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# Thermoelectric Power of Dilute Copper Alloys*

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The thermoelectric power of dilute binary copper alloys containing one atomic percent Zn, Ge, Cd, In, Sn, and Sb was determined over the temperature range extending from about 8°K to 320°K. The thermoelectric powers were obtained by measuring the thermoelectric emf's of thermocouples formed of the alloys and pure copper. The absolute thermoelectric power of pure copper was obtained from measurements on a pure copper versus lead thermocouple.

The results are analyzed in terms of the Friedel theory. It is found that above 40°K satisfactory agreement with that theory can be obtained only if it is assumed that phonon drag makes a significant contribution to the thermoelectric power in the pure material below room temperature. The magnitude and temperature dependence of this assumed phonon drag contribution are in satisfactory agreement with theoretical estimates. Moreover, the effect of alloying on this phonon drag contribution also agrees with theoretical estimates based on reasonable models. In the temperature range below about 40°K we have not been able to give a satisfactory interpretation of our results. Our measurements show that near 40°K the absolute thermoelectric power of pure copper reverses sign, becoming negative, and attains an anomalously low minimum of about $-1.8$ μv/degree near 10°K. If this behavior is due to the presence of minute amounts of impurities in the pure copper which give rise to a thermoelectric anomaly associated with the appearance of a resistivity minimum, then our results can be interpreted without much difficulty. However, the residual resistivity of the pure copper was so low that we do not believe that the low-temperature thermoelectric anomaly can be attributed to the presence of impurities.

A research program on thermoelectric properties of dilute alloys which should shed further light on these questions is outlined.

## 1. INTRODUCTION

THE possibility of studying the electronic band structures of a pure metal by measuring the properties of dilute alloys of that metal has motivated a large number of investigations.[1–3] For example, the work of Salkovitz and Schindler[3] has revealed a number of interesting features of the band structure of magnesium. Of all the metals probably the monovalent ones have been subjected to the closest scrutiny, primarily because it was originally expected that they would most nearly approach the ideal, free electron gas metal. In recent years it has, however, become quite apparent that with the possible exception of sodium, the monovalent metals are far from ideal.[4] Nevertheless, the free electron model has still a great deal of usefulness even for these materials, especially when we restrict our attention to one particular physical property.

In the following pages we shall report on measurements of the thermoelectric emf of thermocouples formed from well-annealed specimens of pure copper and dilute copper alloys. These measurements provide information on the change of the thermoelectric power (TEP) of copper caused by the addition of about one atomic percent of various impurities. The analysis of our results is based on the work of Friedel,[5] which in turn rests on the approximation of nearly free electrons. Since the free electron model predicts the correct magnitude and temperature dependence of the TEP (except at low temperatures) but the incorrect sign for the TEP of pure copper, an interpretation of experimental data based on that model is open to criticism. Moreover, if we discard the rigid band model and instead accept the ideas recently proposed by Cohen and Heine,[6] then the analysis of the results which we shall present herein must be discarded in toto. We make no attempt to justify our procedure, but rather take the attitude that the primary area of interest should be the experimental data, and that in attempting an interpretation of this data the model which leads to physically reasonable results and which is, at the same time, fairly simple should take precedence.

The measurements to be reported herein were motivated by two somewhat related considerations. First, previous work on the residual resistivity of dilute noble metal alloys has clearly demonstrated that considerably more information may be gathered by the study of an alloy *series* rather than by investigations of several alloys chosen more or less at random. In particular, one of the outstanding results of the early work of Linde,[7] namely the dependence of the residual resistivity per atomic percent solute on the square of the valence difference between solvent and solute atoms, was clearly a consequence of this systematic attack on a series of related alloys. We, therefore, decided to follow a like procedure, hoping that a similar pattern might emerge when one compares the changes in thermoelectric power brought about by the addition of solutes of ever increasing valence. Second, the same work of Linde showed that solutes of equal valence but belonging to

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* Supported in part by the Office of Ordnance Research, U. S. Army.

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[1] J. A. Rayne, Phys. Rev. **110**, 606 (1958); Australian J. Phys. **9**, 189 (1956).

[2] W. G. Henry and J. L. Rogers, Phil. Mag. **1**, 237 (1956).

[3] E. I. Salkovitz and A. I. Schindler, Phys. Rev. **91**, 234 (1953); Phys. Rev. **91**, 1320 (1953). E. I. Salkovitz, A. I. Schindler, and E. W. Kammer, Phys. Rev. **105**, 887 (1957).

[4] A. B. Pippard, Phil. Trans. Roy. Soc. London **A250**, 323 (1957).

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

[6] M. H. Cohen and V. Heine, *Advances in Physics* (Taylor and Francis, London, 1958), Vol. 7, p. 395.

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

different rows of the periodic table give rise to different changes in resistivity of a solvent metal. This dependence of the residual resistivity on the inner core of the solute has been related to the degree of lattice distortion brought about by the introduction of the solute atom into the host lattice.[8] This interpretation of the dependence of the residual resistivity on the location of the solute atom in the periodic table was also based firmly on the work of Friedel and so stands, or falls, as does Friedel's.

When we commenced this investigation we were searching for a dependence of the thermoelectric power change on valence as well as on location of the impurity atom in a particular row of the periodic table. We believe that we have found the latter dependence, but attribute it to a mass rather than to the size effect which apparently gives rise to the systematic behavior in the residual resistivities.

## 2. THERMOELECTRIC POWER, FRIEDEL RELATIONS

We shall make use of the relations derived by Friedel, and present here, in brief outline, the salient features of that theory.

According to the free electron model the absolute thermoelectric power $S$ of a metal is given by[9]

$$S=\frac{\pi^2k^2T}{3e}\left(\frac{\partial\ln\sigma}{\partial\epsilon}\right)_\eta=-\frac{\pi^2k^2T}{3e}\left(\frac{\partial\ln\rho}{\partial\epsilon}\right)_\eta \tag{2.1}$$

where $k$ is Boltzmann's constant; $T$, the absolute temperature; $e$, the electronic charge; $\sigma$ and $\rho$ are the electrical conductivity and resistivity, respectively; $\epsilon$ is the electronic energy; and $\eta$ is the Fermi energy. Here the conductivity is given by the following relation

$$\sigma=-\frac{4e^2}{3m^*}\int N(\epsilon)\tau(\epsilon)\epsilon\frac{\partial f_0}{\partial\epsilon}d\epsilon \tag{2.2}$$

where $m^*$ is the effective mass of the electrons; $N(\epsilon)$ is the density of states; $\tau$, the relaxation time; and $f_0$ is the Fermi distribution function; Eq. (2.2) assumes that the effective mass and relaxation time are isotropic. When an impurity atom is introduced into a pure metal, the resistivity is given, to a rather good approximation, by Matthiessen's rule

$$\rho=\rho_0+\Delta\rho \tag{2.3}$$

where $\rho_0$ is the ideal resistivity, and $\Delta\rho$ is the residual resistivity attributable to the impurity atom. The former is temperature-dependent; the latter, temperature-independent. One now assumes that the absolute thermoelectric power of a dilute alloy is given by Eq. (2.1) where for $\rho$ we use the total resistivity according to Eq. (2.3). The difference between the absolute thermoelectric power of the alloy and of the pure metal is then given by

$$\Delta S=-\frac{\pi^2k^2T}{3e}\left[\frac{\partial\ln(\rho_0+\Delta\rho)}{\partial\epsilon}-\frac{\partial\ln\rho_0}{\partial\epsilon}\right]_\eta. \tag{2.4}$$

In writing Eq. (2.4) it is assumed that the alloy is sufficiently dilute so that the Fermi energy of the alloy and of the pure metal are the same. It is a simple matter to correct for the change in the Fermi energy upon alloying under the simplifying assumptions of the free electron model and the rigid band model.[10,11] One then finds that for a concentration of one atomic percent, even when the valence of the solute is four or five, the error introduced by neglecting the change in the Fermi energy is negligible.

A relationship somewhat more useful than Eq. (2.4) was derived by Friedel from the above, namely

$$\frac{\Delta S}{S}=-\frac{(1-\Delta x/x)}{(1+\rho_0/\Delta\rho)} \tag{2.5}$$

where

$$\Delta x=\eta\left(\frac{\partial\ln\Delta\rho}{\partial\epsilon}\right)_\eta;\quad x=\eta\left(\frac{\partial\ln\rho_0}{\partial\epsilon}\right)_\eta. \tag{2.6}$$

In Eq. (2.5) all the parameters except $\Delta x$ are either known or can be measured without great difficulty. The ideal resistivity of pure copper is well known; the residual resistivity caused by the added solute atoms is readily measured; and $x$ is simply related to the absolute thermoelectric power of the pure metal through Eq. (2.1). The parameter $\Delta x$ could be calculated once the scattering potential which one should associate with the impurity atom is known. Some information concerning this potential can, of course, be deduced from the residual resistivity, especially if one employs the sum rule derived by Friedel.[5,12] Unfortunately, however, a variety of potentials of considerably different shapes can lead to the same resistivity and be consistent with the Friedel rule, whereas the dependence of the resistivity on electron energy may vary considerably for these different potentials.[13] Thus, detailed calculations based on a particular choice of scattering potential are not too reliable, although they do indicate the correct magnitude of $\Delta x$. In the following we shall determine $\Delta x$ from the measurements. This procedure does not, in fact, admit as much freedom in fitting the data as one might at first suspect, especially when, as in our

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[8] F. J. Blatt, Phys. Rev. **108**, 285 (1957); Phys. Rev. **108**, 1204 (1957).

[9] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1954), 2nd edition.

[10] J. Freidel, *Advances in Physics* (Taylor and Francis, London, 1954), Vol. 3, p. 446.

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

[12] F. Abeles, Compt. rend. **237**, 796 (1953). F. J. Blatt, Phys. Rev. **99**, 1708 (1955); L. M. Roth, thesis, Harvard University, 1956 (unpublished).

[13] L. M. Roth, reference 12; F. J. Blatt, Phys. Rev. **100**, 666 (1955).

case, the data extends over a considerable temperature range. This is so because the parameter $\Delta x$ in Eq. (2.5) should be: 1, independent of temperature; and, 2, independent of solute concentration. The first requirement follows from the assumption of Matthiessen's rule which states, in effect, that $\Delta\rho$ is temperature-independent, from which it follows that its logarithmic derivative must also be temperature independent. The second condition must hold over that concentration range in which the change in Fermi energy caused by alloying is negligibly small. Hence, subject to the various assumptions already stated, a single determination at a given temperature of the change in the thermoelectric power caused by alloying with a given element should suffice for predictions of the thermoelectric behavior of that alloy at any temperature, and, moreover, for any composition, provided the solute concentration remains small.

The derivation of the Friedel relation is, however, based not merely on the assumptions of free electrons and the rigid band model, but assumes that the thermoelectric power arises entirely as a result of the change in the electron distribution function with temperature, the electron gas being considered an isolated system. In other words, the results would be valid for a free electron gas in which interactions of the gas with its surroundings are neglected except that it is implicitly assumed that there exists some mechanism by which the gas can come to thermal equilibrium with its surroundings. This equilibrium is in fact achieved through the interaction of the electrons with lattice vibrations.

This same interaction, however, should also give rise to a phonon drag contribution.[14] Such an additional thermoelectric effect has already been observed in semiconductors.[15] Its existence in metals has been considered by a number of workers,[16] and is believed to be of comparable magnitude to the free electron thermoelectric effect and quite probably significantly larger within a certain temperature range. Recently the phonon drag effect has been invoked to explain anomalies in the thermoelectric power of the alkali metals.[17]

We shall interpret our experimental results as follows. We first assume that the absolute thermoelectric power of pure copper is entirely of electronic (i.e., no phonon drag) origin. We shall calculate a value of $\Delta x$ for each of our alloys at a fixed temperature and shall then attempt to fit our data over the entire temperature range by use of Eq. (2.5). We shall next assume that

$$S=S_e+S_g$$

where $S_e$ and $S_g$ are the "electronic" and "phonon drag" contributions to the thermoelectric power, respectively. We then apply Eq. (2.5) to $S_e$ only, again compare calculated and experimental results over the entire temperature range and attempt to explain our results within this framework.

The latter procedure requires, unfortunately, one further piece of information, namely the division between $S_e$ and $S_g$ of the measured absolute thermoelectric power of pure copper. Since this information is not attainable by any experimental techniques known to us, we proceed as follows.

We recognize first that all calculations of the phonon drag TEP predict that this contribution falls off as $1/T$ at high temperatures.[18] The absolute TEP of pure copper is known to $T=1173$°K,[19] and we assume that at this high temperature $S_g$ is vanishingly small compared to $S_e$. In support of this contention one may point out that at temperatures in excess of about 400°K, the TEP of pure copper exhibits the nearly linear increase with temperature predicted by the free electron theory.

Since, however, the free electron theory predicts the incorrect sign for $S_e$ we cannot determine this contribution from the results of that theory without further assumptions.[20] We therefore make the further assumption that $S_e$ of pure copper is given by the Sondheimer-Wilson interpolation formula[9]

$$S_e=\frac{\pi^2k^2T}{3e\eta}\left\{\frac{\Delta\rho+3\rho_0[1+(\Theta/2^{\frac{1}{3}}\pi T)^2-(1/4\pi^2)(j_7/j_5)]}{\Delta\rho+\rho_0[1+3(\Theta/2^{\frac{1}{3}}\pi T)-(1/2\pi^2)(j_7/j_5)]}\right\} \tag{2.7}$$

where the product $e\eta$ is to be considered an adjustable parameter. Here $j_n$ denotes the usual transport integrals

$$j_n\left(\frac{\Theta}{T}\right)=\int_0^{\Theta/T}\frac{z^n dz}{(e^z-1)(1-e^{-z})}.$$

In short, we assume that as far as the contribution $S_e$ is concerned the free electron theory predicts the correct temperature dependence, but not the correct sign, nor exactly the correct magnitude. Whatever

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[14] C. Herring, Phys. Rev. **96**, 1163 (1954); F. J. Blatt, "Theory of Mobility of Electrons in Solids," *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, pp. 199–366.

[15] T. H. Geballe, Phys. Rev. **92**, 857 (1953). T. H. Geballe and G. W. Hull, Phys. Rev. **84**, 1134 (1954). H. P. R. Frederikse, Phys. Rev. **91**, 491 (1953); **92**, 248 (1953).

[16] L. Gurevich, J. Phys. U. S. S. R. **9**, 477 (1954); **10**, 67 (1946); E. H. Sondheimer, Proc. Roy. Soc. (London) **A234**, 391 (1956); P. G. Klemens, Australian J. Phys. **7**, 520 (1954); D. K. C. MacDonald, Physica **20**, 996 (1954).

[17] J. M. Ziman, Phil. Mag. **4**, 371 (1959).

[18] I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) **A239**, 247 (1957).

[19] J. Nystrom, Arkiv Mat. Astron. Fysik **A34**, No. 27, 1 (1948).

[20] It has been suggested that the positive TEP of the alkali metals at low temperature could be due to an umklapp phonon drag mechanism.[17] We do not believe that this same mechanism could possibly explain the positive sign of the TEP of copper because both normal as well as umklapp phonon drag effects must decrease with elevated temperatures. There is no indication whatever that the TEP of pure copper tends to reverse sign at elevated temperatures.

mechanism is responsible for the positive sign of $S_e$, is considered to be *temperature-independent*, consistent with the interpretation suggested by Jones.[21] Moreover, whatever changes are produced in $S_e$ as a result of alloying are now presumed to behave according to Eq. (2.5).

It would be difficult, indeed, to justify the foregoing assumptions, and we do not attempt to do so. Instead, we content ourselves with the presentation of the results which have been obtained thus far and with their interpretation according to the above precepts. Considerably more work needs to be done before the tentative conclusions which we shall draw from this work could be considered well established. At the end of this article we shall indicate the direction in which work is currently progressing, and the manner in which that work will shed additional light on the matter at hand.

## 3. EXPERIMENTAL PROCEDURE

### a. Preparation of Alloys[22]

The alloys were prepared by melting the constituents in vacuum. The copper was obtained from the American Smelting and Refining Company and was nominally 99.999% pure. Solute metals were purchased from the same company and from Johnson-Matthey, and their purities were 99.99% or better. The constituents for each alloy were weighed on a Christian Becker balance before they were sealed in a Vycor tube, and the weight of the alloy following melting was similarly determined. The results are shown in Table I. It is apparent that, except for CuGe and possibly CuZn, negligible loss occurred during preparation. Prior to the initial weighing the solute and solvent metals were thoroughly cleaned by an acid etch, rinsed, and dried. Before the Vycor tube containing the samples was sealed, it was evacuated to a pressure of less than $3\times10^{-6}$ mm Hg for four hours or more. During this time the specimens were heated to about 300°C for short intervals to drive off residual gas. Stirring of the melt was accomplished by severely shaking the Vycor capsule while it was in the furnace. Following melting the capsules were quenched in water to inhibit segregation.

TABLE I. Composition of copper alloys.

| Alloys | Solvent wt mg | Solute wt mg | Total wt before melt mg | Total wt after melt mg | Atomic % solute |
|---|---|---|---|---|---|
| CuZn | 6363.7 | 65.5 | 6429.2 | [a] | 0.990 |
| CuGe | 5411.6 | 61.8 | 5473.4 | 5464.0 | 1.048 |
| CuCd | 7264.4 | 129.0 | 7393.4 | 7393.5 | 0.993 |
| CuIn | 7241.2 | 132.7 | 7373.9 | 7373.3 | 1.004 |
| CuSn | 6507.3 | 122.7 | 6630.0 | 6629.6 | 1.000 |
| CuSb | 7414.5 | 143.9 | 7558.4 | 7558.0 | 1.003 |

[a] Not measured.

TABLE II. Annealing schedule.

| Material | Annealing temp. °C | Time-hours | Atmosphere |
|---|---|---|---|
| Pure copper | 1000 | 2 | High vacuum |
| CuZn | 550 | 4 | Helium |
| CuGe | 950 | 2[a] | High vacuum |
| CuCd | 350 | 3 | Helium |
| CuIn | 950 | 2 | Helium |
| CuSn | 850 | 3 | Helium |
| CuSb | 850 | 3 | Helium |

[a] In addition to 8 hours at 500°C and 8 hours at 600°C.

The billets obtained by this procedure were then cleaned and rolled into strips approximately 0.005 inch thick. Throughout the sample preparation frequent etching was used to prevent possible iron contamination. The thermocouples were then formed from ribbons, approximately 0.05 inch wide, cut from the strips.

We report here only the measurements which we have made on annealed samples. The annealing schedule for the various specimens is shown in Table II. We were unable to detect any significant difference between the CuGe alloys annealed at the different temperatures, and the results reported here are for the sample containing the alloy annealed at 950°C.

### b. Resistance Measurements

From Eq. (2.5) it is apparent that an interpretation according to Friedel's theory requires a knowledge of the resistivity of pure copper as well as of the residual resistivity of the alloy. We measured the resistances of our ribbons, both in the annealed as well as unannealed state, at 273°K, 79°K, and 4.2°K. The results of these measurements, as well as some more recent data obtained subsequent to the thermoelectric power investigation reported herein, have already been published.[23] We show in Table III the resistance ratios $R_{4.2}/(R_{273}-R_{4.2})$ of our samples, as well as the values

TABLE III. Resistance ratio $p=R_{4.2^\circ}/(R_{273^\circ}-R_{4.2^\circ})$ and residual resistivity $\Delta\rho$ of annealed copper and copper alloys.

| Sample | $p$ | $\Delta\rho$ $\mu$ ohm-cm |
|---|---|---|
| Cu | 0.00185 | 0.0029 |
| CuZn | 0.15 | 0.23 |
| CuGe | 2.0 | 3.2 |
| CuCd | 0.05 | 0.08 |
| CuIn | 0.57 | 0.88 |
| CuSn | 1.7 | 2.7 |
| CuSb | 2.8 | 4.4 |

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[21] H. Jones, Proc. Phys. Soc. (London) A68, 1191 (1955).

[22] We are grateful to the National Bureau of Standards for permission to use its facilities at the Cryogenics Laboratory, Boulder, Colorado, in the preparation of alloy specimens.

[23] R. H. Kropschot, M. Garber, and F. J. Blatt, Phys. Rev. Letters 2, 91 (1959).

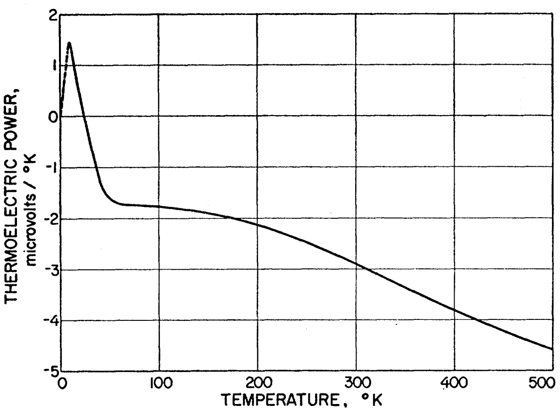

FIG. 1. The thermoelectric power of annealed pure copper against pure lead.

of $\Delta\rho$ calculated from these resistance ratios assuming $\rho_0(273°\text{K})=1.55\ \mu\text{ohm-cm}$.[24]

### c. Thermoelectric Measurements

The thermoelectric emf's were measured with a Leeds and Northrup microvolt amplifier. The amplifier was calibrated against a Leeds and Northrup K-3 potentiometer at regular intervals and was found to give correct readings each time. The temperature difference between the hot and cold junctions of the sample thermocouple was determined by means of calibrated copper versus constantan and gold-2.1% cobalt versus copper thermocouples.[25] These thermocouple emf's were measured with a Leeds and Northrup K-3 potentiometer. We estimate that the error for each individual measurement is ±1.5% for the sample emf measurements and ±0.1°K for the temperature measurements.

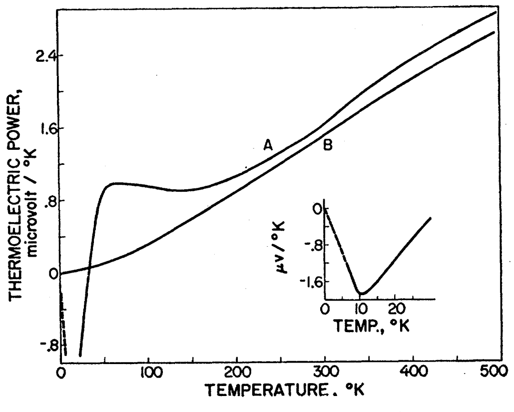

FIG. 2. Curve A, the absolute thermoelectric power of pure annealed copper. Curve B, the Sondheimer-Wilson interpolation formula, Eq. (2.7), matched to Curve A at 1173°K.

The range between 4.2°K and 320°K was spanned in three intervals. The cold junction was maintained either at 4.2°K (immersed in liquid helium), 79°K (immersed in liquid air), or 273.2°K (immersed in distilled water and ice). In every run the hot junction temperature was raised above the cold junction temperature of the following range to permit proper matching of the results. Data were obtained on cooling as well as heating of the hot junction, and the results were found to agree well with each other.

A large number of measurements on each thermocouple were made within each of the three temperature ranges, and at least 150 points span the entire temperature intervals from 4.2°K to 320°K. In the 4.2°K to 90°K range we made an average of 35 measurements per sample, and in this range the data show the largest scatter. We have performed a least squares analysis for all our curves, with the result that indeed the largest deviation occurs for the low-temperature data, but even here the deviation is in every instance less than 0.3 μvolt.

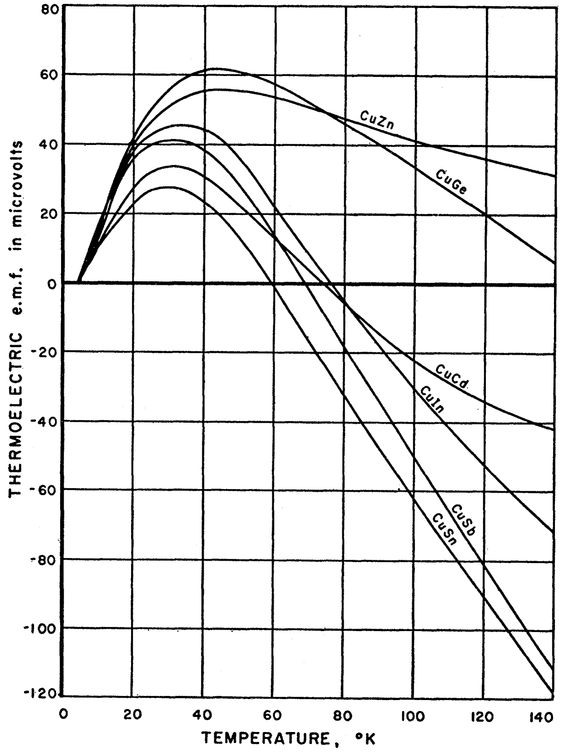

FIG. 3. The thermoelectric emf of annealed copper alloys—annealed pure copper thermocouples. Cold junctions at 4.2°K.

### 4. RESULTS AND DISCUSSION

Figure 1 shows the TEP of a pure annealed copper versus lead thermocouple. Using the results of Christian et al.[26] we determined the absolute TEP of pure

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[24] A. N. Gerritsen, "Metallic Conductivity, Experimental Part," *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 156.

[25] We are grateful to Mr. R. L. Powell and Mr. M. D. Bunch, N.B.S.C.E.L., for making these calibrated thermocouple wires available to us.

[26] J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A245**, 213 (1958).

annealed copper, and this curve is shown in Fig. 2, curve A. Since in our measurements we could not exceed the melting point of lead, we made use of the results reported by Nystrom[19] to extend the absolute TEP of copper to higher temperatures. This information is needed to estimate $S_e$ of pure copper by application of Eq. (2.7), using the procedure mentioned earlier. This assumed $S_e$ curve, curve B, is shown also in Fig. 2.

The thermoelectric emf's of the copper alloy versus pure copper thermocouples are shown in Figs. 3 and 4, and the TEP's of these thermocouples are shown in Figs. 5 and 6. These TEP's are, of course, just equal to $\Delta S$, the change in the TEP upon alloying.

Before we consider the interpretation of the thermoelectric power of these alloys in the light of the Friedel theory and the possible presence of a phonon drag TEP, we wish to say a few words concerning the absolute TEP of our pure copper. From Fig. 2 we note that $S$ is positive above about 30°K, showing a subsidiary maximum near 70°K but reverses sign as the temperature is lowered and displays a pronounced minimum of about $-1.8$ $\mu$volt/°K near 10°K. This behavior is very reminiscent of the behavior reported for extremely dilute copper alloys which exhibit a resistance minimum,[27] and suggests that in fact our "pure copper" was perhaps not as pure as we might have wished. Although we cannot completely rule out this interpretation of our data, we do believe that our results are characteristic of pure copper for the following reasons.

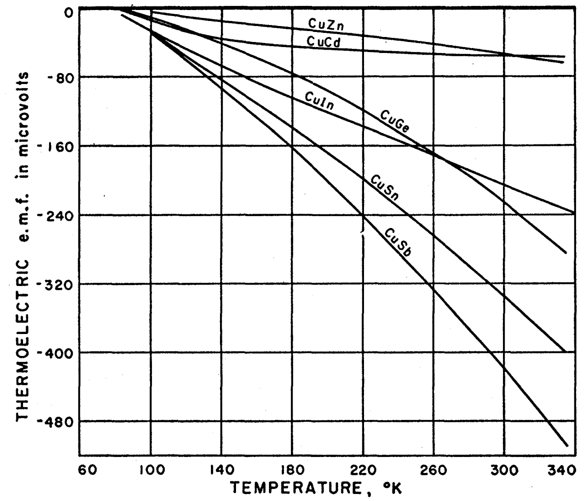

FIG. 4. The thermoelectric emf of annealed copper alloys—annealed pure copper thermocouples. Cold junctions at 79°K.

1. The measured resistance ratio of our pure annealed copper is smaller than that which MacDonald and Pearson[28] quoted for the pure copper which they used in their work on the resistance minimum.

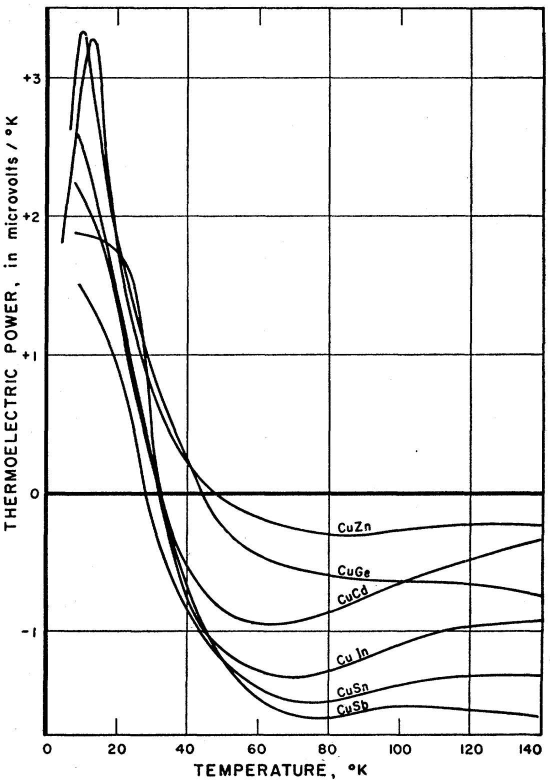

FIG. 5. The thermoelectric power of annealed copper alloys—annealed pure copper thermocouples. Low-temperature region.

2. Recently, Powell has examined the change in TEP upon cold work of copper of very high purity (resistance ratio less than half that of our samples).[29] Our results[30]

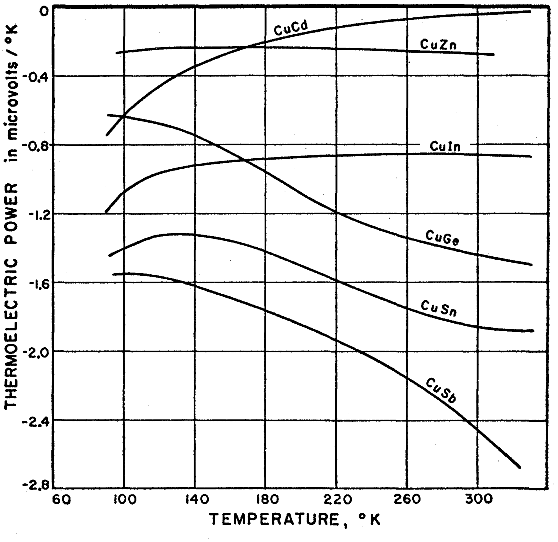

FIG. 6. The thermoelectric power of annealed copper alloys—annealed pure copper thermocouples. Liquid air to room temperature region.

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[27] D. K. C. MacDonald and W. B. Pearson, Acta Met. **3**, 392, 403 (1955); Proc. Roy. Soc. (London) **A219**, 373 (1953).

[28] D. K. C. MacDonald and W. B. Pearson, Phil. Mag. **45**, 491 (1954).

[29] R. L. Powell, H. M. Roder and W. J. Hall, Phys. Rev. **115**, 314 (1959).

[30] R. H. Kropschot and F. J. Blatt, Phys. Rev. **116**, 617 (1959).

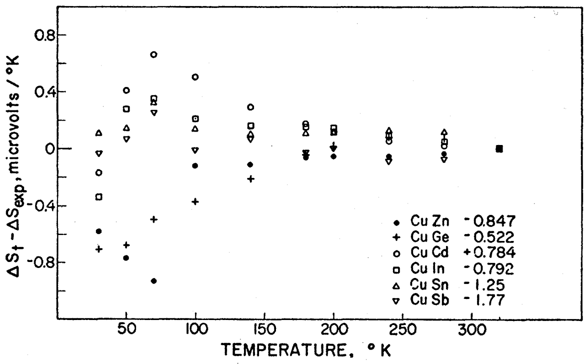

FIG. 7. $\Delta S_t - \Delta S_{\text{exp}}$, the difference between the calculated and measured thermoelectric powers of the copper alloy—pure copper thermocouples, assuming no phonon drag contribution exists.

agree reasonably well with his especially in the low-temperature region.

3. There is now an increasing body of data besides our own which indicates that the noble metals show, at very low temperatures, a *negative* absolute TEP of unusual magnitude. Results of work on pure silver and gold have been reported by MacDonald, Pearson, and Templeton,[31] and a statement that the absolute TEP of *pure* copper is negative at very low temperatures may be found in a recent paper by MacDonald and co-workers.[32,33]

In Fig. 7 we show the comparison between calculated and experimental results for $\Delta S$, using the Friedel relation Eq. (2.5) and neglecting the possible existence of a phonon drag contribution. The calculated $\Delta S$, here denoted $\Delta S_t$, was obtained as follows. We determined the parameter $\Delta x$, here denoted $\Delta x_T$, by matching the measured change in the TEP at 320°K to the Friedel relation. In applying Eq. (2.5) we assumed that the entire absolute TEP of pure copper was of "electronic" origin, and found $x$ from Eq. (2.1). We have used the subscript $T$ to denote that in these calculations the *total* TEP of copper was used in Eq. (2.5). The values of $\Delta x_T$ which give a fit at 320°K are listed in Fig. 7.

It is apparent that there is a very large discrepancy between calculated and experimental results. Indeed, in the neighborhood of 70°K, the temperature at which the absolute TEP of copper shows its subsidiary maximum, the difference between the calculated and experimental results is of the same magnitude as the experimental results themselves. A certain pattern is already quite apparent, however; the discrepancy is positive for those copper alloys which contain solutes that are neighbors to silver, whereas the discrepancy is of opposite sign for the copper alloys which contain solutes neighboring copper in the periodic table.

We now apply Eq. (2.5) to the electronic contribution only, and again calculate a value for the parameter $\Delta x$, now denoted $\Delta x_e$, such that calculated and experimental results agree at 320°K. We need to make two assumptions before $\Delta x_e$ can be determined from the data. The first is that $S_e$ of pure copper is given by curve B, Fig. 2. The second assumption is that at 320°K $\Delta S_g$ is negligibly small so that at 320°K the entire change in the TEP due to alloying is given by Eq. (2.5). Following the same procedure as before we now obtain the results shown in Fig. 8. Here $\Delta S_e$ is the value of $\Delta S$ calculated from Eq. (2.5) using the $\Delta x_e$ values listed in Fig. 8.

A clear pattern now emerges. For the CuZn and CuGe alloys the Friedel theory appears to give quite satisfactory results to temperatures as low as 50°K. However, for the alloys which contain solutes adjacent to silver in the periodic table a large discrepancy still remains, but this discrepancy is practically the same for each of the four alloys. Moreover, the points for these "silver group" alloys follow a curve which is very nearly the curve obtained by taking the difference between curve A and curve B of Fig. 2, shown dashed in Fig. 8. The solid curve is the difference between the absolute TEP of pure copper at temperature $T$ and the absolute TEP of pure copper at 320°K. It should be noted that the dashed curve is just the assumed phonon drag contribution to the absolute TEP of pure copper.

We believe that these results lend themselves to a fairly straightforward interpretation. If, indeed, the absolute TEP of copper is a sum of two contributions

$$S^{\text{Cu}} = S_e^{\text{Cu}} + S_g^{\text{Cu}}$$

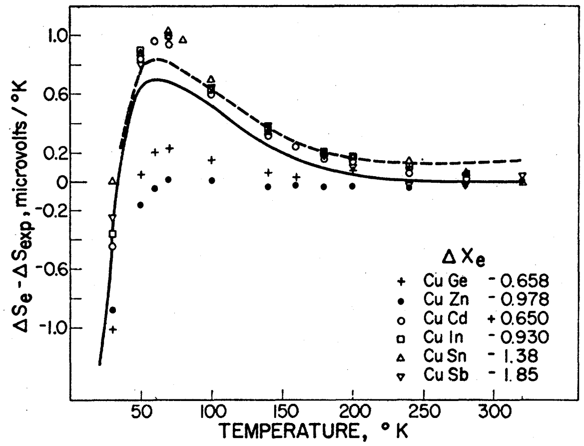

FIG. 8. $\Delta S_e - \Delta S_{\text{exp}}$, the difference between the calculated electronic and the measured thermoelectric powers of the copper alloy—pure copper thermocouples, assuming the existence of a phonon drag contribution to the absolute thermoelectric power of pure copper. Points were calculated under the assumption that $\Delta S_g(320°\text{K}) = 0$. The dashed curve shows the assumed phonon drag contribution in pure copper (Curve A minus Curve B of Fig. 2). Solid curve is the dashed curve minus the value of $S_g$ at 320°K.

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[31] D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Phil. Mag. 3, 657 (1958).

[32] D. K. C. MacDonald, E. Mooser, W. B. Pearson, I. M. Templeton, and S. B. Woods, Phil. Mag. 4, 433 (1959).

[33] Dr. W. B. Pearson has informed us that he has also observed a large negative absolute TEP for pure copper at low temperatures. We are grateful to Dr. Pearson for making these results known to us prior to their publication.

the change in the TEP upon alloying is

$$\Delta S=\Delta S_e+\Delta S_g=S_e^{\text{alloy}}-S_e^{\text{Cu}}+S_g^{\text{alloy}}-S_g^{\text{Cu}}.$$

We have determined $\Delta S_e$ using Eq. (2.5). From Fig. 8 we now see that for impurities of the copper group

$$\Delta S_e^{\text{calc}}-\Delta S_{\text{exp}}\approx 0$$

from which we conclude that

$$S_g^{\text{alloy}}\approx S_g^{\text{Cu}}$$

in the temperature range between 50°K and 320°K.

On the other hand, for impurities of the silver group

$$\Delta S_e^{\text{calc}}-\Delta S_{\text{exp}}\approx S_g^{\text{Cu}}$$

and since

$$\Delta S_g=S_g^{\text{alloy}}-S_g^{\text{Cu}}$$

we conclude that for these alloys in the same temperature range

$$S_g^{\text{alloy}}\approx 0.$$

If, indeed, $S_g^{\text{alloy}}=0$ for the silver group alloys, the analysis of the data which has led to Fig. 8 is not internally consistent, assuming as it does that $\Delta S=0$ at 320°K. What we should do in the light of these results is to add to the measured $\Delta S(320)$ of the silver group alloys the quantity $S_g^{\text{Cu}}(320)$ to obtain $\Delta S_e(320)$. We should then use this value of $\Delta S_e$ in Eq. (2.5) to determine the parameters $\Delta x_e$, and thereafter proceed as before. We did not adopt this procedure at the outset because we had no adequate justification for it. However, in view of the striking features of Fig. 8, we have re-examined the experimental data by this slightly modified procedure, and the results are shown in Fig. 9. Here the dashed curve is the assumed $S_g^{\text{Cu}}$, i.e., the difference between curve A and curve B of Fig. 2. We can offer no satisfactory explanation for the change in sign of the TEP of pure copper at low temperatures, and shall refrain from considering our data in that temperature region beyond the following remarks. If, for example, the anomaly is related to a slight impurity contamination giving rise to a resistance minimum in the "pure" copper, then the low-temperature behavior can be explained fairly readily. One would then simply have a situation in which every impurity which we have introduced has the effect of removing the TEP anomaly of the "pure" copper, a perfectly reasonable supposition Of course, the assignment of a phonon drag TEP to the dashed curve of Fig. 9 in that low-temperature region is then quite incorrect.

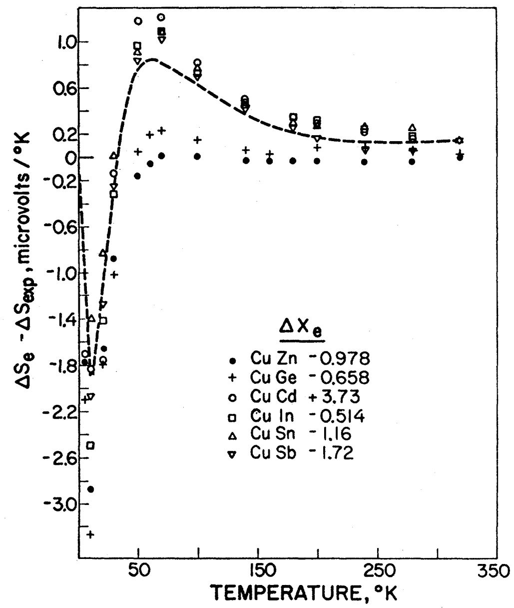

FIG. 9. $\Delta S_e-\Delta S_{\text{exp}}$, the difference between the calculated electronic and the measured thermoelectric powers of the copper alloy—pure copper thermocouples, assuming the existence of a phonon drag contribution in pure copper. The dashed curve is the assumed phonon drag thermoelectric power of pure copper, Curve A minus Curve B of Fig. 2.

In the temperature range extending from about 40°K or 50°K upwards, the dashed curve of Fig. 9 does show the behavior expected of the phonon drag thermoelectric power. The decrease at higher temperatures is approximately proportional to $1/T$, and the maximum occurs at a reasonable temperature and has the expected order of magnitude.

Thus our results suggest that elements of the silver group when alloyed with copper act as very effective scattering centers for phonons and, therefore, annihilate the phonon drag contribution in the alloy. Consequently, the phonon drag effect which exists in pure copper but is absent in the alloy contributes to the TEP of a thermocouple formed from the silver group alloys and pure copper.

Similarly, we must conclude that copper group impurities in concentrations such as we have employed do not scatter phonons very effectively. Phonon drag is therefore present about equally in both the alloy and in pure copper, and, consequently, does not contribute to the measured change in the TEP caused by alloying.

These conclusions appear quite reasonable in the light of the following order of magnitude estimates. In the temperature region in which $S_g$ appears to vary as $1/T$ the relation given by Hanna and Sondheimer[18]

$$\frac{S_g}{S_e}=\frac{N_a\eta}{3kT}\frac{K_g}{K_i} \tag{4.1}$$

should be valid. Here $K_i$ is the ideal electronic thermal conductivity, and $K_g$, the lattice thermal conductivity. The influence of impurities on $S_g$ is then directly related to the effect these same impurities have on $K_g$, the lattice thermal conductivity. Thus

$$\frac{S_g^{\text{Cu}}}{S_g^{\text{alloy}}}=\frac{K_g^{\text{Cu}}}{K_g^{\text{alloy}}}=\frac{W_g^{\text{alloy}}}{W_g^{\text{Cu}}} \tag{4.2}$$

where $W_g=1/K_g$ is the lattice thermal resistivity. We estimate the lattice thermal conductivity of pure copper by assuming that, in the temperature region of interest, the predominant phonon relaxation mechanism is anharmonic coupling. The thermal resistivity is then given by[34]

$$W_a=\frac{10\pi^3\hbar^3\gamma^2 T}{3k^3 M a\theta}. \tag{4.3}$$

Here $\gamma$ is Gruneisen's constant, $a$ is the lattice parameter, and $M$ is the atomic mass. Although Eq. (4.3) is valid only for $T>\theta$, it is probably still a reasonably good approximation at lower temperatures as long as anharmonic coupling is predominant and the lattice thermal conductivity varies as $1/T$.

The thermal resistivity caused by phonon scattering by foreign atoms is given by[35]

$$W_I=\frac{\pi^2 a^3}{0.9hv^2}\left(\frac{\Delta M}{M}\right)^2 cT, \quad T<\theta \tag{4.4}$$

provided scattering caused by lattice strains is neglected. Here $v$ is the velocity of sound, $\Delta M$ is the difference in mass between solute and solvent atoms, and $c$ is the solute concentration.

We now find that for copper Eq. (4.3) gives

$$W_g=1.6\times 10^{-2}T \text{ cm-deg/watt.}$$

The thermal resistivities caused by the presence of impurities are

$W_{\mathrm{I}}=1.0\times 10^{-4}T$ cm-deg/watt for one atomic percent of Zn;

$W_{\mathrm{I}}=3\times 10^{-3}T$ cm-deg/watt for one atomic percent Ge;

$W_{\mathrm{I}}=8.4\times 10^{-2}T$ cm-deg/watt for one atomic percent Cd;

$W_{\mathrm{I}}=12\times 10^{-2}T$ cm-deg/watt for one atomic percent Sb.

As one would expect, silver group impurities are very effective in scattering phonons, whereas zinc gives rise to only a very slight lattice thermal resistivity. Germanium in copper, although more effective than zinc, is nevertheless unimportant compared to anharmonicity as a scattering mechanism for phonons.

If we assume a Matthiessen's rule for $W$

$$W_g=W_a+W_{\mathrm{I}}$$

we conclude that for our samples

$$\frac{S_g(\mathrm{CuZn})}{S_g{}^{\mathrm{Cu}}}\simeq 1.0;\quad \frac{S_g(\mathrm{CuGe})}{S_g{}^{\mathrm{Cu}}}\simeq 0.84$$

and

$$0.12<\frac{S_g(\mathrm{Cu}X)}{S_g{}^{\mathrm{Cu}}}<0.16,$$

where $X$ represents any one of the silver group impurities.

These rough numerical estimates are evidently in good agreement with our previous conclusion, namely

$$S_g{}^{\mathrm{alloy}}\approx S_g{}^{\mathrm{Cu}} \text{ for the alloys CuZn and CuGe,}$$

whereas $S_g{}^{\mathrm{alloy}}\approx 0$ for the alloys CuCd, CuIn, CuSn, and CuSb.

## 5. CONCLUSION

We have measured the change in the TEP of copper due to the addition of various kind of solutes. The results have been analyzed according to the theory of Friedel and we have found that a consistent analysis requires the assumption of a phonon drag contribution to the TEP of pure copper. If this assumption is made we then find that solutes which belong to the silver row of the periodic table have a quite different effect on the TEP of copper than do solutes which are adjacent to copper in the periodic table. We believe that this difference is due to the large mass difference between the two groups of solutes. Specifically, solute atoms whose mass differs greatly from the mass of the solvent atoms present very effective scattering centers to lattice vibrational waves and, consequently, diminish the phonon drag contribution to the TEP. Solute atoms whose mass is nearly the same as the mass of the solvent atoms do not scatter phonons very much and, therefore, the phonon drag contribution in the alloy is nearly the same as in the pure metal. These conclusions are in good agreement with appropriate order of magnitude estimates. However, a considerable amount of additional data should be available to place these conclusions on a firmer basis. We have initiated a program of thermoelectric measurements which, we believe, will provide the data that will ultimately either confirm or definitely contradict our current suggestions concerning the TEP of pure copper and the effect of alloying on it.

First, we have already remarked that the parameter $\Delta x_e$ should be independent of concentration for small concentrations. Obviously, then, further measurements on the same alloys but with different concentrations of the solutes should be very informative. If we then find that the same method of analysis gives adequate agreement with the data using the same values for $\Delta x_e$ over a reasonably wide range of concentrations, we would conclude that our current ideas are indeed correct. An extensive study of the same alloys, containing various amounts of solute is now under way.

Second, silver as an impurity in copper would also give rise to a significant change in the TEP even though in electronic configuration silver and copper are nearly

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[34] P. G. Klemens, "Thermal Conductivity of Solids at Low Temperatures," *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 24, pp. 198–280.

[35] W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, Australian J. Phys. **10**, 454 (1957).

identical. The change in the TEP should be almost entirely due to the absence of a phonon drag TEP in the alloy. The appropriate measurements have also been initiated.

Third, a study similar to that reported herein but using silver as the solvent metal and impurities belonging to the silver and copper rows of the periodic table is nearing completion. If our conclusions are correct we should find that in this case the roles of copper and silver group impurities are reversed. That is, Cd, In, Sn, and Sb should not greatly influence the phonon drag TEP, whereas Zn and Ge, as well as Ga and As, should be effective in eliminating phonon drag.

Fourth and last, it will be of interest to investigate dilute ternary alloys. For example, if a dilute alloy of copper containing Cd and In is prepared, each solute element being present in sufficient abundance to eliminate phonon drag by itself, the additional influence of the other impurity (e.g., Cd) on the TEP of the binary alloy (e.g., CuIn) should reveal itself solely as an effect on the electronic contribution to the TEP. Some studies of ternary alloys have already been initiated by Domenicali.[36] However, his work is not of particular usefulness to us for two reasons. First, one of the solutes in each of his ternary alloys is a member of the transition group. Second, his measurements span that temperature region (room temperature and above) in which the phonon drag effect in the pure metal is already quite small. It is significant, however, that Domenicali is able to predict with a fair degree of reliability the thermoelectric behavior of ternary alloys from a knowledge of the TEP of the binary alloys.

We wish to thank Professor M. Garber for his valuable assistance particularly with the measurements at low temperatures.

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[36] C. A. Domenicali, Phys. Rev. 112, 1863 (1958).

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# Relativistic Self-Consistent Solutions for Atoms of Large Atomic Number*

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Relativistic self-consistent solutions, without exchange, have been obtained for several atoms of large atomic number by use of a general program for a high speed computing machine. A short description of this program and of the self-consistent calculation is given. Eigenvalues for the individual electron subshells of the self-consistent mercury, tungsten, platinum, and uranium atoms are presented. A comparison of the calculation with previous results for the mercury atom is also included.

## I. INTRODUCTION

THE wave function for an atomic system can be obtained by several methods. For atoms of small atomic number one method that has met with much success is the self-consistent field calculation of Hartree.[1] In the usual self-consistent calculations, electronic wave functions that satisfy the Schrödinger equation make up the product wave function for the atom. For atoms of large atomic number these calculations suffer from the neglect of relativistic effects, particularly in the inner shells of the atoms. In the present calculation the method of Hartree is used to obtain the self-consistent wave function for the atom. The single-particle wave functions are, however, assumed to be solutions to the relativistic Dirac equation. Many sizeable relativistic corrections are therefore contained in these solutions. Exchange effects are, however, not included.

Because a modern high-speed computing machine (IBM type 704) was used for the numerical calculations, it was possible to obtain self-consistent solutions of high accuracy. Not only were a large number of grid points used in the calculations but the solutions were iterated many times to assure valid self-consistency. For reasons of flexibility the computations were carried out without the introduction of the usual numerical trial solution to begin the iterations. An iterative procedure was included in the machine program which made the calculation itself entirely automatic. The program used in these calculations may therefore be used for the calculation of the self-consistent solution of an atom of arbitrary electron configuration and atomic number.

Contained in this paper is a description of the method for obtaining the relativistic self-consistent solutions and the numerical techniques used. Also included are results obtained for the solutions to the ground states of several atoms. These include tungsten,

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[1] Douglas R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928).