

## Thermoelectric Power of Dilute Copper Alloys. II\*

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The work of Blatt and Kropschot was extended to dilute CuAg and CuAu alloys; simultaneous measurements of the thermopower and thermal conductivity were made on CuSn alloys. The decomposition of the absolute thermopower of copper into diffusion  $S_d$  and phonon drag  $S_g$  contributions proposed by Blatt and Kropschot was verified. It is based on the observed quenching of  $S_g$  by large-mass solutes due to anisobaric phonon scattering. It was found that  $S_g$  is completely suppressed by approximately 1 at. % of Ag or Sn and by 0.4 at. % of Au. In the temperature region ( $T \approx 60^\circ\text{K}$ ) where anisobaric scattering is important in limiting the lattice conduction  $\kappa_g$ , it was observed that  $\kappa_g$  is reduced considerably less than  $S_g$ . It is suggested that this is due to the characteristic dispersion of phonons of large wave vector. At low temperatures, where the Debye model holds, comparison of  $S_g$  and  $S_d$  with specific-heat data leads to the conclusion that the umklapp contribution  $S_g^U$  is 25% larger in magnitude than the normal contribution  $S_g^N$ . This is in agreement with estimates by Ziman of the relative importance of normal and umklapp processes in copper.

### 1. INTRODUCTION

IT is now generally recognized that two physical mechanisms are responsible for the generation of a thermoelectric voltage in a conductor.<sup>1</sup> The first, thermal diffusion of charge carriers leads to the so-called "diffusion thermopower"  $S_d$ . At sufficiently high and low temperatures, i.e., when the Wiedemann-Franz law is obeyed, it is given by the well-known expression

$$S_d = \frac{\pi^2 k^2 T}{3eE_F} \left( \frac{\partial \ln \sigma}{\partial \ln E} \right)_{E_F} = \frac{2C_e}{3Ne} \left( \frac{\partial \ln \sigma}{\partial \ln E} \right)_{E_F}, \quad (1)$$

where  $\sigma(E)$  is the conductivity of electrons of energy  $E$ ,  $E_F$  is the Fermi energy, and  $C_e$  is the electronic specific heat.

The second mechanism, "phonon drag," was originally suggested by Gurevich<sup>2</sup> and later treated in detail by Herring<sup>3</sup> and Price<sup>4</sup> for semiconductors, and by Klemens,<sup>5</sup> Hanna and Sondheimer,<sup>6</sup> Bailyn,<sup>7</sup> and Ziman<sup>8</sup> for metals. It leads to the "phonon-drag thermopower"  $S_g$ , for which a simple analytic expression cannot be given. Under rather extreme simplifying approximations, among them total neglect of umklapp scattering, one can show that

$$S_g = \frac{C_g}{3Ne} \frac{\tau_{pp}}{\tau_{pp} + \tau_{pe}}, \quad (2)$$

where  $C_g$  is the lattice specific heat,  $\tau_{pe}$  is the phonon-electron relaxation time and  $\tau_{pp}$  is the relaxation time associated with all other phonon scattering events.

Interest in thermoelectricity is founded on the following general considerations. The conductivity of a metal may be written in the form<sup>9</sup>

$$\sigma = e^2 l A / 12\pi^3 \hbar, \quad (3)$$

where  $A$  is the area, in  $k$  space, of the Fermi surface and  $l$  is the mean free path of electrons of energy  $E_F$ . The conductivity depends, therefore, on the product of two parameters of which one  $A$  is a measure of the Fermi surface while the other  $l$  is characteristic of the interaction of conduction electrons with crystal imperfections: phonons, impurities, dislocations, etc. According to (1) the diffusion thermopower is related to the *energy dependence* of these parameters at the Fermi energy. Consequently, the diffusion thermopower is rather more sensitive to the details of the scattering mechanisms and to changes in the Fermi surface with alloying than is the conductivity itself. Our interest in the thermopower of the noble metals is further heightened by the failure of existing theory to explain even the gross features, such as the sign of  $S_d$ , despite current accurate knowledge of the Fermi surface of these metals.<sup>10</sup> The positive thermopower calculated for a spherical Fermi surface and a nonparabolic band<sup>11</sup> is not altogether convincing since one has the feeling that the contact of the Fermi surface at the (111) zone boundaries should play an important role and should be taken into account in any careful calculation. Similarly, the suggestion that electron-electron scattering may provide the explanation of the positive thermopower<sup>12</sup> has yet to be confirmed by detailed calculations.

As regards the phonon-drag contribution, Bailyn<sup>7</sup> and Ziman<sup>8,9</sup> pointed out that in calculations of  $S_g$  one

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<sup>1</sup> D. K. C. MacDonald, *Thermoelectricity* (John Wiley & Sons, Inc., New York, 1962).

<sup>2</sup> L. Gurevich, *J. Phys. U. S. S. R.* **9**, 447 (1945); **10**, 67 (1946).

<sup>3</sup> C. Herring, *Phys. Rev.* **96**, 1163 (1954).

<sup>4</sup> P. J. Price, *Phil. Mag.* **46**, 1252 (1955); *Phys. Rev.* **104**, 1223 (1956).

<sup>5</sup> P. G. Klemens, *Australian J. Phys.* **7**, 520 (1954).

<sup>6</sup> I. I. Hanna and E. H. Sondheimer, *Proc. Roy. Soc. (London)* **A239**, 247 (1957).

<sup>7</sup> M. Bailyn, *Phys. Rev.* **112**, 1587 (1958).

<sup>8</sup> J. M. Ziman, *Phil. Mag.* **5**, 1059 (1960). J. G. Collins and J. M. Ziman, *Proc. Roy. Soc. (London)* **A264**, 60 (1961).

<sup>9</sup> J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960).

<sup>10</sup> P. L. Taylor, *Proc. Roy. Soc. (London)* **A275**, 309 (1963).

<sup>11</sup> H. Bross and W. Häcker, *Z. Naturforsch.* **16a**, 632 (1961).

<sup>12</sup> F. J. Blatt, *Phys. Letters* **8**, 235 (1964).

must be particularly careful to take proper account of normal (N) and umklapp (U) scattering since the phonon drag thermopowers  $S_g^N$  and  $S_g^U$  are normally of opposite sign and cancel each other. Thus the net effect is frequently the difference between two large but nearly equal quantities. These considerations make reliable calculation of  $S_g$  rather difficult, particularly since the results are quite sensitive not only to the shape of the Fermi surface and the  $k$  dependence of the electron-phonon interaction but also to the phonon spectrum. Indeed, the very small values of  $S_g$  at normal temperatures found in all cases studied to date is probably as much due to dispersion in the phonon spectrum as to cancellation between  $S_g^N$  and  $S_g^U$ .<sup>13</sup> At low temperatures, however, where the Debye approximation should be valid, comparison of  $S_g/S_d$  with  $C_g/C_e$  allows a quantitative estimate of the relative efficacy of normal and umklapp scattering. Also in this respect thermopower is more sensitive than electrical conductivity. In the latter phenomenon the effect of N and U processes is additive, both increasing the resistivity. The phonon-drag thermopower seems to provide the most direct and reliable measure of the relative magnitudes of normal and umklapp scattering.

From this cursory introduction one can see that thermoelectricity can be a very useful phenomenon in a study of electronic properties, particularly the interaction of electrons with phonons. In disordered alloys, where more elegant and powerful resonance methods fail due to collision broadening, thermoelectric data can indicate at least gross features of the Fermi surface.<sup>14</sup>

## 2. SEPARATION OF THE DIFFUSION AND PHONON-DRAG THERMOPOWERS

The experimental data do not give us  $S_d$  and  $S_g$  separately but only their sum, and one of the first and most critical problems is that of separating the measured thermopower into these two contributions. This can be achieved by various methods, which we shall now discuss.

At low temperatures, in the residual resistance region,  $S_d$  should be a linear function of the temperature. Also at sufficiently low temperatures and in a reasonably pure metallic sample,  $\tau_{pp} \gg \tau_{pe}$ . Hence, the temperature dependence of  $S_g$  should, according to (2), follow that of  $C_g$ ; i.e., we expect that  $S_g$  goes as  $T^3$  at low temperatures. One can then separate  $S$  into  $S_d$  and  $S_g$  by the same method which is used to decompose the specific heat into its electronic and lattice contributions, that is, by plotting  $S/T$  versus  $T^2$ . The intercept of the resulting straight line is then  $S_d/T$ , and the slope gives  $S_g/T^3$ .

This procedure has been employed with success by de Vroomen, van Baarle, and Cuelenaere<sup>15</sup> and by van

Baarle,<sup>16</sup> as well as by MacDonald and collaborators.<sup>17</sup> It has the advantage over the method selected by us, which we shall describe presently, that measurements on each sample can, at least in theory, be analyzed without reference to any other data. There are some complications, however. The first stems from the fact that if  $S_g^U$  makes a significant contribution to  $S_g$  and if the Fermi surface does *not* contact the Brillouin zone boundary then  $S_g$  will not obey a  $T^3$  law but will contain a term with an exponential temperature dependence at sufficiently low temperatures. Deviations of  $S/T$  versus  $T^2$  from a straight line have been attributed to this quenching of umklapp scattering first predicted by Peierls.<sup>18</sup> As Baily has remarked, one would hardly expect to find a  $T^3$  variation in the alkali metals in the temperature range where  $S_g$  is important.

In the case of alloys this analysis is more problematical. It has generally been assumed that the effect of impurities on  $S_g$  stems from a reduction of  $\tau_{pp}$  through anisobaric phonon scattering. The analysis is then carried out under the assumption that  $\tau_{pe}$  remains unaffected by the solutes.<sup>17</sup> At low temperatures, however, thermal conductivity measurements provide ample evidence that this interpretation cannot be correct and that  $\tau_{pe}$  does depend on the type and concentration of impurities. We shall return to this question later.

Another disadvantage of limiting measurements to low temperatures is the obvious one that nothing is learned of the behavior of  $S_d$  and  $S_g$  at higher temperatures where, in fact, the latter generally displays a pronounced maximum.

The method of separating  $S$  into  $S_d$  and  $S_g$  initially adopted by Blatt and Kropschot<sup>19</sup> also suffers from serious drawbacks. Briefly, it depends on measurements of  $S$  of the pure metal and of several reasonably dilute  $\alpha$ -phase alloys over a wide temperature range. The alloys are carefully selected so that for some of them  $\tau_{pp}^A \ll \tau_{pp}^0$ , where the superscripts denote the alloy (A) and pure metal (0). According to (2) we expect that  $S_g^A \ll S_g^0$  for the group of alloys with  $\tau_{pp}^A \ll \tau_{pp}^0$ , and that  $S_g^A \simeq S_g^0$  if  $\tau_{pp}^A \simeq \tau_{pp}^0$ . Comparison of experimental results with theoretical prediction then gives  $S_d$  and  $S_g$  over a wide temperature range.

This method, which we shall detail in the next section, has the advantage that  $S_g$  and  $S_d$  of the pure metal and of the alloys are obtained over a wide range of temperatures. Moreover, we need make no *a priori* assumption regarding the temperature dependence of  $S_g$ . The very serious drawback is that one in effect assumes at the outset that the Fermi surface of the dilute alloys does not differ significantly from that of the pure metal. If it were otherwise, both contributions

<sup>16</sup> C. van Baarle, A. J. Cuelenaere, G. J. Roest, and M. K. Young, *Physica* **30**, 244 (1964).

<sup>17</sup> A. M. Guénault and D. K. C. MacDonald, *Proc. Roy. Soc. (London)* **A264**, 41 (1961); **A274**, 154 (1963).

<sup>18</sup> R. E. Peierls, *Ann. Physik* **4**, 121 (1930).

<sup>19</sup> F. J. Blatt and R. H. Kropschot, *Phys. Rev.* **118**, 480 (1960). Hereafter referred to as BK.

<sup>13</sup> F. J. Blatt, *Proc. Phys. Soc. (London)* **A83**, 1065 (1964).

<sup>14</sup> W. G. Henry and P. A. Schroeder, *Can. J. Phys.* **41**, 1076 (1963).

<sup>15</sup> A. R. deVroomen, C. van Baarle, and A. J. Cuelenaere, *Physica* **26**, 19 (1960).

could change in an almost unpredictable way as solutes are added. Fortunately, all indications are that in a dilute copper alloy, whatever change the Fermi surface may suffer, it does not exert a noticeable influence on the transport properties. These phenomena reflect principally the effect of impurities in scattering electrons and phonons.

### 3. ANALYSIS OF THE THERMOELECTRIC POWER OF DILUTE ALLOYS

For small concentrations the effect of impurities on the resistivity of a metal can be explained in terms of the reduction of the mean free path as a result of scattering. Matthiessen's rule is, at least in copper, a very good approximation, and so we may write

$$\rho_A = \rho_i + \rho_r,$$

where  $\rho_A$  is the resistivity of the alloy and  $\rho_i$  and  $\rho_r$  are the ideal and residual resistivities, respectively. It now follows from (1) that the diffusion thermopower of an alloy is given by

$$S_d^A = \frac{\rho_i}{\rho_A} S_d^0 + \sum_j \frac{\rho_r^j}{\rho_A} S_d^j, \quad (4)$$

where

$$S_d^j = -\frac{\pi^2 k^2 T}{3eE_F} \left( \frac{\partial \ln \rho_r^j}{\partial \ln E} \right)_{E_F}. \quad (5)$$

Here  $\rho_r^j$  denotes the residual resistivity due to impurity atoms of type  $j$ , and  $S_d^j$  is the corresponding absolute diffusion thermopower due to the presence of type  $j$  impurities in the solvent metal.

Equation (1) is, however, valid only at high and low temperatures, i.e., when the Wiedemann-Franz law is obeyed:

$$\kappa_e / \sigma T = L_0 = 2.45 \times 10^{-8} \text{ (V/deg)}^2, \quad (6)$$

where  $\kappa_e$  is the electronic contribution to the thermal conductivity. In the intermediate temperature range, where significant deviations from (6) occur, a rather complicated expression derived by application of the variational method must be employed instead of (1).<sup>9</sup> In this temperature domain (4) is, therefore, incorrect also. It is generally true, however, as was first demonstrated by Kohler,<sup>20</sup> that the diffusion thermopower of an alloy is given by<sup>1</sup>

$$S_d^A = \frac{W_i}{W_A} S_d^0 + \sum_j \frac{W_r^j}{W_A} S_d^j, \quad (7)$$

where the  $W$ 's denote electronic thermal resistivities, and the electronic thermal resistivity is assumed to obey Matthiessen's rule,

$$W_A = W_i + \sum_j W_r^j.$$

<sup>20</sup> M. Kohler, Z. Physik 126, 481 (1949).

When Eq. (6) is true (7) reduces to (4), the Nordheim-Gorter relation.<sup>21</sup>

This simple equation, (7), allows for very few adjustable parameters since the thermal resistivities and, frequently, also  $S_d^0$  are known from other measurements. As regards  $S_d^j$ , its value will depend on the variation of  $\rho_r^j$  with electron energy, that is, on the energy dependence of the electron-impurity scattering cross section.  $S_d^j$  will therefore be somewhat sensitive to the details of the impurity potential. One might attempt to determine this potential by matching calculated and observed residual resistivities. However, provided certain basic self-consistency requirements are satisfied,<sup>22</sup> the residual resistivity proves to be quite insensitive to the assumed shape, depth and range of this potential.<sup>23</sup> The same is not true of  $\partial \ln \rho_r^j / \partial \ln E$ , and here again we find that the thermopower is more sensitive to the details of electron-impurity interactions than is the resistivity.

Since we cannot calculate  $S_d^j$  from first principles with any degree of accuracy we view it as an adjustable parameter. This does not, however, allow as much freedom as might appear at first sight. Since  $S_d^j$  depends on the logarithmic derivative of  $\rho_r^j$ , i.e., on  $(1/\rho_r^j) \partial \rho_r^j / \partial E$ ,  $S_d^j$  should be independent of impurity concentration  $c_j$  within the limit of validity of Matthiessen's rule. It can be said that  $S_d^j$  is an *intensive* whereas  $\rho_r^j$  is an *extensive* property of the solute atoms. Secondly, since the residual resistivity is the result of elastic scattering of conduction electrons by the impurity centers, a collision process independent of temperature, (5) shows that  $S_d^j$  must depend *linearly* on the absolute temperature. Thus, once we have selected  $S_d^j$  to give a good fit to the measured thermoelectric power of the alloy at one particular temperature and solute concentration, the *same value of  $S_d^j/T$*  must be used in the analysis of data at *all other temperatures*. Moreover, this *same  $S_d^j(T)$*  must be used in (4) to predict  $S_d^A$  of alloys containing type  $j$  impurities in *different concentrations*.

Of course, to determine  $S_d^j$  from measured thermopowers we need to know  $S_d^0$ . In other words, we must somehow achieve, *ab initio*, a separation of  $S^0$  into  $S_d^0$  and  $S_g^0$ , at least at one temperature. For this we rely on the anticipated temperature dependence of  $S_g^0$  at high temperatures. As  $T$  increases  $\tau_{pp}$  decreases as a result of anharmonic phonon-phonon umklapp scattering, whereas  $\tau_{pe}$  remains constant. Since  $\tau_{pp} \propto T^{-1}$  and  $C_g \approx \text{const}$  for  $T > \theta_D$ ,  $S_g^0$  must decrease as  $T^{-1}$  at elevated temperatures. At low temperatures,  $T \ll \theta_D$ ,  $S_g^0 \propto T^3$ , as we have seen already. Thus we expect that

<sup>21</sup> L. Nordheim and C. J. Gorter, Physica 2, 383 (1935).

<sup>22</sup> J. Friedel, Phil. Mag. 43, 153 (1952); *Advances in Physics* (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446.

<sup>23</sup> F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 199. J. Friedel, Can. J. Phys. 34, 1190 (1956).

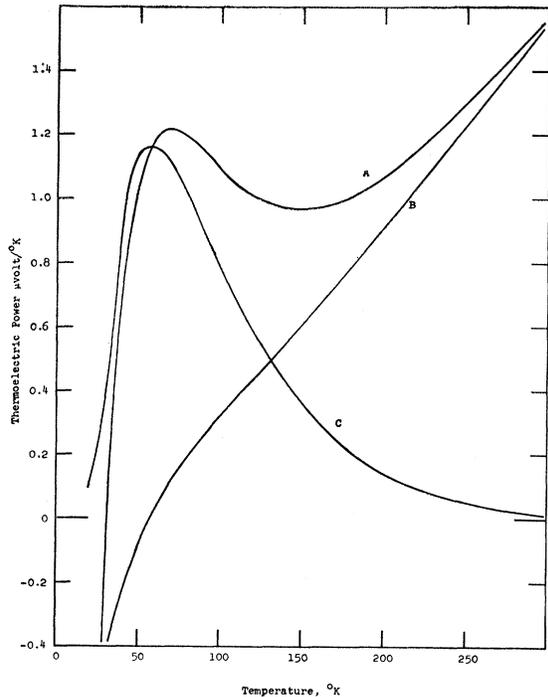


FIG. 1. The thermoelectric power of commercially pure (99.999%) copper: A, Total absolute thermopower of pure copper; B, Calculated diffusion contribution  $S_d$  including effect of iron impurity; C, Phonon-drag contribution  $S_g^0$  the difference of curves A and B.

$S_g^0$  will exhibit a maximum at some intermediate temperature which, in most cases, is near  $T = \theta_D/5$ .

At high temperatures, then,  $S^0 = S_d^0$ , and a good indication that this domain has been attained is a linear increase of thermopower with absolute temperature. Above room temperature  $S$  of copper is proportional to  $T$ , and so we take this "high-temperature" value to be  $S_d^0$ . The diffusion thermopower at lower temperatures can now be obtained by extrapolation using the Sondheimer-Wilson interpolation formula.<sup>24</sup>

Unfortunately, our "pure" copper contained iron in very small concentration. It is now firmly established that these transition metal impurities play a decisive role at low temperatures,  $T \leq 40^\circ\text{K}$  in copper, where they result in the appearance of a resistance minimum and a very large thermoelectric anomaly.<sup>25</sup> Near  $10^\circ\text{K}$  the diffusion thermopower of our pure copper is determined almost entirely by these iron impurities. However, since  $W_r^{\text{Fe}}$  soon becomes negligible compared to  $W_i$  as the temperature is increased,  $S_d^{\text{Cu}}$  is unaffected by these impurities at higher temperatures. Using the known value<sup>25</sup> of  $S_d^{\text{Fe}}$  we obtain, from (7), the diffusion thermopower of our pure copper, shown as curve B in Fig. 1. The measured absolute thermopower is

<sup>24</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1963), 2nd ed.

<sup>25</sup> A. V. Gold, D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, *Phil. Mag.* **5**, 765 (1960).

curve A in Fig. 1. Presumably the difference between these two represents the phonon-drag contribution, curve C in Fig. 1.

The phonon-drag thermoelectric power also suffers changes due to alloying. In this case the influence of impurities manifests itself principally through their effect in reducing  $\tau_{pp}$ , and thereby  $S_g$ , as a result of anisobaric (isotope) scattering of phonons. Scattering of lattice vibrations by atoms whose mass differs from that of the host lattice has been considered theoretically by Klemens,<sup>26</sup> Ziman,<sup>27</sup> and Callaway,<sup>28</sup> and was shown to be an important factor in limiting the thermal conductivity of some copper alloys above  $20^\circ\text{K}$ .<sup>29</sup> Provided the impurity does not distort the lattice, the contribution of anisobaric scattering to  $1/\tau_{pp}$  should be proportional to  $c_j$  and to  $(\Delta M_j/M)^2$ , where  $\Delta M_j = M_j - M_0$  is the difference in mass between an impurity atom and one of the host lattice, and  $M$  is the average atomic mass of the alloy.

Let us consider then the effect on  $S_g$  of adding Zn and Cd to Cu. Since  $M_{\text{Zn}} \approx M_{\text{Cu}}$  we expect no significant reduction in  $\tau_{pp}$  in a dilute CuZn alloy and, therefore, also no significant change in  $S_g$ . On the other hand,  $M_{\text{Cd}} \approx 2M_{\text{Cu}}$ , and estimates based on Klemens' formula indicate that a concentration of 1 at. % of Cd in Cu should reduce  $S_g$  to about  $S_g^0/4$  at the temperature of the phonon-drag maximum. A very rough approximation gives the following relation<sup>6</sup>

$$S_g^A/S_g^0 = \kappa_g^A/\kappa_g^0, \quad (8)$$

where  $\kappa_g$  is the lattice thermal conductivity. As we shall see, (8) is not correct and  $S_g^A$  is in general considerably smaller than this relation predicts. In other words, anisobaric scattering reduces the phonon-drag thermoelectric power considerably more than the lattice thermal conductivity. We shall discuss the reasons for this below.

#### 4. EXPERIMENTAL PROCEDURE

Details of sample preparation have been discussed in a previous publication.<sup>30</sup> The samples used in the present study are listed in Table I. In Table II we have listed the samples used by BK<sup>19</sup> for comparison and for the later discussion.

The conductivities were measured by standard methods, as was the thermoelectric power. In the case of the CuAg and CuAu alloys the cold end of the thermocouple was maintained at the temperature of the cryo-

<sup>26</sup> P. G. Klemens, *Proc. Roy. Soc. (London)* **A208**, 108 (1951); *Phys. Rev.* **119**, 507 (1960).

<sup>27</sup> R. Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A253**, 403 (1959).

<sup>28</sup> J. Callaway and H. C. von Baeyer, *Phys. Rev.* **120**, 1149 (1960).

<sup>29</sup> P. G. Klemens, G. K. White, and R. J. Tainsh, *Phil. Mag.* **7**, 1323 (1962).

<sup>30</sup> M. Garber, B. W. Scott, and F. J. Blatt, *Phys. Rev.* **130**, 2188 (1963).

TABLE I. Binary alloys used by BGS.

Sample	Solute	Concentration at. %	Residual resistivity $\mu\Omega\text{-cm}$
7	Au	0.4	0.21
8	Ag	0.45	0.05
9	Ag	0.96	0.10
10	Sn	0.65	1.75
11	Sn	1.22	3.38
12	Sn	1.84	4.86

TABLE II. Binary alloys used by BK.

Sample	Solute	Concentration at. %	Residual resistivity $\mu\Omega\text{-cm}$
1	Zn	0.7	0.23
2	Ge	0.83	3.1
3	Cd	0.4	0.085
4	In	0.8	0.88
5	Sn	0.95	2.69
6	Sb	0.8	4.38

genic bath, that of the hot end was measured by means of a gold-2.1% cobalt versus silver-37% gold thermocouple which was calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. The thermoelectric voltages from the sample thermocouple were measured with a milli-microvolt potentiometer (Rubicon six-dial) and a photocell galvanometer amplifier (Guildline Instruments) to a precision of  $\pm 2 \times 10^{-9}$  V. The voltages were plotted versus the hot junction temperatures, and the slope of this curve gave the thermopower of the couple. The thermoelectric power so obtained was estimated to be accurate to within  $0.005 \mu\text{V}/^\circ\text{K}$  above  $20^\circ\text{K}$  and to within  $0.02 \mu\text{V}/^\circ\text{K}$  below that temperature.

The three CuSn alloys were measured in an entirely different apparatus described earlier.<sup>30</sup> In this arrangement both hot and cold junction temperatures were raised simultaneously, and a small temperature difference  $\Delta T$  maintained between them. The average thermoelectric power and the electrical and thermal conductances were then measured directly. The thermopowers of these alloys were measured relative to 99.999% pure lead; the absolute thermopowers were obtained using the results of Christian *et al.*<sup>31</sup> Below  $20^\circ\text{K}$  the temperature difference between hot and cold junctions was limited to approximately  $1^\circ\text{K}$ . Above about  $20^\circ\text{K}$  these differences were gradually increased to  $5^\circ\text{K}$  and to about  $10^\circ\text{K}$  near room temperature. Again, the accuracy of the thermoelectric results is best at higher temperatures, where the error is less than  $0.003 \mu\text{V}/^\circ\text{K}$ ; below  $20^\circ\text{K}$  the error is less than  $0.05 \mu\text{V}/^\circ\text{K}$ .

<sup>31</sup> J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) A245, 213 (1958).

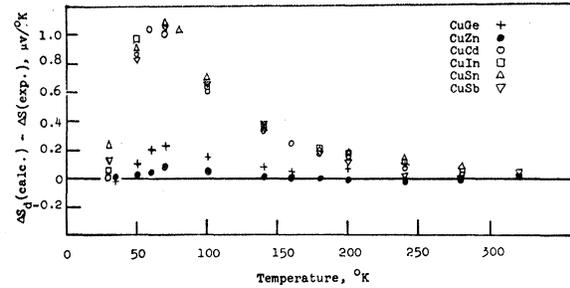


FIG. 2. The difference between the calculated diffusion thermopower and the total measured thermopower for alloy versus pure copper thermocouples (Fig. 7 of BK corrected for iron impurity). This difference is  $S_d^{\text{Cu}} - S_d^{\text{A}}$ .

## 5. RESULTS AND DISCUSSION

### a. Previous Measurements

BK measured the thermoelectric power of thermocouples formed from pure copper and the binary alloys listed in Table II. The measured thermoelectric power in such an arrangement is just the change in the thermoelectric power of copper due to the addition of the solutes. Hence we have

$$\Delta S(\text{expt}) = \Delta S_d + \Delta S_\theta = (S_d^{\text{A}} - S_d^{\text{Cu}}) + (S_\theta^{\text{A}} - S_\theta^{\text{Cu}}). \quad (9)$$

$S_d^j$  was determined for each alloy by fitting the experimental results to Eq. (4) at  $320^\circ\text{K}$  where, presumably,  $S_\theta^{\text{A}} \approx S_\theta^{\text{Cu}} \approx 0$ . Using the parameter  $S_d^j$  obtained in this way,  $S_d^{\text{A}} - S_d^{\text{Cu}}$  was then calculated at the lower temperatures. Figure 2 shows the result of plotting  $\Delta S_d(\text{calc}) - \Delta S(\text{expt})$  for these samples. According to (9) the ordinate should just equal  $S_\theta^{\text{Cu}} - S_\theta^{\text{A}}$ , assuming  $\Delta S_d$  is given correctly by  $\Delta S_d(\text{calc})$ . We see that indeed  $S_\theta^{\text{A}} \approx S_\theta^{\text{Cu}}$  for the CuZn alloy and, somewhat less so, for the CuGe alloy. In the case of all the other binary alloys the points fall on a single curve which is practically identical to the phonon-drag thermopower which we deduced in Fig. 1, indicating that for these alloys  $S_\theta^{\text{A}} \approx 0$ .

The recent work on binary and ternary dilute copper alloys was motivated by the feeling that satisfying through the results of BK might be, the decomposition of  $S^{\text{Cu}}$  into its diffusion and phonon-drag components should be further tested by comparing experimental results with theoretical predictions that are based only on the conclusions of BK and not on any further adjustable parameters. We also decided to measure, in several cases, thermopower and electrical and thermal conductivities simultaneously, so that we might compare directly the change in lattice thermal conductivity with the change in the phonon-drag thermopower and examine the validity of Eq. (8).

### b. CuAg and CuAu Alloys; The Quenching of $S_\theta$ by Anisobaric Scattering

The measurements on the equi-valent alloys serve as an indication of the efficacy of anisobaric scattering

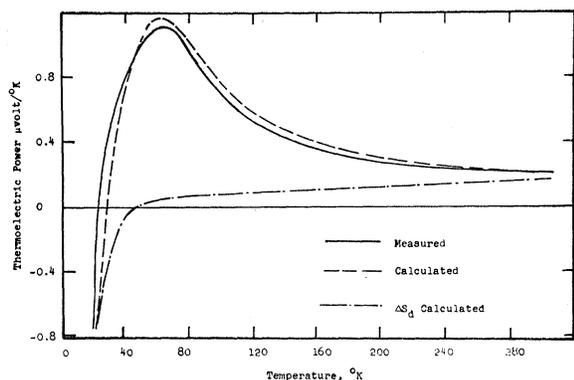


FIG. 3. Measured and calculated thermopowers of Cu versus Cu-0.4 at.%Au couple. The calculated curve is based on the assumption of complete quenching of the phonon-drag contribution.

in quenching the phonon-drag thermopower. As can be seen from Eq. (7) the influence of impurities on the diffusion thermopower depends not only on the parameter  $S_d^j$  but also on the thermal resistivity  $W_r^j$  due to these impurities. Since the electronic thermal resistivities due to silver and gold as solutes in copper are quite small, and there is no reason why  $S_d^j$  should be especially large, these elements should be relatively ineffective in influencing the diffusion thermopower except in the low-temperature range where, in our pure copper samples,  $S_d^{\text{Cu}}$  is determined principally by the iron contamination.

Figures 3-5 show  $\Delta S$  for one CuAu and two CuAg alloys. The calculated curves were obtained on the assumption that 1 at.% Ag as well as 0.4 at.% Au completely quench the phonon-drag contribution in copper. To obtain fair agreement in the case of the 0.45 at.% Ag alloy it was necessary to assume that in this case  $S_g^{\text{A}} = 0.2S_g^{\text{Cu}}$ . Using these results we therefore estimate that in binary copper alloys containing elements to the right of silver in the periodic table  $S_g^{\text{A}} \approx 0$  if  $c_j \gtrsim 0.9$  at.%;  $S_g^{\text{A}} \approx 0.1S_g^{\text{Cu}}$  if  $c_j \approx 0.7$  at.%;  $S_g^{\text{A}} \approx 0.2$

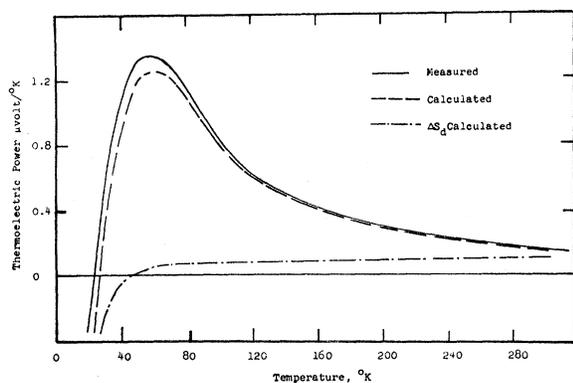


FIG. 4. Measured and calculated thermopowers of a Cu versus Cu-0.96 at.%Ag couple. The calculated curve assumes complete quenching of the phonon-drag contribution.

$S_g^{\text{Cu}}$  if  $c_j \approx 0.5$  at.%. These are, of course, at best rough estimates which are valid only in the temperature region near the phonon-drag peak. We should not wish to appear too dogmatic about these figures; as crude guideposts they should serve adequately. At low temperatures  $S_g^{\text{A}}$  is certainly greater than these figures predict because anisobaric phonon scattering is quite ineffective in reducing the mean free path of long-wavelength phonons. We shall have occasion to return to this point presently.

As expected,  $\Delta S$  in these CuAu and CuAg alloys is, between 40 and 200°K, almost entirely attributable to the quenching of phonon-drag thermopower by the heavy, monovalent impurities in the monovalent host lattice.

### c. The Behavior of $S_g$ and $\kappa_g$ in CuSn Alloys

We now turn to the three CuSn alloys, for which the three transport properties were measured simultan-

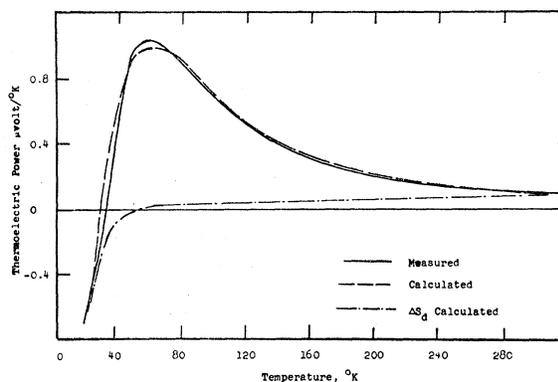


FIG. 5. Measured and calculated thermopowers of a Cu versus Cu-0.45 at.%Ag couple. The calculated curve is obtained by assuming the phonon-drag contribution is 20% of the value for pure copper.

ously. In Fig. 6 we show the calculated and measured thermopowers. The calculated curves were obtained as follows. The ideal thermal resistivity of pure copper was taken from the results of White<sup>32</sup> for the range  $T = 10$  to  $50^\circ\text{K}$ , and from Berman and MacDonald<sup>33</sup> for temperatures between  $50$  and  $90^\circ\text{K}$ . Above  $90^\circ\text{K}$  we used the results of the free-electron theory, that is, Eq. (9.621.5) in Wilson.<sup>24</sup> The residual thermal resistivities  $W_r^j$  were calculated from the measured residual electrical resistivities using Eq. (6). The diffusion thermopower of each alloy was then calculated by means of Eq. (7) using the parameter  $S_d^j$  determined independently by BK. The phonon-drag thermopowers were assumed vanishingly small for samples 11 and 12 and equal to  $0.1 S_d^0$  for sample 10 in accordance with

<sup>32</sup> G. K. White, Australian J. Phys. 6, 397 (1953).

<sup>33</sup> R. Berman and D. K. C. MacDonald, Proc. Roy. Soc. (London) A211, 122 (1952).

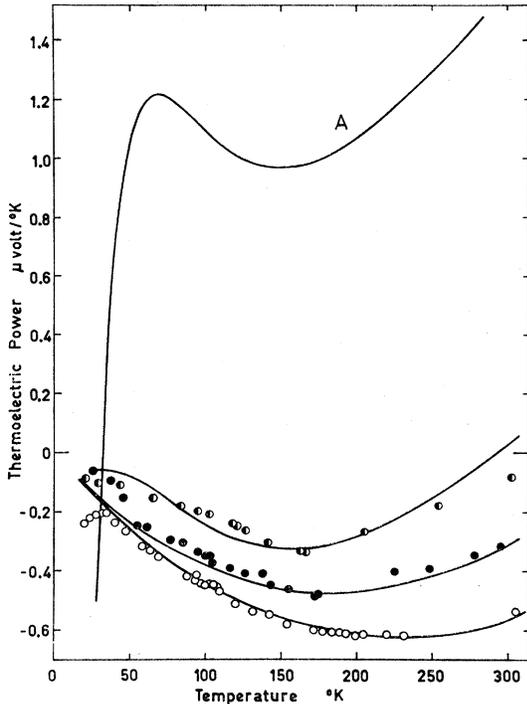


Fig. 6. Absolute thermoelectric power of CuSn alloys. Experimental results are represented by the points:  $\circ$ , Cu-0.65 at.% Sn;  $\bullet$ , Cu-1.22 at.% Sn;  $\circ$ , Cu-1.84 at.% Sn. Solid curves are calculated taking  $S_{Sn}(300^\circ\text{K}) = -1.4 \mu\text{V}/^\circ\text{K}$  and assuming  $S_d^A = 0.1S_d^{\text{Cu}}$  for Cu-0.65 at.% Sn and  $S_d^A = 0$  for the others. Curve A is the absolute thermopower of pure copper, shown for comparison.

our findings on the CuAg alloys and the results of BK. The agreement with the experimental results is remarkably good and provides full support for our decomposition of  $S^{\text{Cu}}$  into diffusion and phonon drag contributions as shown in Fig. 1. Moreover, since the calculation of  $S_d^A$  assumes that the addition of impurities does not modify the Fermi surface, at least insofar as this would affect the transport properties, we conclude that this assumption is justified also. The important point here, it seems to us, is that agreement between experimental results and calculations extends over a fairly wide temperature range even though a single value of  $S_d^i/T$  was used for all three alloys. We would not expect such good agreement if those portions of the Fermi surface of copper which contribute principally to charge transport were significantly modified by alloying with tin. We do not rule out the possibility of fairly substantial changes near the necks of the Fermi surface.

In Fig. 7 we show the lattice thermal conductivities of these alloys in the temperature range 10–100°K. For purposes of the discussion which is to follow we will summarize our previous remarks<sup>30</sup> about this data.

In pure copper two scattering mechanisms are primarily responsible for the lattice thermal resistivity  $W_\theta = 1/\kappa_\theta$ . At high temperatures, that is for  $T > 40^\circ\text{K}$ ,

anharmonic phonon-phonon umklapp scattering leads to a thermal resistivity proportional to  $T$ . As anharmonic scattering diminishes we find that the phonon mean free path is limited ultimately by phonon-electron scattering. In that temperature domain, in copper for  $T < 20^\circ\text{K}$ , the lattice thermal resistivity is proportional to  $T^{-2}$ .

The lattice thermal conductivity is diminished by the addition of impurities in two ways also. At high temperatures anisobaric scattering reduces the phonon mean free path and the effective phonon relaxation time is

$$1/\tau = 1/\tau_u + 1/\tau_a, \quad (10)$$

where  $1/\tau_u$  and  $1/\tau_a$  are the relaxation rates due to umklapp and anisobaric scattering, respectively. They are given by<sup>34</sup>

$$1/\tau_u = BT\omega^2, \quad (11)$$

$$1/\tau_a = (\Omega/4\pi v^3)\mu\omega^4, \quad (12)$$

where  $B$  is constant,  $\omega$  is the phonon frequency,  $\Omega$  is the atomic volume,  $v$  is the velocity of sound, and  $\mu = \sum_j c_j (\Delta M_j/M)^2$ .

In the low-temperature region anisobaric scattering should be quite ineffective in reducing  $\kappa_\theta$  since the

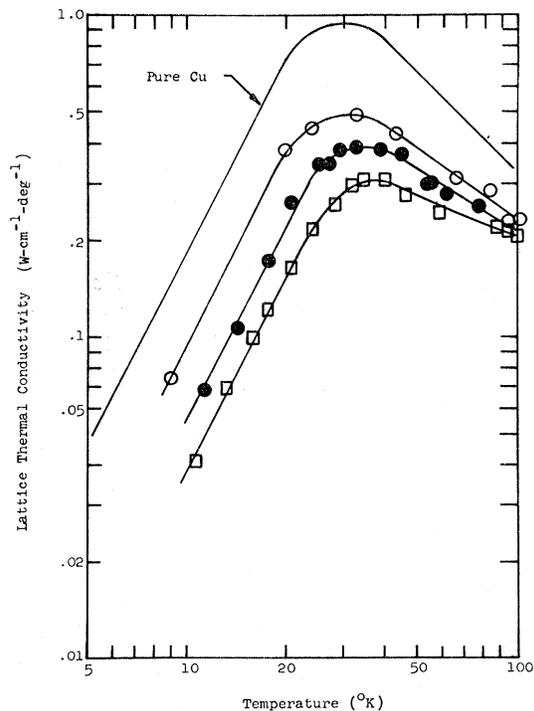


Fig. 7. Lattice thermal conductivities of the CuSn alloys.  $\circ$ —0.65 at.%;  $\bullet$ —1.2 at.%;  $\square$ —1.8 at.% (Fig. 3 of Ref. 30).

<sup>34</sup> P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

scattering process, Rayleigh scattering, is proportional to  $\omega^4$ ; at low temperatures only long-wavelength, low-frequency phonons are excited. Nevertheless, impurities reduce  $\kappa_g$  at low temperatures, as is evident also from our data, and contribute a lattice thermal resistivity proportional to  $T^{-2}$ . The explanation for this observation is due to Pippard<sup>35</sup> who pointed out that the reduction in electronic mean free path enhances the electron-phonon interaction. Accordingly, the theory predicts that  $1/\kappa_g$  should be a function not of the impurity mass but of the residual resistivity, and experimental results confirm this conclusion.<sup>36</sup> (We may note, however, that in the limit of very low temperature and large residual resistivity the theory predicts that  $\kappa_g$  be proportional to  $T$  and increase with increasing  $\rho_r$ . Our results do not reach this domain of  $T/\rho_r$ .)

We now wish to compare the reduction in  $S_g$  and  $\kappa_g$  due to alloying. We reproduce here the expressions for these two quantities valid in the Debye approximation, namely<sup>6</sup>

$$S_g = 3(k/e)(T/\theta)^3 \int_0^{\theta_D/T} \frac{z^4 F(z)}{(e^z - 1)(1 - e^{-z})} dz, \quad (13)$$

$$\kappa_g = Q_\kappa (T/\theta)^2 \int_0^{\theta_D/T} \frac{z^3 F(z)}{(e^z - 1)(1 - e^{-z})} dz, \quad (14)$$

where  $F(z) = \tau_{pp}/(\tau_{pp} + \tau_{pg})$ ,  $z = \hbar\omega/kT$ , and  $Q_\kappa$  is a constant.

In the high-temperature limit ( $z \ll 1$ ) these equations lead to the proportionality of  $S_g$  and  $\kappa_g$ , i.e., to Eq. (8). Since the integrands in (13) and (14) do not differ greatly Eq. (8) should remain a good approximation also at lower temperatures. However, from the fact that (13) contains one higher power of  $z$  than does (14), we can see that at lower temperatures *collision processes which are especially effective in limiting the mean free path of high-frequency phonons will have a more pronounced influence on  $S_g$  than on  $\kappa_g$* . Rough numerical calculations show that for the 0.65 at. % Sn alloy and at  $T = 60^\circ\text{K}$  we should replace (8) by

$$S_g^A/S_g^0 = 0.7(\kappa_g^A/\kappa_g^0). \quad (8a)$$

In other words, at the lower temperature the more exact expressions (13) and (14) predict a greater reduction in  $S_g$  than in  $\kappa_g$  as a result of anisobaric scattering.

Our measurements indicate, however, that  $S_g^A \approx 0.1S_g^0$  whereas  $\kappa_g^A \approx 0.5\kappa_g^0$  for this alloy. Of these two,  $S_g^A$  is rather less precisely known and could, perhaps, be as large as  $0.2S_g^0$ . Despite this uncertainty in  $S_g^A$  there can be no doubt that  $S_g^A/S_g^0$  is, at  $60^\circ\text{K}$ , significantly smaller than even (8a) would predict. Thus we are led to re-examine the approximations on which (13) and (14) are based.

One of these is the neglect of dispersion in the phonon

spectrum and this, we believe, can lead to serious errors, especially at temperatures greater than about  $\theta_D/10$ . Let us recall here the kinetic theory expression<sup>34</sup> for  $\kappa_g$

$$\kappa_g = \frac{1}{3} \int C(\omega) l(\omega) v_g(\omega) d\omega, \quad (15)$$

from which we see directly that the energy transport by phonons in the frequency interval  $d\omega$  is proportional to their contribution to the specific heat, to their mean free path, and to their *group* velocity  $v_g$ . The relatively simple expression for  $\kappa_g$ , Eq. (14), holds only provided  $v_g = d\omega/dq$  is replaced by the phase velocity  $v_p = \omega/q$ . We know that generally  $v_g$  diminishes with increasing wave vector  $q$  and goes to zero as we approach a zone boundary. Consequently, a calculation of  $\kappa_g$  which disregards the  $q$  dependence of  $v_g$  will overestimate the contribution of high-frequency phonons to the lattice thermal conductivity. An immediate corollary is that the same approximation will also overestimate the reduction in  $\kappa_g$  due to centers which scatter predominantly high-frequency phonons. Since anisobaric scattering fulfills condition we expect that

$$(\kappa_g^A/\kappa_g^0)_{\text{exp}} > (\kappa_g^A/\kappa_g^0)_{\text{Debye}}.$$

In contrast to the lattice thermal conductivity, the contribution of phonons to  $S_g$  is determined not by  $v_g$  but by the crystal momentum  $\hbar q$  which they can impart to the electrons through phonon-electron collisions. It is then the high-momentum, rather than the high-frequency phonons which make the dominant contribution to  $S_g$ . In fact, the usual dispersion of the phonon spectrum will *enhance* rather than diminish the contribution of short-wavelength phonons over that obtained in the Debye approximation. This enhancement comes from the fact that for large  $q$  the phonon energy is less than the dispersionless model predicts. Consequently, their occupation number  $n(q)$  is greater than in the Debye model. It then follows also that Rayleigh scattering, with its  $\omega^4$  dependence, will be very effective in reducing  $S_g$ , and we expect that

$$(S_g^A/S_g^0)_{\text{exp}} < (S_g^A/S_g^0)_{\text{Debye}}.$$

We therefore view the experimental results simply as manifestations of the well-known dispersion of the phonon spectrum. These qualitative arguments are also in harmony with the unexpectedly small values of  $S_g^0$  at somewhat higher temperatures (e.g., room temperature) which are characteristic of all metals. It is difficult to believe that  $S_g^N$  and  $S_g^U$  cancel almost exactly in every substance at normal temperatures, and a more palatable explanation of these observations also rests on the universal failure of the Debye approximation at normal temperatures.<sup>13</sup>

In the preceding paragraphs we have made use of expressions for  $S_g$  which disregard U processes altogether. Although we cannot rule out the possibility that,

<sup>35</sup> A. B. Pippard, *Phil Mag.* **46**, 1104 (1955).

<sup>36</sup> P. Lindenfeld and W. B. Pennebaker, *Phys. Rev.* **127**, 1881 (1962).

besides being reduced by the addition of impurities,  $S_g^N$  and  $S_g^U$  may also be made more nearly equal in magnitude, this would seem to be a somewhat fortuitous circumstance.

At sufficiently low temperatures we may hope for greater success of the Debye model. Probably the most careful analysis of experimental data on alloys along such lines is that by Guénault and MacDonald.<sup>17</sup> As a first approximation they used Eq. (13) and calculated the phonon-drag thermopower of their alloys in terms of a single parameter which, in effect, characterizes the Rayleigh cross section. They also assumed that at these low-temperatures anharmonic effects could be neglected and that the phonon-electron relaxation time  $\tau_{pe}$  is insensitive to the addition of impurities.

Unfortunately, this last assumption is probably unjustified. The reduction in lattice thermal conductivity due to impurities at temperatures below the conductivity maximum indicates that  $\tau_{pe}$  is decreased in this temperature range, and the good agreement of the experimental results with the theory of Pippard shows that this reduction is directly related to the residual electrical resistivity rather than to a mass difference between solute and solvent atoms.

Although the interpretation of low-temperature thermoelectric power measurements on alloys is therefore a somewhat uncertain matter, the validity of the Debye approximation at low temperatures can still be used to advantage by restricting attention to pure metals. In particular, estimates of  $S_g^N$  should be reliable at low temperatures. If, then, we assume for the moment that  $S_g^U=0$ , the relation

$$S_g^0/S_d^0=C_g/2C_e, \quad T \ll \theta_D \quad (16)$$

should be obeyed.

In copper,  $C_g/C_e=7 \times 10^{-2} T^2$  at low temperatures.<sup>37</sup> From our data we obtain  $(S_g^0/S_d^0)_{\text{exp}} \simeq 1.2 \times 10^{-2} T^2$ . We conclude that (a)  $S_g^U$  dominates since  $S_g^0 > 0$  and (b)  $S_g^N$  and  $S_g^U$  are of roughly equal magnitude at low temperatures, with  $S_g^U$  about 25% larger than  $|S_g^N|$ . These conclusions are in agreement with Ziman's estimates concerning the relative importance of N and U processes in the noble metals.<sup>38</sup>

<sup>37</sup> W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **98**, 1699 (1955).

<sup>38</sup> J. M. Ziman, *Advances in Physics* (Taylor and Francis, Ltd. London, 1961), Vol. 10, p. 1.

## 6. CONCLUSIONS

From our measurements on CuAg, CuAu, and CuSn alloys in conjunction with the earlier results of BK we draw the following conclusions:

(1) The decomposition of the absolute thermoelectric power of copper into diffusion and phonon-drag contributions proposed by BK is correct.

(2) Using this decomposition, the Kohler relation (7), and reasonable estimates concerning the phonon-drag thermopower in dilute alloys, the thermoelectric power of a dilute binary copper alloy can be predicted with very good accuracy.<sup>39</sup>

(3) The lattice thermal conductivity of the alloys is also in agreement with current theory. At high temperatures,  $T > 40^\circ\text{K}$ , the principal effect of Sn impurities in copper is the reduction in phonon mean free path through anisobaric scattering. At low temperatures,  $T < 20^\circ\text{K}$ , a thermal resistance mechanism appears whose temperature dependence cannot be reconciled with anisobaric scattering of phonons. In this temperature domain it is apparently the reduction in the electronic mean free path, enhancing the electron-phonon interaction, which diminishes the lattice thermal conductivity.

(4) Near the phonon drag peak ( $T \simeq 60^\circ\text{K}$ ) anisobaric scattering is considerably more effective in reducing the phonon-drag thermopower than in diminishing the lattice thermal conductivity. We believe that this is due to the failure of the Debye model, i.e., to dispersion in the phonon spectrum.

(5) Comparison of thermopowers ( $S_g$  and  $S_d$ ) with specific heats ( $C_g$  and  $C_e$ ) at low temperatures indicates that in copper both normal and umklapp processes contribute significantly to  $S_g$ , with  $S_g^U$  roughly 25% larger in magnitude than  $S_g^N$ .

(6) For small Sn concentrations the band structure is not altered significantly, at least not as regards those portions of the Fermi surface that make the dominant contribution to the transport properties.

## ACKNOWLEDGMENTS

It is a pleasure to thank Dr. P. A. Schroeder, B. LaRoy, and D. Sellmyer for their generous help during various stages of this work. This research project received support from the Army Research Office and the National Science Foundation which is herewith gratefully acknowledged.

<sup>39</sup> Good agreement between measured and calculated thermopower is also obtained for ternary copper base alloys. [B. W. Scott, F. J. Blatt, and M. Garber (to be published).]