

## Thermal Conductivity of Dilute Copper Alloys\*

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Lattice thermal conductivities between 10 and 90°K of three copper-tin and five dilute ternary copper base alloys are deduced from measurements of the total thermal conductivity and residual resistivity. The reduction in the lattice thermal conductivity above 40°K is in fair agreement with theoretical estimates which assume that the major effect of solutes on lattice thermal conductivity is through anisobaric phonon scattering. Below 20°K the lattice thermal conductivity is diminished in relation to the residual electrical resistivity, in agreement with a theory due to Pippard and elaborated by Lindenfeld and Pennebaker.

### I. INTRODUCTION

IN recent years there has developed a renewed interest in the thermal conductivity of solids, generated in some measure by theoretical advances<sup>1-5</sup> which, in turn, were stimulated by new, reliable experimental results.<sup>6-12</sup> The current situation is well summarized in the recent review by Mendelssohn and Rosenberg.<sup>13</sup>

In pure metals the major fraction of the total heat current is carried by conduction electrons, phonons contributing very little. Heat transport by lattice waves can, nevertheless, be studied in metals by reducing the electronic thermal conductivity through the introduction of impurities which scatter conduction electrons. Unavoidably, alloying also influences the phonon mean free path, and, in all but very dilute alloys, the phonon distribution as well. Thus, to determine the lattice thermal conductivity of a pure metal we need first as complete an understanding as possible of the manner in which this conductivity is modified by the presence of impurities and imperfections.

As a very rough first approximation, the lattice thermal resistivity  $W_\theta = 1/\kappa_\theta$  is the sum of individual terms, each associated with a particular phonon scatter-

ing mechanism; namely,

$$W_\theta = W_e + W_D + W_U + W_I, \quad (1)$$

where the four terms are due to phonon-electron, phonon-dislocation, phonon-phonon umklapp, and phonon-impurity scattering, respectively. If each of these mechanisms were solely operative, the first two resistivities would vary as  $T^{-2}$ , while the last two would be proportional to  $T$ . The first are dominant at low temperatures, below about 20°K in copper; the latter control the thermal conductivity above about 40°K.

The most immediate and obvious effect of a substitutional impurity on the phonon mean free path derives from the difference between its mass and that of an atom of the host lattice. Anisobaric scattering (sometimes called isotope scattering) of phonons was considered by Klemens<sup>1</sup> whose calculation made use of a cutoff procedure that has been criticized by Ziman.<sup>5</sup> Ziman and co-workers<sup>5</sup> demonstrated that a more elaborate treatment, which, however, necessitates a fair amount of numerical work, gives excellent agreement with experiment. More recently Klemens, White, and Tainsh<sup>14</sup> presented results on copper and silver alloys which they compared with an analytic expression that, though admittedly approximate, appears to describe correctly the lattice thermal conductivity of alloys at temperatures above about 50°K. This is the region where  $\kappa_\theta$  in the pure metal is inversely proportional to the absolute temperature.

Since anisobaric scattering is expected to, and does appear to produce a thermal resistivity approximately proportional to the absolute temperature, this mechanism should not be important at sufficiently low temperatures; i.e., below about 20°K. Nevertheless, it has been universally observed<sup>15</sup> that impurities not only bring forth the expected reduction of  $\kappa_\theta$  at higher temperatures but also contribute a thermal resistivity proportional to  $1/T^2$  at the lower temperatures. Klemens<sup>16</sup> originally suggested that phonon-dislocation scattering may cause this reduction in  $\kappa_\theta$ , and, more

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<sup>1</sup> P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951); Phys. Rev. **119**, 507 (1960).

<sup>2</sup> J. M. Ziman, Can. J. Phys. **34**, 1256 (1956).

<sup>3</sup> J. Callaway, Phys. Rev. **113**, 1046 (1959); J. Callaway and H. C. von Baeyer, *ibid.* **120**, 1149 (1960).

<sup>4</sup> V. Ambegaokar, Phys. Rev. **114**, 488 (1959).

<sup>5</sup> R. Berman, P. T. Nettle, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).

<sup>6</sup> W. R. G. Kemp, P. G. Klemens, A. K. Sreedhar, and G. K. White, Proc. Roy. Soc. (London) **A233**, 480 (1956).

<sup>7</sup> A. M. Toxen, Phys. Rev. **122**, 450 (1961).

<sup>8</sup> G. K. White and S. B. Woods, Phil. Mag. **45**, 1343 (1954).

<sup>9</sup> G. K. White, S. B. Woods, and M. T. Elford, Phil. Mag. **4**, 688 (1959).

<sup>10</sup> G. K. White, Australian J. Phys. **13**, 255 (1960).

<sup>11</sup> J. E. Zimmerman, J. Phys. Chem. Solids **11**, 299 (1959).

<sup>12</sup> M. C. Steele and F. D. Rosi, J. Appl. Phys. **29**, 1517 (1958).

<sup>13</sup> K. Mendelssohn and H. M. Rosenberg, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 223.

<sup>14</sup> P. G. Klemens, G. K. White, and R. J. Tainsh, Phil. Mag. **7**, 1323 (1962).

<sup>15</sup> W. R. G. Kemp and P. G. Klemens, Australian J. Phys. **13**, 247 (1960).

<sup>16</sup> W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, Australian J. Phys. **10**, 454 (1957).

TABLE I. Constitution, annealing, and resistivity of ternary alloys.

Sample	Composition in at. %		Annealing		Residual resistivity, $\mu\Omega\text{-cm}$	
	Initial (by weight)	Final (by chem. anal. $\pm 0.03\%$ )	Temp. ( $^{\circ}\text{C}$ )	Time (h)	Observed	Calculated
14	0.55 Cd	0.23 Cd	600	3	1.06	0.905
	0.97 In	0.76 In				
15	0.54 Cd	0.10 Cd	600	3	0.55	0.46
	0.53 In	0.39 In				
102	0.51 Zn	0.49 Zn	750	2	1.03	1.01
	0.96 In	0.77 In				
103	0.96 Zn	0.99 Zn	750	2	0.73	0.78
	0.47 In	0.42 In				
104	0.29 Zn	0.33 Zn	750	2	0.585	0.55
	0.34 Ga	0.31 Ga				

recently,<sup>14</sup> that the answer may be found in the work of Koshino<sup>17</sup> who considered the interaction between conduction electrons and impurities which participate in the vibratory motion of the host lattice. That work has, however, been criticized by Taylor<sup>18</sup> who finds that Koshino's results are orders of magnitude too large.

In attempting to understand this phenomenon, an important fact, emphasized by White,<sup>19</sup> is that the values of  $T^2/\kappa_g$  for a wide variety of alloys lie about a universal, monotonically increasing curve when plotted against  $\rho_0$ ; that is, below  $30^{\circ}\text{K}$  the increased thermal resistivity appears primarily to be a function of electron free path. For the dilute alloys of copper under consideration, this is also the region where the wavelength of those phonons which carry the major fraction of the heat current becomes equal to and exceeds the electron free path. Pippard<sup>20</sup> has pointed out that under these conditions the standard calculation of phonon-electron scattering<sup>21</sup> is not valid and has given an expression for the phonon free path when  $l_e < \lambda_{ph}$ . Lindenfeld and Pennebaker<sup>22</sup> have applied this theory in a calculation of  $\kappa_g$ , and it appears from their work that the explanation of the problem follows from Pippard's model.

We present here measurements of the thermal conductivity of three copper-tin and five dilute ternary copper base alloys. The lattice thermal conductivities that are deduced from these provide further support for Pippard's argument at low temperatures and also exhibit anisobaric scattering of phonons at temperatures above  $30^{\circ}\text{K}$ . To our knowledge, these are the first such results on ternary alloys presented in the literature, and they are of particular relevance to current theory, showing the transition from anisobaric scattering to the Pippard mechanism as the temperature is decreased.

## II. EXPERIMENTAL DETAILS

### A. Sample Preparation

The samples were prepared from 99.999% pure copper supplied by the American Smelting and Refining Co. and solute metals of at least 99.99% purity obtained from various sources (ASARCO, Jarrell-Ash, Consolidated Mining). The constituents were first etched, rinsed, dried, and weighed to a precision of  $10\ \mu\text{g}$  on a Mettler balance and then melted in vacuum or an inert atmosphere by induction heating. The molten alloys were maintained in that state for about 30 sec to provide for induction stirring and then poured into a cool copper mold. The cast slugs were homogenized in sealed Vycor capsules at  $600^{\circ}\text{C}$  for 6 days. Following this step rods of 0.25-cm diam and 5- to 10-cm length were fashioned by swaging.<sup>23</sup> A final anneal completed the preparation of each sample. After all data had been taken the samples were sent to a commercial laboratory<sup>24</sup> for chemical analysis. As expected, a significant fraction of the more volatile constituents were lost in the course of casting and annealing (see Table I). On the whole, the measured and calculated residual resistivities of the samples are in good agreement. The latter were obtained using the resistivity values quoted by Gerritsen.<sup>25</sup> These, however, are somewhat suspect, since they were obtained from measurements at liquid air and room temperature and are based on the assumed validity of Matthiessen's rule; the true residual resistivities per at. % may differ significantly for these. For example, though Gerritsen gives  $\Delta\rho(\text{Zn}) = 0.32\ \mu\Omega\text{-cm}$ , values ranging between 0.16 and  $0.41\ \mu\Omega\text{-cm}$  have been reported.<sup>26</sup>

### B. Measuring Apparatus

Our apparatus was designed with a view toward simultaneous measurement of three transport properties—electrical resistivity, thermoelectric power, thermal

<sup>17</sup> S. Koshino, Progr. Theoret. Phys. (Kyoto) **24**, 484 (1960).

<sup>18</sup> P. L. Taylor, Proc. Phys. Soc. (London) **80**, 755 (1962).

<sup>19</sup> J. R. Tainsh and G. K. White, J. Phys. Chem. Solids **23**, 1329 (1962).

<sup>20</sup> A. B. Pippard, Phil. Mag. **46**, 1104 (1955).

<sup>21</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.

<sup>22</sup> P. Lindenfeld and W. B. Pennebaker, Phys. Rev. **127**, 1881 (1962).

<sup>23</sup> Hoskins Manufacturing Company, Detroit, Michigan.

<sup>24</sup> Spectrographic Testing Laboratory, Detroit, Michigan.

<sup>25</sup> A. N. Gerritsen, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), 2nd ed., Vol. 19, pp. 137–226.

<sup>26</sup> W. R. Hibbard, Jr., J. Metals (Japan) **6**, 594 (1954).

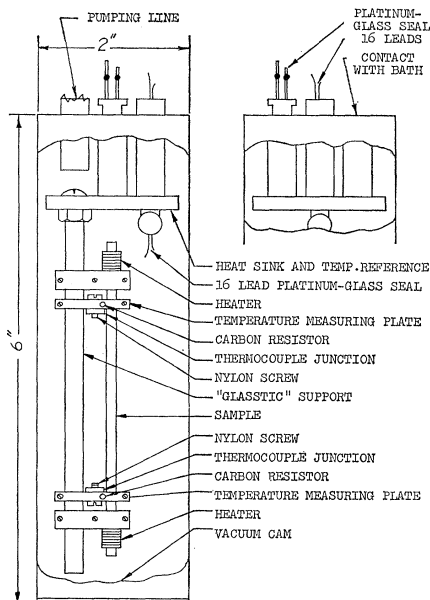


FIG. 1. Specimen assembly.

conductivity—over a fairly wide temperature range.<sup>27</sup> Naturally, the final assembly constitutes a compromise, particularly in the selection of sample shape and choice of a suitable heat leak to the cold bath.

Figure 1 is a drawing of the sample mount. Under operating conditions the entire assembly is, of course, enclosed in a vacuum tight container and pumped to less than  $10^{-5}$  mm Hg. The sample is clamped between the jaws of two copper fittings which carry Manganin heaters of approximately 1000- $\Omega$  resistance as well as the current leads for electrical resistance measurements. Potential leads are attached to the thin copper fittings labeled "temperature measuring plate" since they also carry carbon resistors (not used in the measurements reported here) and thermocouple junctions. These copper fittings have tapered holes and contact the sample around its circumference over a length of  $\frac{1}{64}$  in. The temperatures at these points are measured relative to that of the cryogenic fluid surrounding the assembly by two gold-2.1% cobalt vs silver-37% gold thermocouples whose hot junctions are soldered to small copper plates. These copper plates are, in turn, electrically insulated from the small copper jig by a thin Mylar film coated with vacuum grease, and clamped tightly to the jig with nylon screws to maintain good thermal contact. The thermocouples were calibrated against a platinum resistance thermometer which had been certified by the National Bureau of Standards. The heat leak, a No. 14 copper wire connecting the upper heater to the heat sink which is in contact with the cryogenic fluid, completes the thermal path. The copper fittings which provide

<sup>27</sup> The results on thermopower, whose interpretation requires knowledge of electrical and thermal conductivities, will be presented in a subsequent publication.

mechanical support and electrical contacts for the sample are clamped to a  $\frac{1}{2}$ -in.-diam "Glastic" rod. This material has the desirable property of matching very closely the thermal expansion coefficient of copper, thus minimizing mechanical strains of thermal origin. An attempt to determine the thermal conductivity of this supporting rod by making a run with no sample in the mount proved that it is negligible.

### III. RESULTS

The physical properties actually measured are the total thermal conductivity and the residual electrical resistivity. The lattice thermal conductivity  $\kappa_g$  is obtained from

$$\kappa_g = \kappa - \kappa_e, \quad (2)$$

and  $\kappa_e = 1/W^e$  calculated by adding to the ideal electronic thermal resistivity the residual electronic thermal resistivity  $W_{res}^e = \rho_{res}/L_0T$ . The measured total conductivity, calculated electronic and lattice contributions are shown in Fig. 2 for Sample No. 14, one of the ternary alloys. The curves clearly show that at elevated temperatures  $\kappa_e$  approaches  $\kappa$  so closely that  $\kappa_g$  becomes increasingly uncertain. Moreover, as  $T$  is raised, the rapid increase of the sample's specific heat makes the attainment of thermal equilibrium a tedious and difficult task. These considerations limited our measurements of thermal conductivity to temperatures below 100°K. Sample geometry and a fixed heat leak selected to permit us to raise the average temperature of the sample well above that of the surrounding cryogenic fluid with reasonable power input placed a lower bound on the temperature range which we could cover. With no current flowing through the upper heater and the heat sink at 4.2°K the establishment of a temperature difference of about 0.4°K across the sample raised the average temperature to 8°K or higher. Consequently,

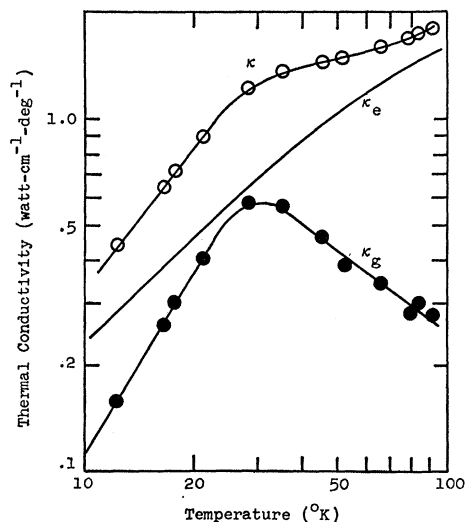


FIG. 2. Total, electronic, and lattice thermal conductivities of a dilute, ternary copper alloy, sample No. 14.

our data span the temperature range between 10 and 90°K.

The pertinent physical data of our samples are given in columns 2 and 3 of Table II. The experimental results are shown in Figs. 3 and 4.

#### IV. DISCUSSION

We consider first the results in the temperature range extending from about 40°K upward.<sup>28</sup> Here the dominant lattice thermal resistivities arise from scattering of phonons by point defects and through umklapp processes. The relaxation rate  $1/\tau'$  for phonons of frequency  $\omega$  is then

$$1/\tau' = 1/\tau_p + 1/\tau_u. \quad (3)$$

These two relaxation rates are given by<sup>14</sup>

$$1/\tau_u = BT\omega^2, \quad (4)$$

$$1/\tau_p = (\Omega/4\pi v^3)\epsilon\omega^4, \quad (5)$$

where  $\Omega$  is the atomic volume,  $v$  is the velocity of sound, and  $\epsilon$  is given by

$$\epsilon = \sum C_i (\Delta M_i/M)^2, \quad (6)$$

if the point defects scatter phonons principally by virtue of the difference between their masses and those of the solvent atoms. If  $N$  processes are neglected, the

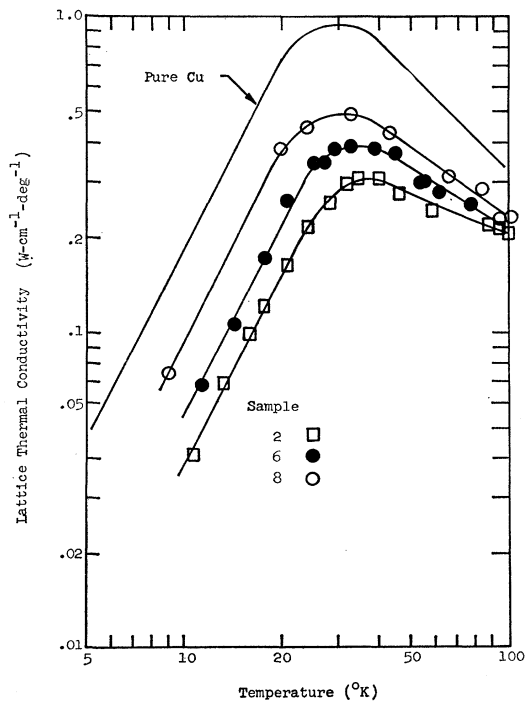


FIG. 3. Lattice thermal conductivities of three copper-tin alloys. Sample 2: 1.84% Sn; Sample 6: 1.22% Sn; Sample 8: 0.65% Sn. The curve for pure copper is taken from reference 8.

<sup>28</sup> Our notation is chosen to agree with that of reference 14.

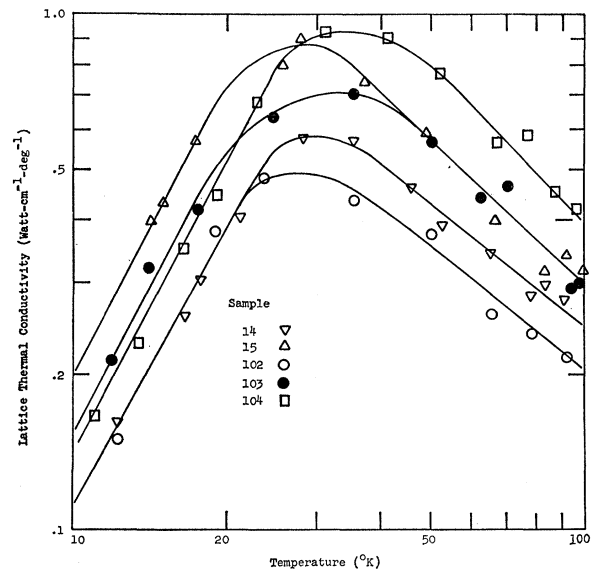


FIG. 4. Lattice thermal conductivities of fine ternary copper alloys. Sample 14: 0.23% Cd+0.76% In; Sample 15: 0.1% Cd+0.39% In; Sample 102: 0.5% Zn+0.77% In; Sample 103: 1.0% Zn+0.42% In; Sample 104: 0.33% Zn+0.30% Ga.

following simple approximate expression for the conductivity may be derived<sup>3,14</sup>

$$\kappa_g = \kappa_u (\omega_0/\omega_D) \tan^{-1}(\omega_D/\omega_0). \quad (7)$$

Here,  $\kappa_u$  is the lattice thermal conductivity due to  $U$  processes only;  $\omega_D$  is the Debye frequency;  $\omega_0$ , defined by  $\tau_u(\omega_0) = \tau_p(\omega_0)$ , is given by

$$\omega_0 = \omega_D \left[ \frac{2}{\pi} \frac{kv}{\Omega q_D \epsilon \kappa_u} \right]^{1/2}, \quad (8)$$

where  $k$  is Boltzmann's constant, and  $q_D$  is the radius of the Debye sphere.

$N$  processes, of course, cannot be neglected. They tend to maintain equilibrium of the phonon spectrum by feeding energy from low-frequency modes, which are not scattered strongly by  $U$  processes or point defects, into the higher frequency modes. Consequently, Eq. (7) would be expected to overestimate the thermal conductivity. Klemens *et al.*<sup>14</sup> have modified (7) to take account of  $N$  processes, at least very roughly, by introducing an effective relaxation time,  $\sigma$ , for  $N$  processes. They find that the somewhat arbitrary choice  $\sigma = \tau_u$  leads to good agreement between theory and experiment.

Columns 6, 7, and 8 of Table II compare our results with the approximate theory of Klemens *et al.* Although this theory is less reliable the lower the temperature, we have, nevertheless, selected  $T = 70^\circ\text{K}$  for this comparison in view of the scatter and uncertainty of data at higher temperature.

Column 6 gives the ratio  $\kappa_g/\kappa_u$  calculated from Eq. (7). The measured ratios are listed in column 7, and, as

TABLE II. Lattice thermal conductivity of copper alloys.

Sample number	Composition (at.%)	Residual resist. ( $\mu\Omega\text{-cm}$ )	$T^2/\kappa_g$ ( $T < 15^\circ\text{K}$ ) ( $\text{deg}^2\text{-cm-W}^{-1}$ )	$\omega_D/\omega_0$ at $70^\circ\text{K}$	$\kappa_g/\kappa_u$ at $70^\circ\text{K}$		
					Eq. (7)	Observed	Calc with $\sigma = 2\tau_u$
2	1.84% Sn	4.86	2500	1.96	0.56	0.47	0.49
6	1.22% Sn	3.38	1820	1.63	0.625	0.52	0.55
8	0.65% Sn	1.75	1100	1.2	0.74	0.6	0.66
14	0.23% Cd+0.76% In	1.06	1000	1.37	0.69	0.63	0.62
15	0.1% Cd+0.39% In	0.55	570	0.995	0.795	0.8	0.74
102	0.5% Zn+0.77% In	1.03	1000	1.215	0.73	0.57	0.65
103	1.0% Zn+0.42% In	0.73	670	0.905	0.815	0.8	0.77
104	0.33% Zn+0.30% Ga	0.585	700	0.09	1.0	1.0	1.0

expected, are generally smaller than those calculated under the assumption that  $N$  processes may be neglected. Column 8 shows the ratios  $\kappa_g/\kappa_u$  calculated with the assumption  $\sigma = 2\tau_u$ , which leads to reasonable agreement with the data. The results on ternary alloys show that in this temperature range, mass difference and not electrical resistivity determines the lattice thermal conductivity. Thus, Sample 104, whose residual resistivity exceeds that of sample 15 has, nonetheless, a thermal conductivity equal to that of copper above  $30^\circ\text{K}$ , although this is not true at lower temperatures. Samples 103 and 15, for which  $\epsilon$  is nearly the same, have identical thermal conductivities above about  $50^\circ\text{K}$ . The relative magnitudes of  $\kappa_g$  for Samples 102 and 14 are puzzling, inasmuch as the former has a slightly lower thermal conductivity although we should have expected the converse. Sample No. 14 is the only one where the concentration of one of the solvents, cadmium, is precariously close to the solubility limit for the binary alloy systems. It is possible then that this alloy may not have been a single-phase solid solution. Precipitation of cadmium would not produce a significant change in residual resistance since the residual resistivity due to indium impurities is dominant. We may remark here that for this same alloy the discrepancy between calculated and measured thermopowers is greater than for any of the others.<sup>29</sup>

Klemens has noted that as a consequence of Eq. (7) the temperature dependence of  $\kappa_g$  in the anisobaric region should change from  $T^{-1}$  to  $T^{-1/2}$  as the concentration of scatterers is increased. This is in qualitative agreement with our observations on the Sn alloys (Fig. 3). However, the results are not accurate enough in this temperature range to permit a quantitative comparison.

We turn now to the temperature range below  $20^\circ\text{K}$ . Here, the lattice thermal conductivity of pure copper should vary as  $T^2$ . The same behavior is, however, displayed by the alloys as well, though anisobaric scattering evident at the higher temperatures cannot give rise to a contribution to the thermal resistance proportional to  $1/T^2$ . All measurements were made on well-annealed

samples; phonon-dislocation scattering is presumably quite small.

The most satisfactory explanation of our results is that based on Pippard's argument<sup>20</sup> and elaborated by Lindenfeld and Pennebaker.<sup>22</sup> Our results, when compared with this theory, lie close to the universal curve deserved for other impurities (Fig. 7 of reference 22; our values of  $T/\rho_0$  lie in the range  $10^6\text{--}10^7^\circ\text{K}\Omega\text{-cm}$ ). In Fig. 5, our results are shown in terms of the relationship

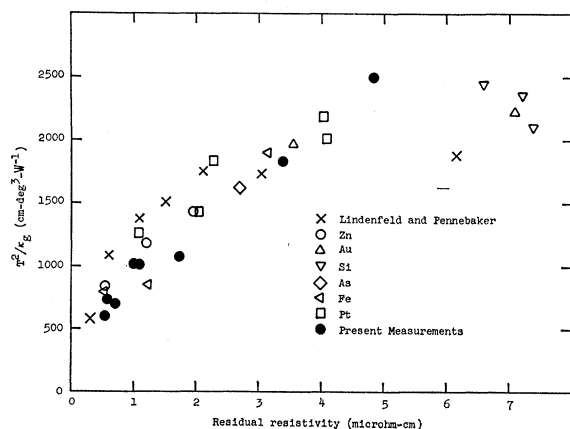


Fig. 5.  $T^2/\kappa_g$  at low temperature for various copper alloys. The sources are references 20 and 21.

between  $T^2/\kappa_g$  and the electronic residual resistivity. It may be noted that in the limit of low  $T$  and large  $\rho_0$ , Pippard's theory predicts a lattice heat conductivity proportional to  $T$  and increasing with  $\rho_0$  (see also reference 11). The transition between the two types of behavior is expected to occur, according to the calculations of Lindenfeld and Pennebaker, for values of  $T/\rho_0 < 10^5$ . This effect should, therefore, be observable at helium-3 temperatures for the more concentrated alloys.

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