

Thus

$$L S = \frac{1 - [(9\pi/4)^{1/2}\pi]^{-1}(r_s/a_n)p^{-1}(1+2q)6[h(1)-h'(1)]}{1 + [(9\pi/4)^{1/2}\pi]^{-1}(r_s/a_n)p^{-1}(1+2q)u^{-2}}$$

$$= u^2 \left[(9\pi/4)^{1/2} \frac{a_n}{r_s} \frac{p}{1+2q} - \left\{ 3(1 - \frac{1}{2}\beta)^2 - \ln \frac{2}{\beta} \right\} \right]. \quad (\text{A28})$$

We see that the exchange effect does not drop out for two reasons: (1), the numerator retains a value not equal to 1 reflecting the dependence of the matrix element on k , and (2), the denominator, although allowing G to be negligible compared to F , has an effect arising from the use of one-electron energy functions differing from the free electron one through the use of $p \neq 1$ and $q \neq 0$

Thermoelectricity and Resistivity in Metal Alloys at Low Temperatures

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A simple model is proposed for the "resonant scattering" of electrons from foreign atoms in a crystal lattice. The model assumes the existence of highly selective scattering mechanisms characterized by widths of the order of 10^{-4} electron volts and larger; in this sense it is similar to the model of Korringa and Gerritsen (1953), although the present model makes use of only the general analytical characteristics of the relaxation time and does not specify the details of the scattering mechanism. Mott's well-known approximation formula $S = (\pi^2 k^2 T / 3e) [d \ln \sigma(E) / dE]_{E=E_F}$ for the absolute thermoelectric power of a metal alloy is strictly valid and physically meaningful only at temperatures $kT \ll a$, where $2a$ is the width of the resonance. At temperatures $kT \gg a$ the formula leads to useful and valuable information on the thermoelectric properties of alloys, but the formula in this temperature region has only a rather artificial physical meaning. In the intermediate temperature region where kT is comparable to a , the Mott formula is entirely invalid. But it is in precisely this intermediate temperature range that the resistance and thermoelectric anomalies occur, so that Mott's approximation cannot be used for the treatment of these anomalies. The model satisfactorily explains many of the details of this anomalous behavior. It is suggested that the solvent metals used in the experimental studies of these effects will have to be much purer than those presently available before we shall be able to specify unambiguously the effects of a given kind of impurity.

I. INTRODUCTION

THERE is an increasing interest nowadays in the electric and magnetic properties of noble metals and their alloys.¹ Among the many interesting and unsolved problems in this field is that of understanding the nature of the electron scattering which causes certain well-known anomalies² or departures from the "simple" behavior exemplified, for example, by Matthiessen's rule. That these problems are by no means simple is demonstrated by the fact that it has been found extremely difficult to explain even the sign of the absolute thermoelectric power of the pure metals at room temperature.³ Schmitt⁴ and Yosida⁵ have attempted to explain the low-temperature "resistivity maximum" in CuMn alloys on the basis of a spin-dependent interaction between the scattered electron and the d electrons of the impurity ion; their work not only supplies a specific mechanism for the electron scattering but also

attempts to connect the electrical with the magnetic properties of CuMn alloys. However, the work of Schmitt and Yosida has led only to a very qualitative understanding of a few rather general aspects of the problem and furnishes little in the way of details of the known electrical behavior of noble metal alloys.

Earlier, Korringa and Gerritsen⁶ proposed a "resonance scattering" model which led to a fairly detailed description of the low-temperature resistivity and magnetoresistance of dilute alloys of copper, silver, or gold containing manganese. While their treatment has some quantum mechanical basis, their arguments for the existence of "resonance states" very near the Fermi level are not very convincing. However, since the transport properties of these alloys are determined primarily by the scattering of the electrons having kinetic energies within a few kT of the Fermi level energy E_F , it would seem that the actual scattering mechanism (or mechanisms) must be highly "selective" or "discriminating." This selectivity will probably turn out to be due at least in part to some kind of spin-sensitive interaction,⁷ as proposed by Korringa, Schmitt, and

¹ See, e.g., the *Report on the International Conference on the Electronic Properties of Metals at Low Temperatures, Geneva, New York, August 25-29, 1958* [Revs. Modern Phys. (to be published)].

² D. K. C. MacDonald, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, Part 1.

³ M. Bailyn, *Phys. Rev.* **112**, 1587 (1958); M. Tsuji, *J. Phys. Soc. (Japan)* **13**, 133, 818, 979 (1958).

⁴ R. W. Schmitt, *Phys. Rev.* **103**, 83 (1956).

⁵ K. Yosida, *Phys. Rev.* **107**, 396 (1957).

⁶ J. Korringa and A. N. Gerritsen, *Physica* **19**, 457 (1953).

⁷ A recent contribution has been made by A. D. Brailsford and A. W. Overhauser, *Phys. Rev. Letters* **3**, 331 (1959). A very similar calculation has also been made recently by A. J. Dekker (private communication).

Yosida. This means, of course, that the usual theoretical treatments will have to be modified to include the dependence of scattering probability of an electron upon its spin as well as upon its kinetic energy, so that one can no longer speak simply of a function $\tau(E)$ giving the relaxation time in terms of the energy alone. It is certainly an open question whether or not such a more general kind of scattering can be interpreted both physically and mathematically in a phenomenological way as a rapid dependence of an "effective relaxation time" with energy. On the supposition that it will in fact be possible to so represent the true scattering effects in terms of a relatively simple picture, we have investigated the consequences of the "narrow resonance" model and have found a rather encouraging agreement between the model and the known experimental facts.⁸ Needless to say, we have not determined any of the several parameters involved from first (or even second!) principles; however, in view of the fact that the model makes use of only three or four parameters (each of which has a definite physical meaning) whereas the theory explains and correlates many more than three or four specific and rather intricate properties of noble metal alloys, this general agreement seems to us to be something more than fortuitous. The model shows how the scattering responsible for the low-temperature anomalies is also operative at much higher temperatures; our experimental work⁹ on these alloys at temperatures from -196° to 800°C indicates a widespread and gradual change of impurity resistivity which extends over this entire range and joins smoothly with the low-temperature behavior. Thus we are of the opinion that undue emphasis has been placed on the specifically low-temperature aspects of the problem, and that these low-temperature peculiarities are simply manifestations of effects which extend up to the melting point of the alloys. Furthermore, it should be remembered that certain nontransition solute atoms in polycrystalline wires also give an *increasing* resistivity with decreasing temperature; examples of this are CuSi, CuGe, and CuSn with solute concentrations less than about 1 atomic percent.^{9,10} Pearson *et al.*¹⁰ have found that CuSn single crystals do not show a resistivity minimum, whereas polycrystalline specimens do when appropriately annealed. This effect is as yet unexplained, but it indicates that nontransition solutes in certain states of aggregation also behave anomalously.

The basis for most treatments of thermoelectric

⁸ While a mere change of name contributes absolutely nothing to the validity of a theory, we suggest that a more appropriate name for the present picture would be "high-selectivity scattering model" rather than "resonance model."

⁹ C. A. Domenicali, *Phys. Rev.* **112**, 1863 (1958); details of experimental work to be submitted to *J. Appl. Phys.*

¹⁰ J. O. Linde, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 402; see also N. Bäcklund, *J. Phys. Chem. Solids* **7**, 94 (1958); and W. B. Pearson, D. M. Rimek, and J. M. Templeton, reference 1, p. 211.

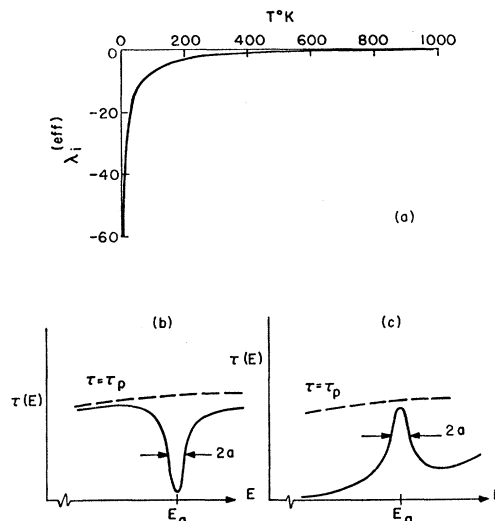


FIG. 1. (a) Variation of λ_i^{eff} with temperature for Cu+0.30 at. % Fe. Values obtained with the use of Eq. (2). Thermoelectric power data for $0 < T < 50^\circ\text{K}$ taken from reference 15, and for $88^\circ\text{K} < T < 1000^\circ\text{K}$ from reference 9. (b) and (c). Schematic representation of "resonance" in scattering cross section of impurity atoms dissolved in noble metals or alkali metals. The widths of the resonances are supposed to be small compared with the energy E_a .

power of metals and metallic alloys has been the "Mott formula"

$$S = [(\pi^2 k^2 T) / (3 |e|)] [d \ln \rho(E) / dE]_{E=E_F}, \quad (1)$$

where k is Boltzmann's constant, T is the Kelvin temperature, $|e|$ is the magnitude of the electron charge, and $\rho(E)$ gives the energy dependence of the resistivity of the metal. The sign given in (1) refers to electrons as the sole carriers of the electric current. By using a simple model of scattering of electrons by solute atoms in a noble-metal solvent, it has been found possible to get interesting and useful information on the nature of this scattering.^{9,11-14} If the scattering is predominantly due to impurities, we can write Eq. (1) in the form

$$S = AT [d \ln \rho_i(E) / dE]_{E_F} \equiv AT \lambda_i, \quad (2)$$

where $A \equiv \pi^2 k^2 / (3 |e|) = 0.0243$ (ev-microvolt)/deg², and λ_i represents the logarithmic derivative evaluated at the Fermi level in the alloy; this parameter λ_i is characteristic of each chemical impurity and in general depends upon the temperature as well as upon concentration of impurity.

If we use experimental values^{9,15} of S to determine λ_i

¹¹ J. Friedel, *J. phys. radium* **14**, 561 (1953); P. de Faget de Casteljau and J. Friedel, *J. phys. radium* **17**, 27 (1956).

¹² C. Domenicali and F. A. Otter, *Phys. Rev.* **95**, 1134 (1954).

¹³ F. J. Blatt, *Phys. Rev.* **100**, 666 (1955).

¹⁴ M. Tsuji, *J. Phys. Soc. (Japan)* **13**, 133 (1958). See also N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1934); and H. Jones, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, Part 1.

¹⁵ G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde, *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **35**, 10, 15, 25 (1932).

in Eq. (2), we find in some cases a very rapid increase in the magnitude of this quantity with temperature below about 50° or 100°K. The values of λ_i required at temperatures in the liquid helium range may be as much as two orders of magnitude larger than those required at or above room temperature.² Figure 1(a) gives an idea of this variation for iron in copper. It can be seen from the work of Borelius *et al.*,¹⁵ MacDonald and Pearson,¹⁶ and others, that the thermoelectric behavior of dilute alloys at low temperatures is very sensitive to the nature and amount of dissolved foreign atoms. We shall show how this behavior and that of the electrical resistivity can be explained on the basis of a simple model very similar to that of Korringa and Gerritsen,⁶ except that the present model makes use of only the general analytical characteristics of the relaxation time and does not specify the details of the scattering mechanism.

II. FORMULAS FOR RESISTIVITY AND THERMOELECTRIC POWER

Our model is the following. We take the total resistivity ρ to be the sum of ρ_T , the thermal scattering, and ρ_i , the solute or impurity scattering: $\rho = \rho_T + \rho_i$. The scattering cross section $Q_i(E)$ of a given foreign atom dissolved in a metal consists of two parts, one of which is slowly varying with kinetic energy E of the scattered electrons, the other of which represents a rapidly varying "resonance" type of scattering. If the Fermi level E_F in the metal lies within a few kT of the "resonance energy" E_a , then there will be an unusually large sensitivity of electrical properties upon impurity concentration, temperature, and any other experimentally variable parameters which affect the values of the transport integrals to be discussed below. The electron relaxation time is related to the scattering cross section by the expressions

$$\tau = \tau_i \tau_p / (\tau_i + \tau_p), \quad \tau_i = (m/2)^{1/2} n_i^{-1} \gamma(E),$$

$$\gamma(E) \equiv [E^{1/2} Q_i(E)]^{-1}, \quad (3)$$

where τ_i and τ_p are the impurity and phonon contributions, respectively, m is the electron mass and n_i is the concentration of impurity of species " i ." In an alloy the relaxation time τ varies with impurity concentration in such a way that we always have $0 < \tau < \tau_p$. We have introduced the variable $\gamma(E)$ in order to avoid carrying along the factor $(m/2)^{1/2} n_i^{-1}$. Since we are postulating that the scattering consists of a "normal" (slowly varying) part and an "anomalous" (rapidly varying) part, we can represent the function $\gamma(E)$ by one of the two curves in (b) or (c) of Fig. 1. In (b) the resonance gives an anomalously large scattering in the vicinity of $E = E_a$ while in (c) there results an anomalously small scattering. Now whatever may be the precise details of

this scattering, we can always represent curves such as in Figs. 1(b) and (c) by a function of the form

$$\gamma(E) = G(E) + \gamma_0 \exp[-(E - E_a)^2/a^2], \quad (4)$$

where $G(E)$ is a polynomial $G(E) = g_0 + g_1(E - E_F) + g_2(E - E_F)^2$, say.

In our discussion we shall use only the term g_0 , and we shall hereafter consider the low-temperature behavior of dilute noble-metal base alloys *in which the impurity resistivity predominates over the thermal (and other) scattering*.

For values of the width a comparable to kT the approximations involved in deriving Mott's formula (1) can be shown to be invalid, and we must then use the formula¹⁴

$$eTS = K_1 / (K_0 - E_F), \quad (5)$$

where

$$K_n = \frac{2(2m)^{1/2}}{3\pi^2 \hbar^3} \int_0^\infty E^{n+1/2} \tau(E) \frac{df_0}{dE} dE. \quad (6)$$

Here m and e are the electron mass and charge (to be taken as a negative number for electrons), \hbar is $(2\pi)^{-1}$ times Planck's constant, and f_0 is the Fermi distribution function. From a consideration of Eqs. (5) and (6) applied to the curves in Figs. 1(b) and (c) it can be seen that Mott's formula is valid for the ranges $kT \ll a$ and $kT \gg a$; in the first case because the "Fermi surface" electrons can be treated as monoenergetic, in the second case because the resonance peak is so narrow that only a small fraction of the Fermi electrons "see" this peak and the remaining electrons "see" the slowly varying or "normal" part of the $\tau(E)$ curve. It is this second, high-temperature case which we treated in our earlier work.⁹

Formula (5) can be written in the simple and interesting form

$$\int_0^\infty (E - E_F) \eta(E) dE = eTS \int_0^\infty \eta(E) dE, \quad (7)$$

where

$$\eta(E) = E^{1/2} \tau(E) (df_0/dE). \quad (8)$$

Thus the Peltier heat eTS measures the "position," relative to the Fermi level, of the "center of mass" of the function $\eta(E)$. In order to obtain a large thermoelectric power, for example, we must have a $\tau(E)$ which places the "center of mass" of $\eta(E)$ as far away from the Fermi level as possible.

Equation (7) is exact to the extent that Eqs. (5) and (6) are exact. However, for our purposes it is convenient to get rid of the fractional exponent of E in Eq. (8) by expanding $E^{1/2}$ in a Taylor series about $E = E_F$ and thus

¹⁶ D. K. C. MacDonald and W. B. Pearson, *Acta Met.* **3**, 392, 403 (1955).

to use the (excellent approximation)

$$eTS =$$

$$\frac{\int_0^\infty (E - E_F) \xi(E) dE + (3/2E_F) \int_0^\infty (E - E_F)^2 \xi(E) dE}{\int_0^\infty \xi(E) dE}, \quad (9)$$

where now

$$\xi(E) = \tau(E) (df_0/dE). \quad (10)$$

In this same approximation the electrical resistivity is given by¹⁴

$$\rho^{-1}(E) = -[2e^2(2m)^{1/2}E_F^{3/2}/(e\pi^2\hbar^3)] \int_0^\infty \xi(E) dE. \quad (11)$$

For convenience of integration we use the approximation

$$df_0/dE = -(1/4kT) \exp[-(E - E_F)^2/(kT)^2], \quad (12)$$

which has the correct value of df_0/dE at $E = E_F$. Using Eqs. (3), (4), and (9)–(12), we find the desired expressions for the “impurity thermoelectric power” S_i and for the “impurity” resistivity ρ_i , as follows.

$$S_i(t) = \frac{k}{|e|} \frac{(\gamma_0/g_0)t\Delta(1+t^2)^{-1/2} \exp[-\Delta^2(1+t^2)^{-1}]}{1 + (\gamma_0/g_0)(1+t^2)^{-1/2} \exp[-\Delta^2(1+t^2)^{-1}]}, \quad (13)$$

$$\rho_i(t) = \rho_\infty \{1 + (\gamma_0/g_0)(1+t^2)^{-1/2} \times \exp[-\Delta^2(1+t^2)^{-1}]\}^{-1}. \quad (14)$$

The following notation has been used:

$$t = T/T_a, \quad \Delta = (E_F - E_a)/a, \quad kT_a = a, \quad (15)$$

and ρ_∞ is the value of $\rho_i(t)$ at $t = \infty$. The ratio $k/|e|$ has

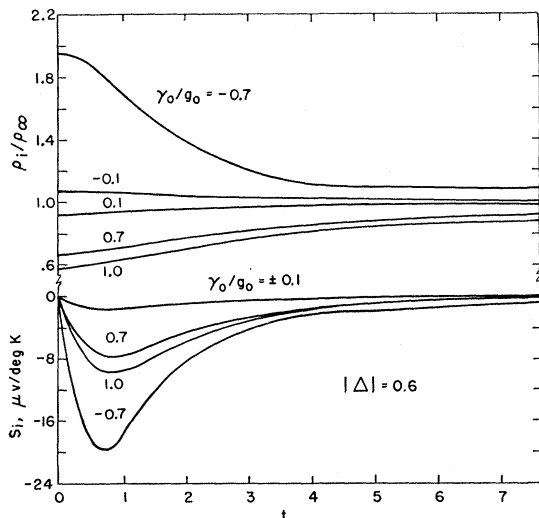


FIG. 2. Dependence of ρ_i/ρ_∞ and S_i upon temperature $t = T/T_a$ for $|\Delta| = 0.6$. The sign of the thermoelectric power S_i is determined by the sign of the product $(\gamma_0/g_0)\Delta$, as seen from Eq. (13).

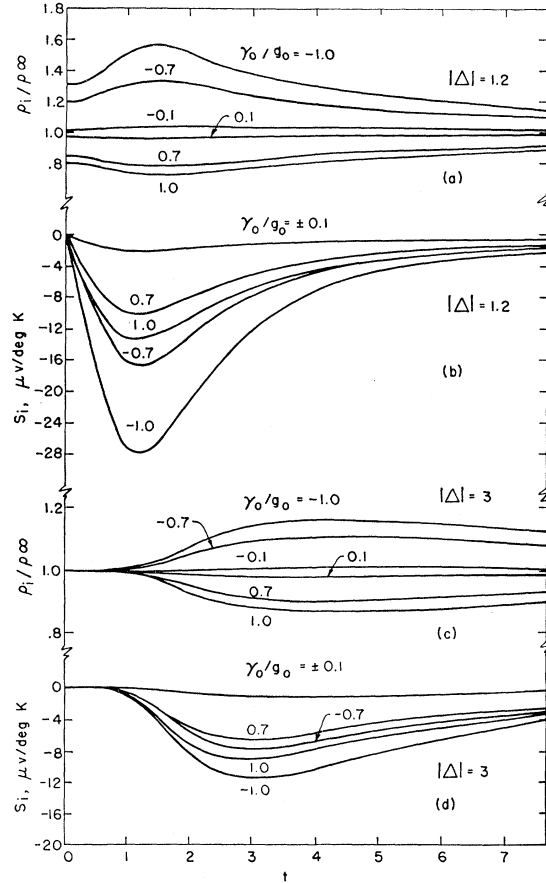


FIG. 3. Same as in Fig. 2, except here $|\Delta| = 1.2$ and $|\Delta| = 3$.

the value 86.4 microvolts per Kelvin degree. For our purposes, when a is small, and Δ and γ_0/g_0 are of order unity we can take ρ_∞ to be the room temperature *impurity* resistivity $\rho_i = \zeta_i p_i$, where ζ_i is Linde's "atomic resistivity" or resistivity per atomic percent and p_i is the impurity concentration in atomic percent. The sign of S_i in Eq. (13) is determined by the sign of both γ_0 and Δ ; since a is necessarily positive the sign of S_i is thus only partly determined by whether the "resonance energy" E_a is above or below the Fermi level. We should emphasize that Eqs. (13) and (14) refer to a *single* species of impurity whereas all the alloys as well as all "pure" metals which have been studied experimentally have almost certainly contained unknown amounts of trace impurities which often have given misleading information on the effects of the single solute intentionally added. Thus it makes little sense to speak of the electrical properties of "pure gold" on the basis of measurements made on a specimen whose resistivity ratio $\rho_{300^\circ\text{K}}/\rho_{4.2^\circ\text{K}}$ is of the order of 100 or less.

We show in Figs. 2 and 3 the dependence of ("impurity") S_i and of resistivity ρ_i upon temperature t for several values of the parameters Δ and γ_0/g_0 . By maxi-

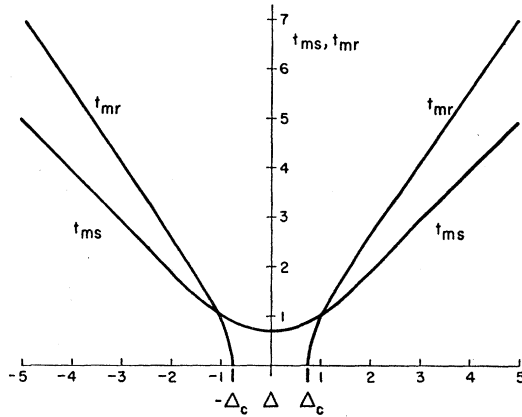


FIG. 4. Variation of the temperatures t_{mr} and t_{ms} at which extrema occur in the impurity resistivity and impurity thermoelectric power, respectively. The curve for t_{ms} is calculated on the assumption that the denominator in Eq. (13) is constant.

mizing ρ_i^{-1} (for convenience) we find that the extrema in resistivity $\rho_i(t)$ occur at values of t given by

$$t_{mr}=0 \quad \text{and} \quad t_{mr}=(2\Delta^2-1)^{\frac{1}{2}}. \quad (16)$$

For $\Delta < 2^{-\frac{1}{2}}$ there is no extremum in the impurity resistivity at any finite temperature. Obviously, if ρ_i decreases with increasing temperature over some range of t , the total resistivity $\rho = \rho_T + \rho_i$ may still show a minimum. To find the extremum of S_i we take (for convenience) the denominator in Eq. (13) to be approximately constant and differentiate only the numerator with respect to t . This approximation is justified because the denominator (which is proportional to the electrical conductivity) typically varies by only a few percent over the entire low-temperature range in actual alloys. We find then

$$t_{ms} = \frac{1}{2} \{ (2\Delta^2 - 1) + [(2\Delta^2 - 1)^2 + 8]^{\frac{1}{2}} \}. \quad (17)$$

The variation of t_{ms} and of t_{mr} with Δ are shown in Fig. 4. It is seen that there will be some solutes for which we find an "anomalous" thermoelectric behavior but for which there is no resistivity extremum. It is of interest to notice in Fig. 4 that $t_{mr} > t_{ms}$ for $|\Delta| > 1$ while $t_{mr} < t_{ms}$ for $|\Delta| < 1$. Thus if we begin with a large negative value of Δ and move toward $\Delta = 0$, always with fixed a , the absolute temperature T_{mr} of the impurity resistivity extremum becomes smaller until the "critical" value $-\Delta_c$ is reached, where $\Delta_c = 2^{-\frac{1}{2}}$; for $|\Delta| < \Delta_c$ there is no extremum. This disappearance of the resistance extrema may be called the "saturation effect," because as will be discussed presently, we shall assume that the further addition of solute atoms affects mainly the parameter Δ ; that is, the so-called "saturation effect" on the resistivity extrema accompanying increased solute concentration results from the variation of t_{mr} indicated in Fig. 4. (It must be kept in mind, however, that the position of the minimum in resistance is determined in most cases by the superposition

of ρ_T onto ρ_i .) In the same way, the position t_{ms} or T_{ms} of the extremum in S_i may be said to "saturate" in the sense that, for fixed a , the position of T_{ms} remains nearly constant for small Δ , or $|\Delta| < 1$.

The solute concentration may affect S_i and ρ_i in several different ways. The addition of a solute may alter the separation $E_F - E_a$ (and therefore the parameter Δ) simply by shifting the Fermi level as determined by the number of conduction electrons in the conduction band. While E_F itself may also change with concentration, it does not seem reasonable that this change alone would determine the separation $E_F - E_a$, for the following reason. The nature of the effective scattering potential around an impurity is primarily determined by (a) the nature of the dissolved atom and (b) the fact that this atom is surrounded by very large numbers of essentially free electrons, and that the scattering is nearly (but not completely) indifferent to the actual depth of the Fermi sea. One finds⁹ that a given impurity atom behaves in very much the same way whether it is dissolved in copper, in silver, or in gold, except for small but systematic quantitative differences.¹⁷ Thus, an expansion of the alloy lattice resulting, for example from a temperature change, would be expected to have little if any effect on the scattering potential. In our present picture, the observed changes in "effective" scattering parameters result from the changing amount of "overlap" of the factors (df_0/dE) and $\tau(E)$ in the transport integrals as the temperature is changed. This

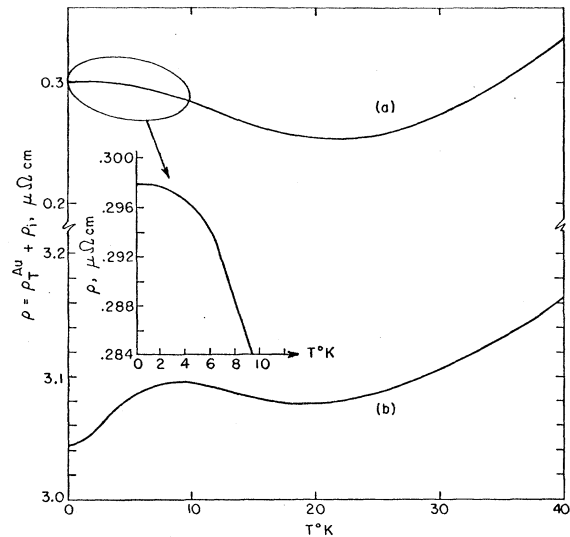


FIG. 5. Typical theoretical behavior of the total resistivity $\rho = \rho_T + \rho_i$ for fixed concentration of a single impurity in gold. The impurity is characterized by the following parameters: (a) $\rho_\infty = 0.16 \mu\text{ohm-cm}$; $\gamma_0/g_0 = -0.75$; $T_a = 11.6^\circ\text{K}$; $\Delta = \pm 0.7$; (b) $\rho_\infty = 3.0 \mu\text{ohm-cm}$; $\gamma_0/g_0 = -0.1$; $T_a = 5^\circ\text{K}$; $\Delta = 1.4$. The thermal contribution ρ_T for gold is taken from references 2 and 19.

¹⁷ Further experiments in progress, carried out by M. D. Blue of our Laboratory, indicate that the effective λ_i of nickel or of manganese is about the same in a 50% Au+50% Cu solvent as in pure gold or pure copper. Additional work of this sort is being done with iron and cobalt solutes.

leads to the temperature dependent parameter λ_i which we used in our earlier work⁹ and which can be interpreted as the *effective* logarithmic derivative of the curve of scattering cross section vs temperature. On the other hand, the effect of solute concentration upon S_i and ρ_i might better be understood as resulting from an interaction between impurity atoms; such an interaction may affect the separation $E_F - E_a$ or the width a or the height γ_0/g_0 , or it may affect several of these parameters. It seems quite reasonable to suppose that some (or perhaps all) of these parameters would be concentration dependent. For our purpose we have placed the entire emphasis upon changes in $E_F - E_a$ with concentration; since, for fixed temperature parameter t , the quantities $E_F - E_a$ and a enter into the S_i and ρ_i expressions only through their ratio $\Delta = (E_F - E_a)/a$, one sees that the same general behavior results from taking either $E_F - E_a$ or a as concentration dependent. The values of a which we use are of order 10^{-3} ev, so that only minute changes in either $E_F - E_a$ or a are required to produce large changes in Δ .

By superposing values of ρ_i (for given ρ_∞ , γ_0/g_0 , Δ and a) and ρ_T for hypothetical gold alloys at various absolute temperatures T , one easily finds a variety of resistivity-temperature curves of the form actually found experimentally; such hypothetical resistivity curves are typified by Figs. 5 and 6. If we use Eq. (14)

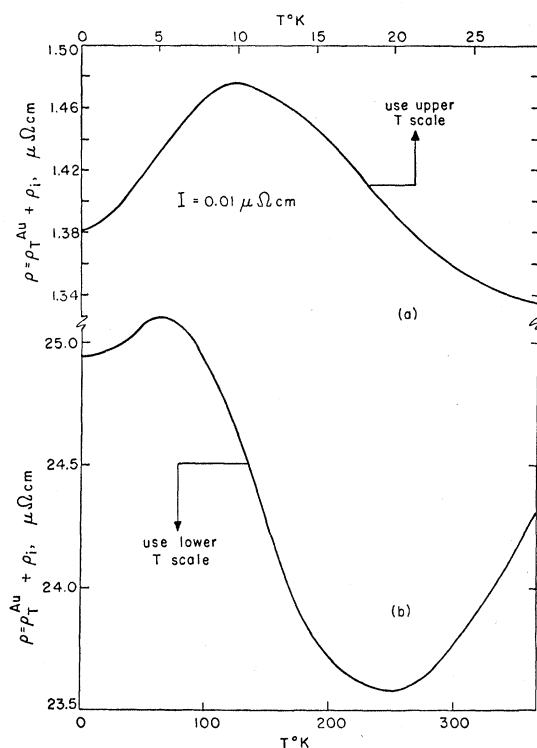


FIG. 6. Same as in Fig. 5, except with the following parameters: (a) $\rho_\infty = 1.0$ $\mu\Omega\text{-cm}$; $\gamma_0/g_0 = -0.75$; $T_a = 10^\circ\text{K}$; $\Delta = 1.0$. (b) $\rho_\infty = 25$ $\mu\Omega\text{-cm}$; $\gamma_0/g_0 = +1.0$; $T_a = 100^\circ\text{K}$; $\Delta = 2.5$.

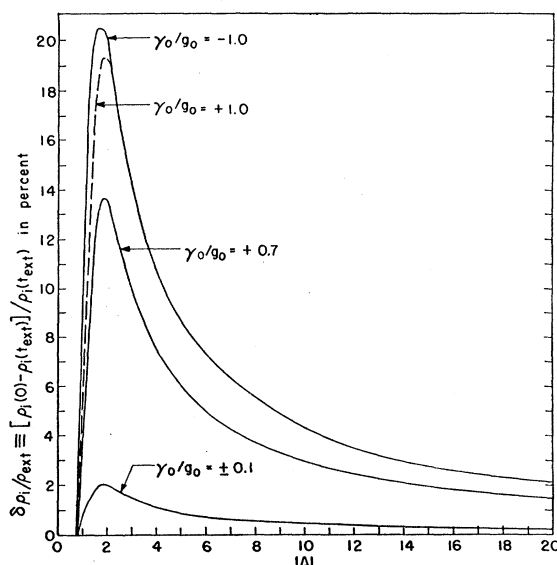


FIG. 7. Theoretical dependence of $|\delta\rho_i/\rho_{\text{ext}}| = |\rho_i(0) - \rho_i(t_{\text{ext}})|/\rho_i(t_{\text{ext}})$ in percent, upon the parameter $\Delta = (E_F - E_a)/a$.

to find the ratio

$$R = |\delta\rho_i/\rho_{\text{ext}}| = |\rho_i(0) - \rho_i(t_{\text{ext}})|/\rho_i(t_{\text{ext}}), \quad (18)$$

in which the extremum value ρ_{ext} occurs at $t = t_{\text{ext}}$ as given by Eq. (16), we find the interesting results shown in Fig. 7. This means that as $|\Delta|$ increases from zero to the value $\Delta_c = (2)^{-1/2}$ there is no extremum, as we have already seen, and as $|\Delta|$ increases beyond Δ_c the "relative size of the extremum," given by R , increases rapidly to a maximum and then decreases much more slowly. It can easily be shown that the maximum of R occurs at a value $|\Delta| = |\Delta|_m$ which is very insensitive to the value of γ_0/g_0 . In fact, $|\Delta|_m$ varies between about 1.7 for $\gamma_0/g_0 = -1.0$ and approximately 3 for $\gamma_0/g_0 = +100$. Recalling that we are postulating a dependence of $E_F - E_a$ upon concentration of impurity, we can expect the ratio R to be very sensitive to this concentration. On the other hand, we must also remember that Fig. 7 refers only to ρ_i whereas the measured resistivity is $\rho = \rho_T + \rho_i$. For a particular curve of ρ_i which happens to show a minimum, the superposition of the monotonically increasing $\rho_T(T)$ will of course cause the minimum in $\rho = \rho_T + \rho_i$ to move toward lower temperatures. To illustrate the behavior of ρ with composition and absolute temperature, we have chosen a set of values of ρ_∞ for a hypothetical impurity X in gold to match approximately those which are given for the "pure" gold of Alekseevskii and Gaidukov.¹⁸ In order to place the resistivity minimum in the correct temperature region, we take $T_a = 4^\circ\text{K}$ ($a = 3.3 \times 10^{-4}$ ev), and in order to obtain a large value of $R = |\delta\rho_i/\rho_{\text{ext}}|$ we use $\gamma_0/g_0 = +1.0$. The value of Δ for infinite dilution

¹⁸ N. E. Alekseevskii and Iu. P. Gaidukov, J. Exptl. Theoret. Phys. U. S. S. R. 31, 947 (1956) [translation: Soviet Phys. JETP 4, 807 (1957)].

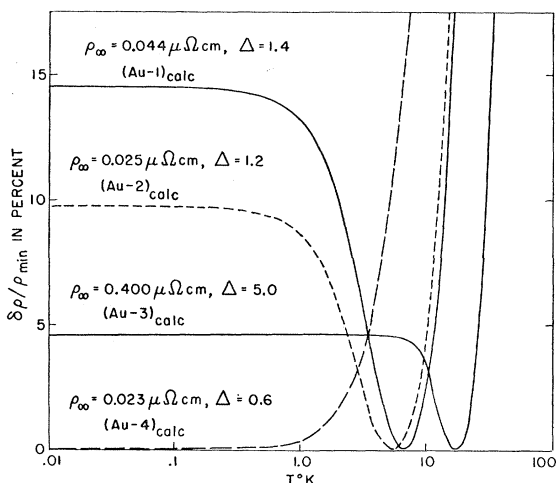


FIG. 8. Theoretical variation of $\delta\rho/\rho_{\min}$ (in percent) with $\log T$, for comparison with experimental results of Alekseevskii and Gaidukov (reference 18).

is taken to be 0.4. The change in the separation $E_F - E_a$ is arbitrarily taken to be of the order of 0.07 eV per atomic percent, so that the corresponding change in $|\Delta|$ with p_i is given by

$$d|\Delta|/dp_i = (7 \times 10^{-2} \text{ eV/at. } \%) / (3.3 \times 10^{-4} \text{ eV}) \approx 200/\text{at. } \%. \quad (19)$$

Our value 0.07 eV/at. % was actually estimated as a change in Fermi level assuming the resonance energy E_a to remain fixed, and this is admittedly an artificial way of calculating this change. Alternatively, as has already been pointed out, we might suppose that the separation $E_F - E_a$ has only a small dependence upon the height E_F itself and that $E_F - E_a$ changes upon further addition of solute atoms via some sort of interaction between these solute atoms. Using an atomic resistivity of 8 $\mu\text{ohm-cm/atomic percent of } X$, a typical value for iron or cobalt in copper or in gold, we find successive values of p_i of about 0.0015, 0.002, 0.003, and 0.025%. This then gives, from Eq. (19), the approximate values of $\Delta = 0.65, 0.8, 1.0$, and 5.1 for the gold specimens numbered, respectively, Au-4, Au-2, Au-1, and Au-3 by Alekseevskii and Gaidukov. In view of all the approximations we have made (including the assumption that the wires contained only one kind of impurity), we used some values of ρ_i/ρ_{∞} which we had calculated earlier for the neighboring values $\Delta = 0.6, 1.2, 1.4$, and 5 in order to place our hypothetical alloys in the appropriate regions of the curves in Fig. 7. Thus we did not bother to recalculate ρ_i/ρ_{∞} for the specific values of Δ given above. For the temperature dependence of ρ_T we used the "ideal gold" curve given in the International Critical Tables¹⁹ and the theoretical values given by MacDonald.² After superposing the

calculated ρ_i values and those for ρ_T , we find the minimum in the sum $\rho = \rho_i + \rho_T$ by graphical means, and thereafter compute the ratio $\delta\rho/\rho_{\min} = [\rho(T) - \rho(T_{\min})]/\rho(T_{\min})$. This ratio is shown for the four alloys labelled (Au-1)_{calc} through (Au-4)_{calc} in Fig. 8. It is seen in this figure that the order of arrangement of the alloys at the high-temperature region is Au-4, -2, -1, -3, whereas Alekseevskii and Gaidukov find the order Au-2, -4, -1, -3. In our calculations for the curve marked (Au-4)_{calc} we used the value of ρ_i at $T = 0^\circ\text{K}$ for $\rho_i(t_{\text{ext}})$ in Eq. (18); presumably Alekseevskii and Gaidukov did the same, so that there would appear to be a fundamental discrepancy between experiment and theory, since one would expect the purest material to be the first to rise rapidly with temperature at the high-temperature end of Fig. 8. Since their specimen Au-4 has a ratio $\rho_{295^\circ\text{K}}/\rho_{\min}$ of only 172, it must contain a fairly high level of impurities, and the reversed order of their specimens Au-4 and Au-2 may be due to the presence of several kinds of impurity atoms.

It is interesting to see how the temperature T_{\min} of the resistivity minimum in Fig. 8 depends on the resistivity ρ_{\min} at the minimum. This dependence is shown in Fig. 9, and is seen to have the same shape as was found by Pearson²⁰ for dilute Cu-Fe and Cu-Sn alloys. It is clear that the position of the minimum is simply that temperature T_{\min} at which the derivative $d\rho_T/dT$ happens to be equal (and opposite) to the derivative $d\rho_i/dT$, and the latter depends in turn upon the impurity concentration in a rather complicated way as can be seen from Fig. 8, for example. Of course, if the ρ_i vs T curve passes through a minimum at a temperature where ρ_T is negligible, then the position of this minimum will depend only upon the characteristics of the impurity scattering, as is shown by Fig. 4. Putting aside metallurgical considerations and for all other factors equal, one would prefer to work with copper as a solvent because its Debye temperature is about twice

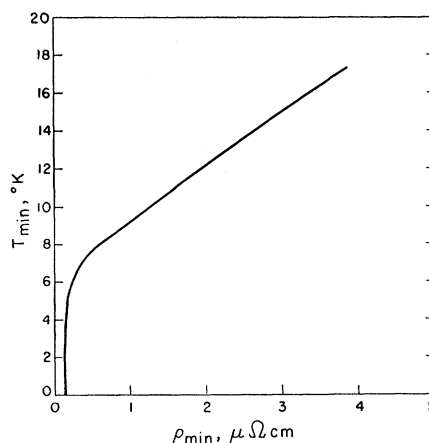


FIG. 9. Theoretical dependence of T_{\min} upon ρ_{\min} for the hypothetical alloys of Fig. 8.

¹⁹ International Critical Tables (McGraw-Hill Book Company, New York, 1926), Vol. VI, p. 127.

²⁰ W. B. Pearson, Phil. Mag. 46, 920 (1955).

that of gold, so that the thermal scattering is less significant in copper (at a given low temperature) than in gold.

It is also seen that the linear portion of our $\delta\rho/\rho_{\min}$ curves covers less than an order of magnitude of absolute temperature, whereas the work of Croft *et al.*²¹ and further work of Gaidukov²² indicates that $\delta\rho/\rho_{\min}$ can be linear in $\log T$ over about two orders of magnitude in the absolute temperature. We are not able to explain such a behavior on the basis of our model, for a single species of impurity atom. On the other hand, this behavior can be easily explained by the presence of two or more species of foreign atoms in the alloy.

If we consider a dilute alloy containing only a single species of foreign atom, we can arrive at certain generalizations concerning the resistivity and thermoelectric behavior. In order to exhibit a resistivity maximum in a temperature region where thermal scattering is negligible, a foreign atom must be characterized by a negative value of γ_0/g_0 .²³ If this atom causes the thermoelectric power to become negative (as is usually the case), then from Eq. (13) it is clear that Δ must be positive. Very few solute elements have been found which definitely cause a resistivity maximum; examples are AuCr,²⁴ AuMn,²⁴ CuMn,²⁴ AgMn,¹⁰ and AuFe.^{10,25} The thermoelectric behavior of AuFe, AuMn, and AuCr has been studied by Borelius *et al.*¹⁵ While the absolute thermoelectric power of their Au+2.08 at. % Mn and Au+3.65 at. % Cr appears to become positive (and small) at temperatures below 10° or 15°K, there seems to be little doubt that iron in concentrations greater than 0.065 at. % causes the thermoelectric power of gold to be quite large and negative. Let us consider the effects of adding small amounts of iron to pure gold. We take the value of Δ for iron in gold at extremely small dilution to be positive and to have a value less than $(2)^{-1/2}$. Assuming again that the parameters γ_0/g_0 and a are independent of iron concentration p_{Fe} , and that the addition of iron further increases $E_F - E_a$ and therefore Δ , we see from Fig. 4 that the temperature of the minimum in S_i should gradually increase while the resistivity at first shows no maximum. The further addition of iron continues to raise the temperature T_{ms}

of the S_i extremum and ρ_i now develops a maximum whose temperature T_{mr} increases rapidly at first but then becomes linear with Δ , as in Fig. 4. If Δ is some function $\Delta = \Delta(p_{Fe})$, then the temperature T_{mr} of the resistivity maximum will have for large Δ the same dependence on the concentration p_{Fe} . Experimentally it is in fact observed that both T_{mr} and T_{ms} increase with increasing iron concentration in gold,^{15,10} so that our model leads to a correct interpretation of the facts. Gerritsen and Linde²⁶ found a linear relationship between the resistance ratio $r_T = R_T/R_{273^\circ K}$ and the temperature T_{max} of the resistance maximum for silver-manganese alloys. From an experimental study of the dependence of both T_{ms} and T_{mr} on concentration in various alloy systems, it would be possible from our equations to determine the dependence of the several scattering parameters Δ , a , and γ_0/g_0 upon concentration.

The possibility of observing S_i vs T curves of the form shown in Fig. 3(d) is demonstrated by the results of MacDonald and Templeton²⁷ on "pure" potassium whose residual resistance ratio $R_{273}/R_{4.2}$ had the value 400.

Finally, it must be realized that the purest available solvent metals are yet far from being sufficiently clean to permit an easy and unambiguous separation of the effects due to each kind of chemical impurity when one works with very dilute alloys. The resistance and thermoelectric power of not-so-pure alloys would be expected to be rather complex, with perhaps several minima and maxima as found by Gerritsen and Linde,²⁴ for example. It is also conceivable that the presence of minute impurities might cause an apparent "discontinuity" in thermoelectric power of the sort found by Borelius *et al.* (See their Fig. 2 on page 29 of reference 15.)

While it is very important that we develop methods for further purifying metals, it is also important that we carry out systematic investigations on somewhat more concentrated alloys; in this way one can avoid some of the difficulties of obtaining super-purity metals and at the same time help to understand these more concentrated alloys for their own sake.

III. DISCUSSION

We have attempted to explain the low-temperature behavior of resistivity and thermoelectric power of metal alloys on the basis of a simple model of "resonance scattering" of conduction electrons by impurity atoms. Although we have not discussed in detail the high-temperature behavior in terms of this model, it can be seen that the present approach "joins smoothly" with our earlier one⁹ in the sense that in the higher temperature ranges we can use Mott's formula (1) and talk about "effective slopes" of the scattering cross section curve $Q_i(E)$. The resonance model appears to give the correct behavior over the entire temperature range from

²¹ A. J. Croft, E. A. Faulkner, J. Hatton, and E. F. W. Seymour, *Phil. Mag.* **44**, 289 (1953).

²² Iu. P. Gaidukov, *J. Exptl. Theoret. Phys. U. S. S. R.* **34**, 836 (1958) [translation: *Soviet Phys. JETP* **34**(7), 577 (1958)].

²³ These remarks refer to cases in which T_a is of the order of 10°K or less; for large T_a it is possible to have both a maximum and a minimum even though γ_0/g_0 is positive. Of course, in the latter case the "anomalous" behavior will appear at ordinary temperatures as may be seen in Fig. 6(b). Such a behavior is in fact shown by some copper-manganese alloys containing about 9 to 10 atomic percent of "deoxygenated" manganese prepared in our Laboratory. (See second part of reference 9 and also J. O. Linde, *Physica* **24**, S109-117 (1958). Linde finds that the temperature of the resistivity minimum in AuV alloys increases from the liquid helium region for 0.4% V to about 350°K for 1.6% V, and to possibly several hundreds of degrees above room temperature for 5.5% V in gold.)

²⁴ A. N. Gerritsen and J. O. Linde, *Physica* **18**, 877 (1952).

²⁵ A. N. Gerritsen, *Physica* **23**, 1087 (1957).

²⁶ A. N. Gerritsen and J. O. Linde, *Physica* **17**, 573 (1951).

²⁷ D. K. C. MacDonald and I. M. Templeton, *Phil. Mag.* **3**, 917 (1958).

0°K to near the melting point. We have interpreted the temperature dependence to be the result of the complicated overlapping or "scanning" of the function $\tau(E)$ by the derivative function df_0/dT .

In our earlier model we assigned a $Q_i(E)$ curve with a very broad resonance (Ramsauer effect) to certain kinds of impurity atoms, and we assumed that this curve was *fixed in energy* in such a way that the Fermi level moves along this Q_i curve when temperature changes cause the crystal lattice to expand or contract. We made use of effective λ_i values, which give essentially the logarithmic derivative of the cross section with energy. We can see that our earlier model cannot possibly explain the anomalous behavior characteristic of the low-temperature region, since the temperature coefficient of volume expansion is extremely small in the liquid helium range. It seems more reasonable to suppose that the Q_i vs E curves are *fixed relative to the Fermi level for a given alloy*, in such a way that as the temperature changes the resonance energy E_a moves along with the Fermi level E_F . The application of stress to the crystal lattice would also move both E_F and E_a *together*, so that even large hydrostatic pressures would alter neither the resistivity nor the thermoelectric power to the extent that one would calculate on the basis of the associated volume changes in the lattice.

We can now see how the temperature dependent λ_i values originate, in terms of the resonance model. At normal temperatures the parameter λ_i is a measure of

the slope of the $Q_i(E)$ curves which is "seen" by the large majority of electrons with energies within a few kT of the Fermi level. A small fraction of these electrons will have energies for which the slope of $Q_i(E)$ is extremely large, but this small minority of electrons may nonetheless contribute significantly to the integrals in Eq. (6) and thus have an appreciable effect in determining the effective λ_i . When we use Mott's formula at normal temperatures for impurity atoms which exhibit a resonance, we are actually *ignoring the resonance*, then tacitly considering Q_i to be a slowly varying function which permits the use of Mott's approximation, Eq. (1), and finally lumping the contribution of this minority of electrons into an "effective" λ_i . Our earlier work⁹ and that of Friedel,¹¹ Blatt,¹³ and others whose arguments make use of Mott's formula, leads to useful results and enables us to explain phenomenologically as well as to predict the behavior of rather complex alloys. But the use of Mott's formula in cases where there is a sharp resonance—if indeed such things exist in alloys!—is essentially an artifice. We have pointed out that Eq. (1) is also properly applicable at very low temperatures where $kT \ll a$.

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