investigation of the temperature-dependent electrical-resistivity anisotropy of pure tin. Five oriented pure-tin single crystals (less than 3-ppm impurity) were measured between 8 and 300 °K. The anisotropy was determined to be a strongly varying function of temperature for tin. A greatly simplified model for an anisotropic metal is employed to explain the gross features of the a-versus-T data.

The orientation dependence of the resistivity of a tetragonal crystal such as tin may be written in the form

$$\rho(\theta)=\rho_\perp\,[1+(a-1)\cos^2\theta]\,, \tag{1}$$

where θ is the angle between the tetrad axis and the current direction, $\rho_\perp$ is $\rho(90°)$, and a, which we