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Thermoelectric Power and Electron Scattering in Metal Alloys*†

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The thermoelectric power of a metal depends on the details of how the current carriers in the metal are scattered by the various deviations of the crystal from a perfect lattice. A semiempirical theory of thermoelectric power in metal alloys is described, which is based on a formula due to Mott and others. The theory relates absolute thermopower to the energy dependence of the scattering cross section $Q_i(\epsilon)$ of a lattice imperfection, and deduces numerical values for the first few "scattering coefficients" in a Taylor expansion of $Q_i(\epsilon)$ about the Fermi level μ_0 in the pure solvent metal. The few known empirical "rules" of thermoelectric power in binary alloys of Cu, Ag, and Au, of alkali metals, and of Al are interpreted in terms of these scattering coefficients. The correlation with high-temperature thermoelectric properties of such alloys is shown to be quite satisfactory, but the low-temperature properties present several difficulties which cannot be properly discussed without further extensive experiments at very low temperatures. The usefulness of thermoelectricity as a tool for studying the nature of lattice imperfections is discussed briefly.

INTRODUCTION

It has long been known[1,2] that the thermoelectric power of a metal depends upon the *details* of how the current carriers in the metal are scattered by the various deviations of the crystal from a perfect lattice. The most important of these deviations are thermal vibrations and potential perturbations caused by foreign atoms, vacancies and interstitial atoms in the lattice, and dislocations. In contrast to this the electrical resistivity of the metal is determined by the gross or "total" scattering and is relatively insensitive to the precise details of how a scattering center might discriminate between fast and slow electrons. Hence, although a number of papers have been written on the quantum kinetics of thermoelectric power, few of these have carried the theory to the point of making actual numerical calculations for a variety of metals and alloys. One of the main difficulties in the field of thermoelectricity is that there has been found very little "empirical consistency" in the variation of thermopower from metal to metal and from alloy to alloy. (Thermoelectricity has no "Matthiessen Rule," no "Wiedemann-Franz Relation.") There have been attempts to formulate "additivity rules" for thermopower, for example by Kohler,[3] and in this case the additive quantity is the ratio of thermopower to thermal conductivity. Kohler emphasizes the importance of using *absolute* thermopower instead of relative thermopower in such additivity relations. Unfortunately, a disadvantage of such relationships is that they involve other parameters besides thermopower, so that a comparison with experiment necessitates having simultaneous thermopower and thermal conductivity data for the same specimens.

Introducing the Wiedemann-Franz relation into his formulas, Kohler deduces the following rule: If two noble-metal alloys A and B are formed into a thermocouple, metal A is thermoelectrically positive against B if the residual or impurity resistivity of B is greater than that of A, and this results from the fact that the noble metals (Cu, Ag, Au) have *positive* absolute thermopowers. On the other hand, Kohler's formula predicts the reverse polarity for the relative thermopower of the thermocouple if the solvent metal is one of the alkali metals which has a *negative* absolute thermopower. It is found experimentally[4] that if almost any foreign atom is added in small amounts to Cu, Ag, or Au, the resulting alloy is thermoelectrically negative relative to the pure solvent. Manganese dissolved in copper is one exception[5,6] and the absolute thermopowers of α-phase (Cu-rich) Cu−Mn alloys attain values higher and higher above that for pure copper as the temperature increases (at least as far as data are available, namely, +700°K). Ti and Cr in Cu appear to be additional exceptions,[7] but the thermopower data available for these alloys are not extensive.[8] Apart from these three cases, we know of no other exceptions to Kohler's rule. In the *International Critical Tables* the compilation by Caswell gives the thermopower of Ag−Tl alloys as positive relative to pure silver, but the sign convention of Bernoulli,[9] from whose work Caswell's

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† During the final typing of our manuscript our attention was called to a recent paper by J. Friedel, J. phys. et radium **14**, 561 (1953), on much the same problem as we discuss here. There seems to be at least one very important difference between our two points of view. Friedel assumes that for small impurity concentrations the Fermi level of the metal remains fixed upon alloying; in contrast to this, we attribute the main features of thermopower behavior to precisely this variation of Fermi level upon alloying, even for very small impurity concentrations. It is interesting that both we and Friedel have speculated on the existence of an "internal Ramsauer effect."

[1] A. Sommerfeld, Z. Physik **47**, 1, 43 (1928).

[2] L. Nordheim and C. J. Gorter, Physica **2**, 383 (1935).

[3] M. Kohler, Z. Physik **126**, 481 (1949).

[4] G. Borelius, *Handbuch der Metallphysik*, edited by G. Masing, (Leipzig, Akademische Verlagsgesellschaft m.b.h., 1935), Vol. 1, part 1, p. 404.

[5] A. L. Norbury, Phil. Mag. **2**, 1188 (1928).

[6] J. L. Thomas, J. Research Natl. Bur. Standards **16**, 149 (1936).

[7] See W. H. Keesom and C. J. Mattijs, Physica **2**, 623 (1935).

[8] We have begun an experimental study of the systems Cu−Mn, Ag−Mn, Au−Mn, Cu−Ti, and Cu−Cr.

[9] A. L. Bernoulli, Ann. Physik **33**, 690 (1910).

data are taken, is the reverse of that commonly used nowadays.

Another fairly general trend was found by Norbury,[5] who pointed out that the initial slopes of thermopower *vs* composition curves increase with increasing valence, for various elements dissolved in copper.

We propose to show that present quantum theories for thermoelectric power can lead to interesting and important information about electron scattering in solids. The formulation of Mott[10] is particularly convenient for our purposes inasmusch as his formula for absolute thermopower is given in terms of the energy dependence of resistivity. We shall concentrate primarily on dilute, substitutional, binary alloys of various foreign atoms in Cu, Ag, or Au, but the general approach should be useful in other alloy systems as well. In fact, we hope soon to extend the study to ternary alloys, and to scattering by lattice vacancies, interstitials, and dislocations. The arguments given here should be applicable to alkali metal-base alloys, and do indeed seem to apply to very recent results of MacDonald and Pearson.[11] However, the solubility of most nonalkali atoms in the alkali metals is extremely small.

A. FORMULAS FOR ABSOLUTE THERMOPOWER AND RESISTIVITY

According to Mott[10] the absolute thermopower S of a metal or alloy is given by

$$S=(\pi^2k^2T/3|e|)[\partial \ln\rho(\epsilon)/\partial\epsilon]_{\epsilon=\mu}. \qquad (1)$$

Here k is the Boltzmann constant, e is the electron charge, T is the absolute temperature, ϵ is the energy of the electrons at the surface of the Fermi distribution, and μ is the actual value of ϵ in the particular metal in question. The formula is valid for pure metals for temperatures $T\gg\Theta_D$, where Θ_D is the Debye temperature; and for $T\ll T_0$, T_0 being the "degeneracy" temperature of the free electron gas in the metal. The values of T_0 for Cu, Ag, and Au are of the order of 50 000°K, whereas for Fe, Ni, Pt, Pd, etc. (transition metals), T_0 is probably an order of magnitude smaller, roughly speaking. The formula is valid for any functional relation between energy and wave number, $\epsilon=\epsilon(\mathbf{k})$, provided that the scattering is isotropic. Finally, the formula is applicable to alloys even at low temperatures, provided that the impurity resistivity ρ_i is much greater than the resistivity ρ_T resulting from lattice vibration or phonon scattering.

The significance of the derivative in (1) is as follows. If the energy ϵ of the "surface electrons," i.e., those which actually carry the current, could be varied without otherwise altering a given metal or alloy, then the resistivity $\rho(\epsilon)$ would vary. The way in which the resistivity would vary thus determines the thermopower, according to Eq. (1), the logarithmic derivative being evaluated at the actual Fermi level $\epsilon=\mu$ of the electrons in the lattice. There is no way in which the level μ can be varied in an actual metal without simultaneously introducing other changes. For example, if one dissolves foreign atoms in Cu, the Fermi level will usually change; however, in so doing we also introduce new scattering centers whose cross sections have their own peculiar energy dependence, so that we should then need to separate these scattering effects from one another. Likewise, by squeezing the metal we can change the Fermi level, but we will at the same time alter the effective potential distribution around each atom and thereby change not only μ but also the *function* $\rho(\epsilon)$ itself. However, we can use relation (1) by postulating some reasonable energy dependence for the resistivity ρ, then comparing the deductions from the formula with the known thermoelectric properties of metals.

We write the total resistivity $\rho(\epsilon)$ of the binary alloy in the usual form,

$$\rho(\epsilon)=\rho_T(\epsilon)+\rho_i(\epsilon), \qquad (2)$$

where $\rho_T(\epsilon)$ represents the "thermal" resistivity arising from phonon scattering of the electrons and $\rho_i(\epsilon)$ represents that arising from perturbations of the solvent lattice potential caused by the presence of the impurity atoms. In the cases that it is possible to speak of a mean free path one can express the impurity resistivity $\rho_i(\epsilon)$ in terms of an effective, total scattering cross section $Q_i(\epsilon)$ which is in general a function of the energy of the current-carrying electrons:[12,13]

$$\rho_i(\epsilon)=[(2m)^{\frac{1}{2}}n_i/e^2n_0]\epsilon^{\frac{1}{2}}Q_i(\epsilon), \qquad (3)$$

where m, e are electronic mass and charge, n_i is the density of impurity atoms in the alloy, and n_0 is the density of "free electrons" in the lattice. It should be emphasized that Eq. (3), and therefore our entire theory, is based on the one-electron approximation. If we let x be the fraction of impurity atoms in the alloy, β be the number of conduction electrons contributed per impurity atom, and suppose for simplicity that each solvent atom (Cu, Ag, Au, Na, or K, etc.) contributes a single conduction electron per atom, then the ratio n_i/n_0 in (3) becomes $x/[1+(\beta-1)x]$ and (3) becomes

$$\rho_i(\epsilon)=21.1\frac{x}{1+(\beta-1)x}\epsilon^{\frac{1}{2}}Q_i(\epsilon), \quad \mu\Omega-\text{cm}, \qquad (4)$$

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[10] N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Oxford University Press, London, 1936).

[11] D. K. C. MacDonald and W. B. Pearson, Proc. Roy. Soc. (London) **A221**, 534 (1954). The most often quoted experimental work on the thermopower of alkali metals is that of C. C. Bidwell, Phys. Rev. **23**, 357 (1924). More recent work is that of E. Heiber, Ann. Physik **23**, 111 (1935).

[12] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1939), p. 541.

[13] The assumption that mean free path (or cross section) is energy independent is valid only for very special scattering potentials. For example, the "hard-sphere approximation" leads to $\partial l/\partial\epsilon=0$; but for more realistic scattering potentials there results in general an energy dependence of mean free path l on energy. For simplicity we assume throughout this paper that the effective electron mass is simply the free electron mass.

the energy ϵ now being expressed in electron volts, $Q_i(\epsilon)$ in A^2 units (i.e., in units of 10^{-16} cm^2), and $\rho_i(\epsilon)$ in microhms-cm. The actual residual resistivity of the alloy is given by (4) evaluated at $\epsilon=\mu$. We assume that the alloys are relatively dilute ($x\leq 0.1$ approximately, i.e., $\leq$ 10 atomic percent); and since the Fermi energy μ of an ideal free-electron gas varies with the $\frac{2}{3}$ power of the electron density, we see that, if we neglect lattice parameter changes upon alloying, the Fermi level varies with composition x in the following manner for small $(\beta-1)x$:

$$\mu=\mu_0[1+(\beta-1)x]^{\frac{2}{3}}\cong\mu_0[1+\tfrac{2}{3}(\beta-1)x]. \tag{5}$$

Inserting this into Eq. (4) and again using approximations appropriate to small $(\beta-1)x$, one finds for the actual resistivity of the alloy

$$\begin{aligned}\rho_i(\mu)&=21.1x[1-\tfrac{2}{3}(\beta-1)x]\mu_0^{\frac{1}{2}}Q_i(\mu)\\&=0.211p\left[1-\frac{\beta-1}{150}p\right]\mu_0^{\frac{1}{2}}Q_i(\mu);\end{aligned} \tag{6}$$

the units here are of course the same as in (4), and the atomic percentage $p=100x$.

It is customary[14] to define the so-called "atomic resistivity change" ζ as the *initial* slope of the resistivity *vs* percent impurity curve, so that if we assume in Eq. (2) that ρ_T is independent of p, we find from Eq. (6) that

$$\zeta=[\partial\rho_i(\mu)/\partial p]_{p=0}=0.211\mu_0^{\frac{1}{2}}Q_i(\mu_0). \tag{7}$$

It has been found that ζ can be expressed in the form

$$\zeta=k_1+k_2z^2, \tag{8}$$

where k_1 and k_2 are nearly constant for dilute binary solid solutions of various atoms in Cu, Ag, or Au, and $z=N-11$, N being the group number (column number) of the added element in the column-of-eighteen periodic table of the elements. Equation (8) represents the empirical rule found by Norbury[15] and Linde[16] and explained by Mott.[17]

Now it is clear that what is needed is the energy dependence of the scattering cross section $Q_i(\epsilon)$. Suppose that this function be expanded in a Taylor series about the Fermi energy $\epsilon=\mu_0$ in the pure metal. We can write this expansion in the form

$$Q_i(\epsilon)=Q_0[1+\alpha_1(\epsilon-\mu_0)+\alpha_2(\epsilon-\mu_0)^2+\cdots], \tag{9}$$

where

$$Q_0=Q_i(\mu_0),\quad Q_0\alpha_1=[\partial Q_i(\epsilon)/\partial\epsilon]_{\mu_0},$$
$$2Q_0\alpha_2=[\partial^2Q_i(\epsilon)/\partial\epsilon^2]_{\mu_0},\ \cdots.$$

We shall see that in most cases only the linear term (in α_1) in (9) is needed for the thermopower calculations, while in some cases the α_2 term is also necessary. In Sec. E we shall correlate the terms in (9) with an analytic expression derived by Mott[17] for calculating resistivities of binary alloys.

If we substitute Eq. (2) into (1), we find

$$\begin{aligned}(3|e|/\pi^2k^2)(S/T)&=[\partial\ln\rho(\epsilon)/\partial\epsilon]_\mu\\&=(\rho_T+\rho_i)^{-1}[\partial\rho_T(\epsilon)/\partial\epsilon+\partial\rho_i(\epsilon)/\partial\epsilon]_\mu.\end{aligned} \tag{10}$$

The second term in the brackets is $\rho_i[\partial\ln\rho_i(\epsilon)/\partial\epsilon]_\mu$, and from (3), (5), and (9) we find

$$\rho_i\left[\frac{\partial\ln\rho_i(\epsilon)}{\partial\epsilon}\right]_\mu=\rho_i\left[\frac{1}{2\epsilon}+\frac{1}{Q_i}\frac{\partial Q_i}{\partial\epsilon}\right]_\mu\cong\rho_i\left[\frac{1}{2\mu_0[1+(\beta-1)p/150]}+\frac{\alpha_1+2\alpha_2\mu_0(\beta-1)p/150}{1+\alpha_1\mu_0(\beta-1)p/150+\alpha_2\mu_0^2(\beta-1)^2p^2/(150)^2}\right]. \tag{11}$$

At temperatures $T\gg\Theta_D$ we have, from Mott's formula (1) applied to the pure metal,

$$S_0=[\pi^2k^2T/3|e|][\partial\rho_T(\epsilon)/\partial\epsilon]_{\mu_0}\cdot[\rho_T(\mu_0)]^{-1},$$

so that

$$[\partial\rho_T(\epsilon)/\partial\epsilon]_{\mu_0}=3|e|\rho_T(\mu_0)S_0/(\pi^2k^2T), \tag{12}$$

in which S_0 is the absolute thermopower of the solvent metal at temperature T. The first term in the brackets in (10) is the derivative $\partial\rho_T/\partial\epsilon$ evaluated at $\epsilon=\mu$, the Fermi level in the *alloy*, whereas in (12) this derivative is evaluated at $\epsilon=\mu_0$, the level in the *pure solvent metal*. There are several reasons for supposing that these two derivatives are almost exactly equal. First, if we make the reasonable assumption that the phonon scattering is of the same nature in the three similar metals Cu, Ag, and Au, we can suppose that the derivative $\partial\rho_T/\partial\epsilon$ is practically uniform over a large electron-energy range, since these *pure* metals have very nearly equal thermopowers despite the large differences in Fermi energy μ_0. Thus whereas the level μ_0 changes by a factor of approximately 2 in passing from pure Cu to pure Au, the Fermi level μ in noble-metal base alloys varies only slightly from μ_0 (in the pure metal) as we dissolve even up to 10 atomic percent of a foreign atom in the solvent. Secondly, the absolute thermopowers of all the *pure* metals extended over a range of only some 50 μv/deg despite the large variation in crystal structure, Fermi level, and phonon distribution functions; this indicates that the quantity $\partial\rho_T/\partial\epsilon$ does not vary rapidly with energy. This situation is to be contrasted with the very great effect on the thermopower of the noble metals when only minute amounts of impurities are added to the solvents. Thirdly, from the quantum-mechanical point of view one would expect the *purely phonon scattering itself* to be determined primarily by the distribution-in-energy of the phonons, and this

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[14] G. Borelius, reference 4, p. 336.

[15] A. L. Norbury, Trans. Faraday Soc. **16**, 570 (1921); A. L. Norbury and K. Kuwada, Phil. Mag. **4**, 1338 (1927).

[16] J. O. Linde, Ann. Physik **10**, 52 (1931); **14**, 353 (1932); **15**, 219 (1932).

[17] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

would surely not change radically as a result of the introduction of a small percentage of foreign atoms; it follows that the *rate of change* of this scattering with electron energy would be quite small.[18] For these reasons we feel justified in assuming that the derivatives of $\rho_T(\epsilon)$ in Eqs. (10) and (12) are equal or very nearly so; i.e., we set

$$[\partial\rho_T(\epsilon)/\partial\epsilon]_\mu=[\partial\rho_T(\epsilon)/\partial\epsilon]_{\mu_0}. \tag{13}$$

Upon substituting (11), (12), and (13) into (10) and solving for S, we find

$$S=[\rho_T+\rho_i]^{-1}\cdot\left\{S_0\rho_T+\frac{\pi^2k^2}{3|e|}\cdot\rho_iT\left[\frac{1}{2\mu_0[1+(\beta-1)p/150]}+\frac{\alpha_1+2\alpha_2\mu_0(\beta-1)p/150}{1+\alpha_1\mu_0(\beta-1)p/150+\alpha_2\mu_0^2(\beta-1)^2p^2/(150)^2}\right]\right\}, \tag{14}$$

where S is the absolute thermopower of the alloy containing p atomic percent of a foreign atom in solid solution in Cu, Ag, Au, Li, Na, $\cdots$, S_0 and ρ_T are, respectively, the absolute thermopower and resistivity of the *pure* solvent metal at temperature T°K, and ρ_i is given by Eqs. (6) and (9). Inserting numerical values for the constants in (14) one finds the formula

$$S=[\rho_T+\rho_i]^{-1}\left\{S_0\rho_T+0.0243\rho_iT\left[\frac{1}{2\mu_0[1+(\beta-1)p/150]}+\frac{\alpha_1+2\alpha_2\mu_0(\beta-1)p/150}{1+\alpha_1\mu_0(\beta-1)p/150+\alpha_2\mu_0^2(\beta-1)^2p^2/(150)^2}\right]\right\}, \tag{15}$$

in which now S, S_0 are in microvolts/deg K, ρ_T and ρ_i must be in microhm-cm in order to be consistent with Eq. (6), $\pi^2k^2/(3|e|)=0.0243$ (ev-microvolt)/deg,^{2} μ_0 is in ev, α_1 in (ev)$^{-1}$, α_2 in (ev)$^{-2}$, and p is atomic percent. Equation (15) is the basis of our discussion of the thermopower of noble-metal base alloys at temperatures above the Debye temperature of the solvent metal. It should be emphasized that (15) is valid only for $T>\Theta_D$, because of our use of Eq. (12) for the pure metal. We shall discuss in Sec. F the formulas which apply at low temperatures.

B. APPLICATIONS TO DILUTE BINARY ALLOYS OF Cu, Ag, Au, Li, Na, etc., $T\gg\Theta_D$

Equation (15) for the absolute thermopower of an alloy, together with the relations (6) and (9) for ρ_i and Q_i, contains the following parameters:

(1) μ_0, the Fermi level at T°K in the pure metal. This parameter is almost temperature independent in "ideal gas" metals if there is no expansion of the lattice. We shall neglect these changes with T, although the variation resulting from thermal expansion can be very significant. In fact, this latter variation may have a great deal to do with deviations from linearity of S with T at very low temperatures.

(2) β, the number of conduction electrons contributed per atom by the solute. For this parameter one should attempt to be consistent with the arguments of Friedel,[19] Jones,[20] and Haworth and Hume-Rothery,[21] although it appears that the "best" value for β depends in many cases upon the particular physical property with which one is concerned.

(3) Q_0, the "zero-order" approximation to the scattering cross section in Eq. (9). We shall see that the terms in α_1 and α_2 in Eq. (9) are generally only very small fractions. Thus, while the resistivity[7] is determined by the "zero-order" approximation Q_0, the thermopower (15) is strongly dependent on the way in which the cross section varies with the speed of the current-carrying electrons. From Eqs. (7) and (9) we see that the atomic resistivity change ζ is determined by Q_0, and this fact allows us to deduce values of Q_0 from experimentally-found values of ζ, for example from the extensive measurements of Linde.[16] The parameter Q_0 enters into the S expression (15) through the factor ρ_i in the numerator and denominator.

(4) α_1 and α_2, the first- and second-power coefficients in the expansion for the scattering cross section (9). These parameters can in principle be computed by an elaborate program of curve fitting, in which the expression (15) is made to fit known experimental data. Such a program would be of questionable value, since most available thermoelectric data on alloys is subject to fairly large errors and since the alloys themselves have contained varying amounts of unspecified impurities. It will always be possible of course to fit a given S *vs* p curve if one is willing to use additional terms in the cross section expansion (9). For these reasons we shall show how the scattering parameters Q_0, α_1, and α_2 determine the thermopower by giving curves for some hypothetical alloys, and we shall give only a few applications to actual binary alloys, namely Cu$-$Zn, Cu$-$Si, Cu$-$Sn, and Cu$-$Ni.

Following Linde and Mott we introduce the quantities q_0, q_1, and z,

$$Q_0\equiv q_0+q_1z^2,\quad Q_0,\ q_0,\ q_1 \text{ in A}^2\text{ units}, \tag{16}$$

in which z has the same meaning as before and q_0 and q_1 are generally taken to be approximately constant for a given solvent. Actually, it is known from resistivity data on noble-metal base alloys that q_0 and q_1 vary by as much as a factor of 2 from one solute atom to another.[14] At temperatures above 400°K the absolute

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[18] In this respect it might be mentioned that the transition-metal base alloys require special consideration, in contrast to those alloys with Cu, Ag, or Au as solvent.

[19] J. Friedel, Phil. Mag. 43, 153 (1952).

[20] H. Jones, Phil. Mag. 44, 907 (1953).

[21] J. B. Haworth and W. Hume-Rothery, Phil. Mag. 43, 613 (1952).

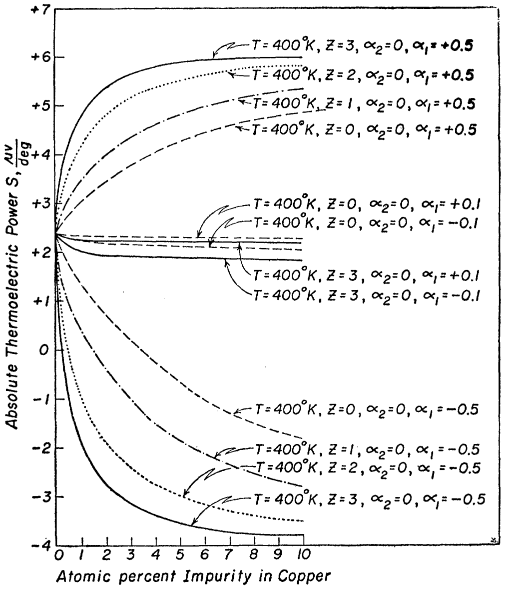

FIG. 1. Thermopower *vs* impurity concentration for hypothetical alloys.

thermopower S_0 and resistivity ρ_T of pure copper satisfy the relation $S_0\rho_T/T=3.46\times10^{-5}T$ sufficiently well for our purposes, with S_0 in μv/deg and ρ_T in $\mu\Omega$-cm. The resistivity is given by $6.00\times10^{-3}T$ $\mu\Omega$-cm. Using the abbreviation $y\equiv(\beta-1)p/150$ and restricting ourselves for the present to small values of α_1, α_2, β, and y, i.e., for

$$|\alpha_1|\leq0.2,\quad |\alpha_2|\leq0.4,\quad -1\leq\beta\leq+2,\quad |z|\leq5,$$

approximately, the formula (15) becomes

$$S\cong S_0\cdot\frac{1+(305/T)(q_0+q_1z^2)p[0.118+\alpha_1+8.5\alpha_2y]}{1+(72.3/T)(q_0+q_1z^2)p}. \tag{17}$$

This relation will serve to show the general behavior of the absolute thermopower as the several scattering parameters are varied; this behavior is illustrated in Fig. 1, in which are shown the values of S at 400°K for hypothetical alloys of copper as given by Eq. (17). The value of S_0 for pure copper at 400°K is $+2.38$ μv/deg, as given by Borelius *et al.*[22] and by Nyström.[23] We notice first that the general shape of the curves is that characteristic of most noble-metal alloys. Secondly, it is seen that the initial slope of the S *vs* p curve is positive only for values of α_1 greater than some critical value $\alpha_1{}^c$. This critical value can most easily be found by taking the limiting form of Eq. (17) for very small p,

$$\begin{aligned} &S/S_0\rightarrow1-(36.3Q_0p/T)(1-8.39\alpha_1),\\ &[\partial(S/S_0)/\partial p]_{p=0}=-36.3T^{-1}(q_0+q_1z^2)(1-8.39\alpha_1); \end{aligned} \tag{18}$$

we then find

$$\alpha_1{}^c=0.12. \tag{19}$$

Thus, a binary copper alloy will be thermoelectrically positive relative to pure copper if $\alpha_1>0.12$, negative to pure copper if $\alpha_1<0.12$, and this is so for all temperatures (above Θ_D). We conclude from the rule of Borelius and Kohler mentioned in the Introduction that most atoms dissolved in Cu have values of α_1 less than about $+0.12$, whereas Mn and possibly Ti and Cr have α_1 values larger than 0.12 when dissolved in Cu. The solvents Ag and Au would have values of $\alpha_1{}^c$ which are slightly different from 0.12, since $\alpha_1{}^c$ will be seen [Eq. (23)] to depend on μ_0 and on the thermopower S_0 for the pure solvent metal. Finally, it is seen from Fig. 1 and from Eq. (18) that for fixed values of α_1, q_0, and q_1, the initial slopes of the S/S_0 curves increase with increasing z, in agreement with the "rule" of Norbury mentioned in the Introduction. However, if one dissolves in succession the Row-4*b* atoms Zn, Ga, Ge, and As in Cu, according to Eq. (18) the initial S/S_0 *vs* p slopes will not necessarily increase with z^2 *alone*, since these slopes depend also on q_0, q_1, and α_1. This dependence on q_0, q_1, and α_1 should be particularly noticeable when one compares the thermopowers of such alloy series as Cu—Zn, Cu—Cd in Column II-B, or Cu—Si, Cu—Ge, Cu—Sn, and Cu—Pb in Column IV-B, since the parameter z certainly cannot be expected to be the only determining factor for the scattering. It turns out that the S *vs* p curves for this latter series at first dip down and then turn upwards again, the minimum lying around 2 or 3 atomic percent. The curves for Cu—Si and Cu—Sn at several temperatures are shown in Fig. 2. Data for Cu—Sn at 400°K do not seem to be available above about 2 atomic percent; however, since the S *vs* p curves generally have the same shape at the higher temperatures, we have used the data of

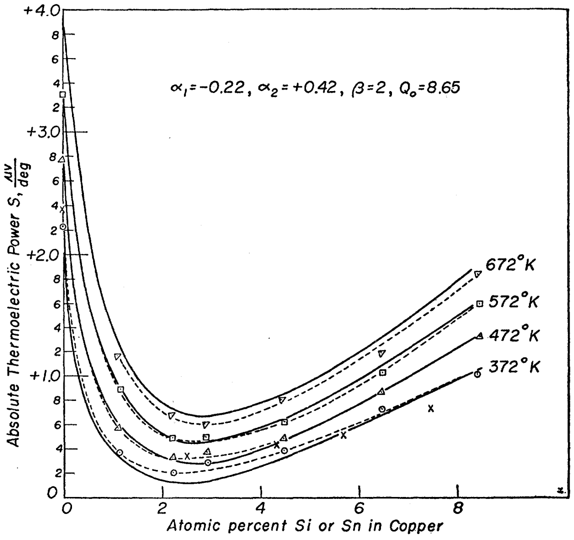

FIG. 2. Thermopower *vs* silicon content at various temperatures. The solid curves are theoretical, the dotted curves experimental. For comparison, experimental data on Cu—Sn alloys at 400°K are included (crosses).

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[22] Borelius, Keesom, and Johansson, Leiden Comm. **196a** (1928) or Proc. Acad. Sci. Amsterdam **31**, 1046 (1928).

[23] J. Nyström, Arkiv. Mat. Astron. Fysik **A34**, No. 27 (1948).

Andrewartha and Evans,[24] who give mean relative thermopowers against copper between 283°K and 373°K, and after conversion to absolute thermopower we have then shifted the curve upward to coincide with $S_0=2.38$ μv/C° at 400°K for $p=0$. These data are shown by the crosses in Fig. 2. There are no thermopower data available for Cu—Ge, and Pb has only a very small solubility in Cu. Thus two of the four IV-B atoms Si, Ge, Sn, and Pb when dissolved in Cu show the behavior illustrated in Fig. 2. This behavior requires the use of the $\alpha_2(\epsilon-\mu_0)^2$ term in $Q_i(\epsilon)$, Eq. (9), and the values of the scattering coefficients α_1 and α_2 for Si in Cu are given in the figure. The data of Norbury[5] for Sn in Cu up to ~700°K give a somewhat steeper drop in S than is shown in Fig. 2, with increasing Sn content, but his alloys contained up to only 2 atomic percent Sn. We have therefore chosen to use instead the results of Andrewartha and Evans.

The actual experimental values for Cu—Zn alloys[5] are compared in Fig. 3 with the calculations using Eq. (17).

The metals Fe, Co, and Ni have unusually large effects on the thermopower of Cu, Ag, and Au, and their behavior is typified by the S *vs* p curves for Cu—Ni at 400°, 500°, 600°, and 700°K in Fig. 4. As before, the value of Q_0 used was determined from ζ values found experimentally. The initial slopes of the experimental S *vs* p curves can in principle be used to determine α_1; however, there seems to be little information on very dilute alloys at higher temperatures, so that it is better to use "hypothetical" curves such as those in Fig. 1 as a guide, and to adjust the scattering parameters slightly to get a good fit with experimental curves. The parameters necessary for describing the impurity scattering in Cu—Ni, Cu—Fe, and Cu—Co are too large to permit the use of Eq. (17), and one must return to the original expression (15). The theoretical curves in Fig. 4 were calculated to fit some very meager data on Cu—Ni obtained in our laboratory. The shapes of the curves are identical with those of Norbury,[5] but Norbury's thermopowers have larger negative values than ours.

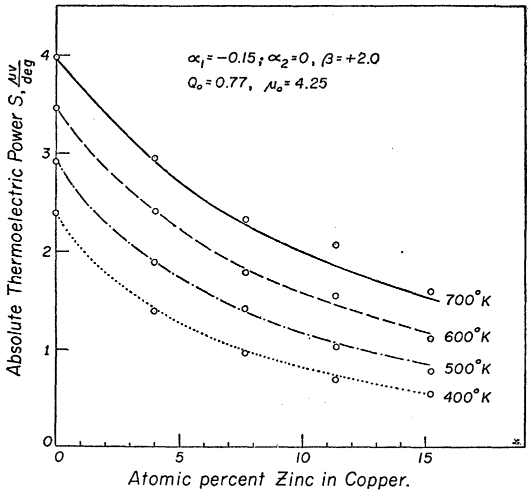

FIG. 3. Thermopower *vs* zinc content at various temperatures. All four curves are theoretical. Circles show experimental data.

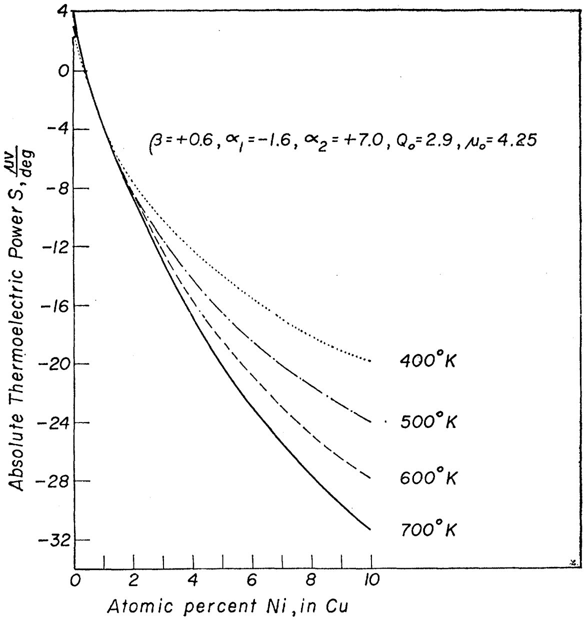

FIG. 4. Thermopower *vs* nickel content at various temperatures. All four curves are theoretical.

Coles[25] has compared the electronic structures and physical properties of the systems Cu—Ni and Ag—Pd and has pointed out the striking difference between the S *vs* p curves for these two systems. Palladium reduces the absolute thermopower of Ag, but at a slow rate, of the order of 0.3 μv/deg per atom percent Pd; on the other hand, Ni reduces the thermopower of Cu at a rate of roughly 3 μv/deg per atom percent Ni. This means that the α_1 for Pd in Ag is much smaller than the α_1 for Ni in Cu.

C. RESISTIVITY

We come now to the question of how the scattering parameters α_1 and α_2 affect the resistivity ρ_i. From Eqs. (6), (9), and (5) it is seen that for Cu-, Ag-, and Au-base alloys

$$\rho_i=0.211\mu_0^{\frac{1}{2}}Q_0p\left[1-\left(\frac{\beta-1}{150}\right)p\right]\times\left[1+\alpha_1\mu_0\left(\frac{\beta-1}{150}\right)p+\alpha_2\mu_0^2\left(\frac{\beta-1}{150}\right)^2p^2\right]. \quad (20)$$

It is found for many dilute, noble-metal base alloys, that the ρ_i *vs* p curves increase approximately linearly with

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[24] G. G. Andrewartha and E. J. Evans, Phil. Mag. **31**, 265 (1941).

[25] B. R. Coles, Proc. Phys. Soc. (London) **B65**, 221 (1952).

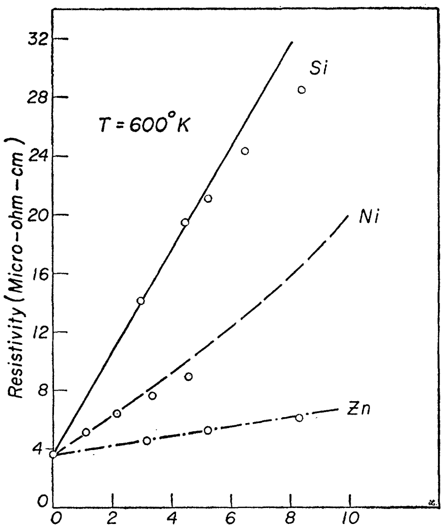

FIG. 5. Resistivity *vs* impurity concentration. All three curves are theoretical. The points show experimental data.

p. From Eq. (20) it is seen that the deviation of ρ_i from linearity with p is very sensitive to the values of the parameter β, the number of electrons contributed per atom of the solute. In cases where the thermopower varies slowly with p and for which therefore small values of α_1 and α_2 are required, the bracketed terms in (20) remain so near unity that comparison with experiment is difficult. It is no easy matter to determine accurately the impurity content of alloys. Nevertheless, in the cases of Cu−Zn and Cu−Si alloys, agreement with the theory is satisfactory as seen from Fig. 5. On the other hand, in the case of Cu−Ni, for example, large values of α_1 and α_2 are required to fit the thermopower curves. Now it has been customary to assign the value zero to the "valency" β of transition metals dissolved in Cu, Ag, and Au. If we use $\beta=0$ in Eq. (15) for thermopower, we require such large values of α_1 and α_2 (in the Cu−Ni case, for example) that at $p=10$ atomic percent the bracketed term in ρ_i from Eq. (20) attains values of about 2, which of course represents an enormous deviation from linearity. Experiment shows that ρ_i *vs* p for dilute Cu−Ni alloys is practically a straight line. (See Fig. 5.) But it has been shown by Jones[20] and by Haworth and Hume-Rothery[21] that in Cu alloys with Fe, Ni, Co, and Mn, both binary and ternary (with Zn or with Al), the valency of these transition metals is not only nonzero but actually varies with composition. They find, for example, that Ni, Co, Fe, and Mn behave as though they possessed valencies of about 0.6, 0.8, 1.0, and 1.9, respectively, in the systems Cu−Zn−Ni, Cu−Zn−Co, Cu−Zn−Fe, Cu−Zn−Mn, Cu−Al−Co, Cu−Al−Fe, and Cu−Al−Mn. In fact, Haworth and Hume-Rothery hold that the effective valence of Ni in Cu is radically different at the Cu-rich side of the phase diagram from what it is at the Ni-rich side. If, therefore, we use values of the order of $\beta\approx 0.6$ electron/Ni atom in Eqs. (15) and (20) we arrive at much more satisfactory agreement with experiments on the impurity resistivity of this alloy system. This situation we consider to be support for the metallurgical properties discussed by Jones, Haworth, and Hume-Rothery, although from Fig. 5 it is seen that the ρ_i *vs* p curves for Cu−Ni bend the wrong way.

D. APPLICATIONS TO OTHER ALLOY SYSTEMS

We attempt first to apply the theory to the alloys of aluminum. Crussard[26] has made a rather extensive study of dilute aluminum alloys and his results have been explained qualitatively by Galt[27] on the basis of Mott's equation (1). However, Galt does not consider scattering from the impurities themselves, and assumes as does Mott[10] that the effect of these impurities is simply to vary the Fermi level in the metal. According to our picture this assumption is not allowable.

Because of the difference in number of conduction electrons per atom between Cu and Al, our formula (15) for absolute thermopower must be altered slightly. Instead of using the factor $(\beta-1)p/150$ we should write $(\beta-3)p/150$, where we have assumed that Al has three valence electrons per atom. We mention this detail only to emphasize the fact that Eq. (15) applies as it stands only to Cu, Ag, Au, Li, Na, K, $\cdots$, etc., and the factor $(\beta-3)$ will not enter into the formulas we wish to discuss in connection with aluminum alloys.

We concern ourselves only with the following "rule" laid down by Crussard: The absolute thermopower of Al ($\Theta_D=390$°K) is negative (at ordinary temperatures); when small amounts of a metal preceding Al in the column-of-eight periodic table are dissolved in Al, the absolute thermopower is algebraically increased (becomes less negative); when the dissolved metal follows Al in this table the thermopower is algebraically decreased (becomes more negative). It can be shown that for $p\rightarrow 0$, Eq. (15) becomes

$$S/S_0\rightarrow 1+0.211\mu_0^{\frac{1}{2}}Q_0\rho_T^{-1}p \times[0.0243TS_0^{-1}(2^{-1}\mu_0^{-1}+\alpha_1)-1], \quad (21)$$

if we neglect the higher terms in the $Q_i(\epsilon)$ expression (9). Equation (18) is a special case of (21) applied to Cu. The initial slope of (21) is then

$$(\partial S/\partial p)_{p=0}=0.211\mu_0^{\frac{1}{2}}Q_0S_0\rho_T^{-1} \times[0.0243TS_0^{-1}(2^{-1}\mu_0^{-1}+\alpha_1)-1]. \quad (22)$$

From (22) it is seen that in general

$$(\partial S/\partial p)_{p=0} \text{ is positive for } \alpha_1\gtrless\left(\frac{S_0}{0.0243T}-\frac{1}{2\mu_0}\right) \text{ when } S_0 \text{ is} \begin{cases}\text{positive}\\ \text{negative}\end{cases}. \quad (23)$$

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[26] C. Crussard in Report of Conference on Strength of Solids, H. H. Wills Laboratory, Bristol (Physical Society, London, 1948), p. 119; Compt. rend. **226**, 1003 (1948).

[27] J. K. Galt, Phil. Mag. **40**, 309 (1949).

Taking $S_0 = -0.00563T$°K for Al and $\mu_0^{\text{Al}} = 4$ ev, we find $(\alpha_1^c)^{\text{Al}} = -0.356(\text{ev})^{-1}$.

The application of Eq. (15) to Ni-, Fe-, and Co-base alloys is more difficult than in the alloys already considered. However, it should be possible to apply the basic arguments given here even in the cases of these alloys.

E. CORRELATION WITH THEORETICAL FORMULAS FOR SCATTERING CROSS SECTION

In order to arrive at a connection between our empirically determined scattering parameters Q_0, α_1, α_2, etc., and the atomic structure of the impurity scattering centers we have chosen a formula of Mott[17] which relates the impurity resistivity of binary alloys of Cu, Ag, Au, Li, Na, K, etc., to the velocity of the current-carrying electrons in the metal. Mott uses a one-electron approximation, of course, and takes the electron to be free ($\mathbf{v} = \hbar\mathbf{k}/m$). The foreign atom is shown to introduce a perturbing potential of the form $V = (1/r)\exp(-r/r_0)$, the so-called screening potential. Mott's final formula for the scattering cross section of a foreign atom is[28]

$$Q_i(\epsilon) = 2\pi(ze^2/mv^2)^2 f(y), \tag{24}$$

where z has the same meaning as our z, $e = 4.80\times10^{-10}$ esu, $m = 9.1\times10^{-28}$ g, v is the velocity of the scattered electron in cm/sec, $Q_i(\epsilon)$ is in cm², and $f(y)$ is

$$f(y) = \ln\left(1+\frac{1}{y}\right) - \frac{1}{1+y}, \tag{25}$$

with the abbreviation $y = \hbar^2/(4m^2v^2r_0^2)$. Here r_0 is the "screening radius" in the scattering potential and is the reciprocal of the usual screening constant q_0. If the cross section is expressed in A² and the energy in electron-volts, Eq. (24) becomes

$$Q_i(\epsilon) = 326(z^2/\epsilon^2)f(y). \tag{26}$$

We have seen in Eq. (9) that for a given dependence $Q_i(\epsilon)$ of cross section on energy, the Taylor expansion for this $Q_i(\epsilon)$ will be in the form of (9) if we set $\Delta \equiv 0.953/r_0^2$ and

$$\alpha_1 \equiv \left[\frac{1}{Q_i}\frac{\partial Q_i}{\partial\epsilon}\right]_{\mu_0} = \left[\frac{\partial \ln Q_i(\epsilon)}{\partial\epsilon}\right]_{\mu_0}$$
$$= \frac{\mu_0(3\mu_0+2\Delta) - 2(\mu_0+\Delta)^2\ln(1+\mu_0/\Delta)}{\mu_0(\mu_0+\Delta)^2\ln(1+\mu_0/\Delta) - \mu_0^2(\mu_0+\Delta)}, \tag{27}$$

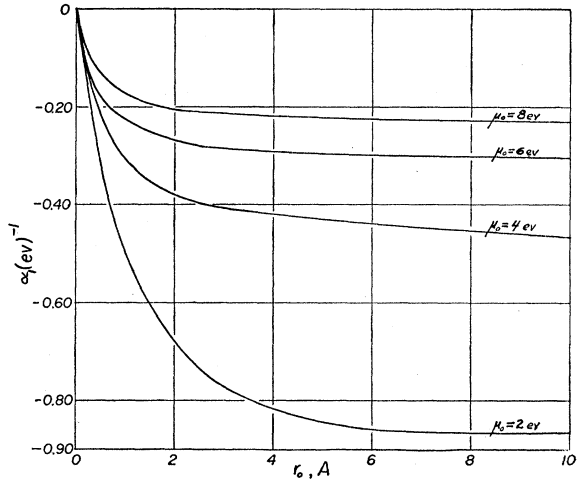

FIG. 6. First scattering parameter α_1 *vs* effective radius r_0, for various Fermi levels μ_0.

the last step requiring some algebraic manipulation. In Fig. 6 we show how α_1 depends on μ_0 and on the screening radius r_0. We have not attempted to calculate the second-order coefficient α_2. Mott has found that resistivity data call for screening constants of the order of $1/q_0 \sim 0.3\text{A} = r_0$, whereas calculations made on the basis of the Thomas-Fermi method give larger values of r_0. The values of α_1 for $r_0 \sim 0.3$A from Fig. 6 are of the order of $\alpha_1 \sim -0.1$, being negatively larger the smaller the Fermi energy μ_0. Thus we see that Mott's cross section formula leads to just the right range of α_1 values for the thermopower *vs* composition curves discussed above. On the other hand, we see that formula (26) for Q_i does not permit *positive* values of α_1. According to Eq. (19) the thermopower of a binary alloy with copper base cannot be thermoelectrically positive relative to pure copper unless $\alpha_1 > +0.12$, and we have mentioned that Mn and possibly Ti and Cr form dilute solutions in Cu which are positive against copper.[8]

F. FORMULAS FOR LOW TEMPERATURES

Mott's formula (1) is valid at lower temperatures than Θ_D provided $\rho_i \gg \rho_T$, so that the scattering is predominantly by impurities, or more generally, "lattice imperfection scattering." The formula for S at low temperatures can be obtained from Eq. (15) simply by letting $\rho_T \to 0$. Thus

$$S = 0.0243T\left[\frac{1}{2\mu_0[1+(\beta-1)p/150]} + \frac{\alpha_1 + 2\alpha_2\mu_0(\beta-1)p/150}{1+\alpha_1\mu_0(\beta-1)p/150 + \alpha_2\mu_0^2(\beta-1)^2p^2/(150)^2}\right], \tag{28}$$

where again S is in μv/deg, μ_0 in ev, α_1 in (ev)$^{-1}$, α_2 in (ev)$^{-2}$, and p is atomic percentage of the foreign atom (or vacancies, etc.).

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[28] There is a succession of typographical errors in the transcription of Mott's resistivity formula from his paper to Mott and Jones' book, and to p. 545 of F. Seitz's *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1939). Mott's formulas for $\Delta\rho$, his Eq. (17) on page 290 of reference 17 and that just above his Eq. (17), should have a factor of 2π in the numerator. This factor seems to have been used, however, in Mott's numerical calculations. On p. 294 of Mott and Jones (reference 10) and on p. 545 of Seitz, the resistivity formula should have e^2 in the denominator, not e^4. On the same page of Seitz's book, the expression for Mott's abbreviation y should have m^2 in the denominator, not m.

The main point of interest in this formula is the linear temperature dependence. The Fermi level μ_0 will decrease slightly with increasing temperature because of thermal expansion,[29] and although this decrease is in the right direction to account for some of the deviation of many S *vs* T curves from linearity, we have not yet investigated these effects sufficiently to arrive at any definite conclusions.

The most extensive low-temperature thermoelectric measurements on metals and alloys are those performed in the Leiden Laboratory by Borelius, Keesom, Johansson, and Linde.[30] These workers measured the thermopower of a large number of very dilute alloys of Cu, Ag, and Au at temperatures down to 4°K. The solutes included Fe, Co, Ni, Ti, Cr, Mn, Pd, As, and Au, and the reference metal was a so-called "Silbernormallegierung" (Ag+0.37 atom percent Au) chosen because of its suitability for Thomson-coefficient measurements. Now the absolute thermoelectric powers of these alloys, according to the measurements of Borelius *et al.*, do not vary linearly with temperature even at temperatures so low that the impurity resistivity should exceed the thermal contribution by factors of tens or even hundreds. It is very unlikely that the scattering parameters α_1 and α_2 are temperature dependent. It is conceivable, although unlikely, that the effective valence of some elements may be sufficiently sensitive to interatomic distances to make β temperature sensitive. The experiments of Borelius *et al.* show that the thermopowers of the dilute Cu−Fe, Au−Fe, and Cu−Co alloys are not greatly sensitive to the amount of foreign atom dissolved, and this fact would indicate that even the variation of β with temperature is unlikely, as one can deduce from Eq. (28); for if β were mainly responsible for the large negative values of the bracket in (28), which would be required to give large negative S in these alloys, then changes in solute content should give rise to large variations in S. In the case of Cu−Ni, the α_1 required to give the experimental order-of-magnitude thermopower at 10°K is about -4 (even with $\alpha_2=+7$, the value used for a good fit at high temperatures), and this value is several times larger than the high-temperature value (-1.2).

The recent findings of Pullan[31] on silver and tin at liquid helium temperatures are more encouraging. Pullan shows that the thermopower of tin becomes more nearly linear with temperature as the impurity content increases; and that while $S\sim T^{1.79}$ for high purity, well annealed silver with very low residual resistivity, the thermopower of the same silver in the cold-drawn state satisfies the relation $S=+0.011T$ μv/deg. According to Eq. (28), the coefficient $+0.011$ calls for an α_1 of approximately $+0.35$ (for $\mu_0{}^{\mathrm{Ag}}=3.3$ ev). The lattice imperfections caused by cold drawing of silver would thus have a *positive* scattering coefficient $\alpha_1=+0.35$

It is obvious that a great deal more experimental work needs to be done on the thermoelectric properties and on the resistivity of dilute noble metal alloys, and it would be most helpful to have both S and ρ for the same specimens.

G. CONCLUSIONS

We have shown that the theory of thermoelectric power as developed by Mott and others[32] can be used to explain many intricacies of thermoelectricity in metal alloys. The theory can also be used in reverse to derive information about electron scattering in metals. Furthermore, if a systematic study were made of the thermoelectric properties of quenched, cold-worked, and otherwise imperfect lattices, it should be possible to learn much about the nature of such imperfections. Finally, our specifications of the values which the scattering parameters must have, in order to explain the thermoelectric properties of imperfect metallic lattices, more precisely define one of the problems to be solved by the quantum theory, namely, the calculation of scattering cross sections of scattering centers in solids.[33]

The authors wish to express their appreciation to Dr. F. C. Nix for his valuable encouragement in this work, and to the Squier Signal Laboratories for their continued support.

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[29] The temperature variation of μ_0 at *constant volume*, involving a factor [1-const $(T/T_0)^2$], is completely negligible for our purposes.

[30] Borelius, Keesom, Johansson, and Linde, Leiden Comm. **206a** (1930); **206b** (1930); **217d** (1932); **217e** (1932). Most if not all of these communications also appear in the Proc. Acad. Sci. Amsterdam (Koninkl. Ned. Akad. Wetenschap. Proc.).

[31] G. T. Pullan, Proc. Roy. Soc. **A217**, 280 (1953).

[32] A formula identical with Mott's equation (1) is also a consequence of the recent theoretical work of A. W. Sáenz, Phys. Rev. **91**, 1142 (1953). See, e.g., his Eqs. (4.13).

[33] One might ask, for example, whether or not there exists an "internal or crystalline Ramsauer effect."