

Deviations from Matthiessen's Rule in Aluminum, Tin, and Copper Alloys*†

P. ALLEY‡ AND B. SERIN

Department of Physics, Rutgers University, New Brunswick, New Jersey

(Received May 18, 1959)

The electrical resistance of aluminum, tin, and copper alloys was measured at 4.2°K, 77°K, and from 198°K to 348°K. The aluminum alloys contained zinc, magnesium, germanium, or silver in various concentrations. The alloys of tin contained indium, antimony, or bismuth; and those of copper contained zinc. At temperatures above 77°K, the impurity resistivity, $\delta\rho$, for a given solvent may be described by the equation $\delta\rho = \alpha(T)\rho_r$, where ρ_r is the residual resistivity, measured at 4.2°K, and T is the temperature. This result is independent of the nature of the solute. α is constant in the temperature region 198°K to 348°K. For aluminum and tin $\alpha(273) = 1.12$, whereas for copper $\alpha(273) = 1.05$. The value of $\alpha(77)$ is about the same as at 273°K for aluminum and copper, but for tin $\alpha(77) = 1.08$. The temperature coefficient of the impurity resistivity for 198°K $< T < 348$ °K was no larger than 1×10^{-3} (°K)⁻¹. It is pointed out that while several different theoretical models qualitatively describe these results, none can be quantitatively compared with experiment.

1. INTRODUCTION

IT is customary to consider $\rho(T)$, the electrical resistivity of a metal at temperature T , to be the sum of two parts, written as

$$\rho(T) = \rho_{id}(T) + \delta\rho(T). \quad (1)$$

The first term, $\rho_{id}(T)$, would be the resistivity in an ideally pure and perfect crystal, and arises solely from the scattering of the conducting electrons by the thermal motion of the lattice atoms. The second term, $\delta\rho(T)$, is the resistivity arising from all other causes, such as the electron scattering by impurities and by any other lattice defects, which for the sake of generality we take also to be a function of the temperature.

Numerous observations have shown that $\delta\rho(T)$ is a very slowly varying function of the temperature compared to $\rho_{id}(T)$. The approximation of assuming $\delta\rho$ constant has come to be called Matthiessen's rule, since he first observed that it provides a reasonable description of the behavior of most metals. Conversely, any dependence of $\delta\rho$ on temperature is called a deviation from the rule.

It is also generally observed that as the absolute temperature approaches zero, $\rho_{id}(T)$ approaches zero as a high power of T . As a result, $\rho(T)$ approaches $\delta\rho(T)$ at low temperatures. Moreover, $\delta\rho(T)$ at these temperatures is a constant which is called the residual resistivity ρ_r ; that is to say, $\lim_{T \rightarrow 0} \rho(T) = \delta\rho = \rho_r$. It is clear that Matthiessen's rule holds exactly only when $\delta\rho$ equals ρ_r at all temperatures.

Although deviations from the rule were qualitatively evident in many investigations of the dependence of the resistance of different metals on temperature (see Krautz and Schultz¹ for references to earlier work), the first systematic investigation of this question seems to

be the work of Krautz and Schultz¹ on tungsten. They varied the resistivity of their specimens by subjecting them to varying amounts of cold drawing, and found that in the temperature range from about 100°K to 400°K $\delta\rho$ for any given specimen was constant but appreciably larger than ρ_r . The difference varied somewhat from one specimen to another, $\delta\rho$ being between 14% and 22% larger than the residual resistivity. Between 14°K and 100°K, $\delta\rho$ increased monotonically from ρ_r to this larger value. More recently, Krautz and Schultz² have measured two alloys (Au+1% Ag, and Ag+0.6% Au), and observed somewhat similar behavior in that $\delta\rho$ was about 8% greater than ρ_r in the high-temperature region. However, it appeared that $\delta\rho$ went through a maximum of about $1.10\rho_r$ at a temperature somewhat below 100°K before decreasing to ρ_r at very low temperature. We will discuss other experimental results as well as the theory in Sec. 4.

In this investigation, we have determined the electrical resistance at 4.2°K, 77°K, and in the range 198°K $\leq T \leq 348$ °K, of a total of 31 dilute alloys having either aluminum or tin or copper as solvents. As we will show, the data for each solvent may be described by the equation

$$\delta\rho = \alpha(T)\rho_r, \quad (2)$$

where α is constant (and greater than unity) in the high-temperature range. At 77°K, α can be somewhat smaller than at the higher temperatures. At 4.2°K, α equals unity.³ Thus, our results are in qualitative agreement with the observations of Krautz and Schultz, but we find no evidence for a maximum in the extra resistivity $\delta\rho$.

2. EXPERIMENTAL PROCEDURE

The aluminum and the tin samples were prepared by methods completely described in earlier publications.^{3,4}

* This work was supported by the Office of Naval Research and the Rutgers University Research Council.

† This paper is based in part on a dissertation submitted by P. Alley to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree.

‡ Present address: Franklin and Marshall College, Lancaster, Pennsylvania.

¹ E. Krautz and H. Schultz, *Z. Naturforsch.* **9a**, 125 (1954).

² E. Krautz and H. Schultz, *Z. Naturforsch.* **12a**, 710 (1957).

³ Budnick, Lynton, and Serin, *Phys. Rev.* **103**, 286 (1956).

⁴ Chanin, Lynton, and Serin, *Phys. Rev.* **114**, 719 (1959).

The aluminum specimens were in the form of 3.2-mm diameter rods, 60 mm long. They were annealed in vacuum for seven days at 540°C. The tin specimens were about the same length but had diameters between 1 mm and 2 mm and were annealed at 185°C for at least 30 days. Ingots of the two copper alloys were kindly prepared for us by the American Smelting and Refining Company, and specimens 60 mm long of 1.6-mm square cross section were machined from them, as was a pure specimen from a rod of OFHC copper. These were also vacuum annealed at 540°C for a week. The compositions of all samples are listed in Table I.

Current leads were soldered to the ends of the specimens. The potential contacts were in the form of spring loops of piano wire attached to small bakelite blocks which could be clipped on to the samples, and the piano wire was sharpened at the contact end so that it dug into the specimen. Potential leads were soldered to the wire.

Five alloy specimens and a pure sample were mounted on a form which was placed inside a Dewar vessel containing an appropriate temperature bath. The samples were supported vertically by having the lower potential contact block rest on a horizontal support, but were not held tightly in any way, so that they were free to expand or contract without danger of straining. The form also carried a heater and a stirrer. The latter served to mix vigorously the liquid which was being used as a

temperature bath in order to insure that its temperature was uniform. For measurements between 1.9°K and 4.2°K a liquid helium bath was used; and a bath of liquid nitrogen provided the 77°K point. In the temperature region between 198°K and 348°K an ethyl alcohol bath was used. Its temperature was varied either by heating it with the heater or cooling it with various refrigerants introduced into the flask.

The temperature of the bath (with exception of the liquid helium points) was determined by measuring the emf produced by a thermopile consisting of five copper-constantan thermocouples in series. The cold junctions were placed in a bath of distilled water ice, and the hot junctions were arranged around the specimens so as to give the average temperature. This thermopile served principally to determine the ice point very accurately. The temperature does not enter critically at any other place in our treatment of the data, but we used the thermopile at all temperatures because it was convenient.

It was essential in these measurements to determine the resistance of the pure specimen at the identical temperature at which the resistance of each alloy specimen was measured. With the helium bath and the nitrogen bath this presented no problem, since the temperature did not vary appreciably during the time of measurement; but it was necessary to take account of the temperature drift of the alcohol bath. We found that this bath changed temperature uniformly and at a rate not exceeding 0.2°C/min. In order to take account of this drift we took the measurements in the following sequence: (a) thermopile emf, (b) resistance of pure specimen, (c) resistance of alloy specimen, (d) resistance of pure specimen, (e) thermopile emf. The instant that each measurement was taken, the time was recorded by making an appropriate mark on a recorder chart moving at constant speed. By plotting the thermopile emf and the resistance of the pure specimen each as a function of time, we could find the temperature at any time and the resistance of the pure specimen at the moment that each alloy specimen was measured. The time was recorded with an accuracy of about 0.05 min. The resistance of each specimen at the ice point was determined by plotting it as a function of thermopile emf and interpolating to zero emf. We took measurements at about nine different temperatures in the range between 198°K and 348°K.

The resistance of a specimen was determined in standard fashion by having a standard resistance in series with it, and comparing the potential drop across the standard with that across the specimen with current flowing. The voltages were measured with potentiometers, and the effects of thermal emf's were eliminated. In all cases the resistance was determined with an accuracy of 1 part in 10⁴.

3. TREATMENT OF DATA

The resistances of the pure specimen and of one of its alloy specimens give respectively measures of $\rho_{id}(T)$

TABLE I. The impurity resistivity ratio values, \bar{Z} , are listed at 4.2°K, 77°K, and 273°K.

Atomic percentage	$\bar{Z}(4.2)$	$\bar{Z}(77)$	$\bar{Z}(273)$
Al+ 0.50% Zn	0.051	0.058	0.058
+ 1.0 % Zn	0.079	0.095	0.094
+ 1.95% Zn	0.168	0.187	0.187
+ 3.1 % Zn	0.287	0.292	0.309
+ 4.2 % Zn	0.298	0.319	0.324
Al+ 0.25% Mg	0.016	0.021	0.022
+ 0.50% Mg	0.076	0.084	0.084
+ 1.0 % Mg	0.106	0.120	0.121
+ 1.4 % Mg	0.205	0.221	0.222
Al+ 0.11% Ge	0.037	0.045	0.043
+ 0.16% Ge	0.054	0.062	0.064
+ 0.26% Ge	0.073	0.085	0.087
Al+ 0.11% Ag	0.050	0.058	0.058
+ 0.21% Ag	0.091	0.100	0.101
Sn+ 2.5 % In	0.153	0.170	0.176
+ 3.5 % In	0.200	0.219	0.222
+ 4.5 % In	0.240	0.270	0.284
+ 5.7 % In	0.328	0.353	0.370
Sn+ 1.85% Sb	0.120	0.130	0.131
+ 3.8 % Sb	0.242	0.257	0.266
+ 6.0 % Sb	0.374	0.401	0.428
+ 8.0 % Sb	0.439	0.479	0.526
Sn+ 0.79% Bi	0.067	0.080	0.081
+ 2.3 % Bi	0.194	0.213	0.216
+ 2.75% Bi	0.212	0.236	0.242
+ 3.4 % Bi	0.333	0.355	0.366
+ 6.0 % Bi	0.474	0.507	0.527
+ 8.0 % Bi	0.382	0.413	0.449
+10.0 % Bi	0.426	0.451	0.470
Cu+ 2.0 % Zn	0.277	0.294	0.294
+ 4.0 % Zn	0.615	0.637	0.637

and $\rho(T)$, and one could, in principle, use Eq. (1) to determine $\delta\rho(T)$. For reasons which will be discussed subsequently, we were unable to use this direct procedure, but found it necessary to analyze the data in terms of appropriate resistance ratios in a manner similar to that adopted by Krautz and Schultz.¹

We call $R(T)$ and $R(273)$ the measured resistances of an alloy specimen at temperature T and 273°K, respectively, and $R_p(T)$ and $R_p(273)$ the corresponding quantities for the pure specimen. Then letting $r(T) = R(T)/R(273)$, $r_p(T) = R_p(T)/R_p(273)$, and $Z(T) = \delta\rho(T)/\rho(273)$, one can show that Eq. (1) may be written as

$$r(T) = r_p(T)[1 - Z(273)] + Z(T). \quad (3)$$

Moreover, if

$$\bar{Z}(T) = \delta\rho(T)/\rho_{id}(273), \quad (4)$$

it follows that

$$\bar{Z}(T) = Z(T)/[1 - Z(273)]. \quad (5)$$

Thus if one knew $Z(273)$, he could use Eq. (3) to calculate $Z(T)$ from the measured values of r_p and r , and find $\bar{Z}(T)$ from Eq. (5), thereby determining the ratio of $\delta\rho(T)$ to the resistivity of a pure specimen at the ice point.

The primary reason for using this ratio method is that it eliminates having to know the geometrical factor $f = (\text{area of specimen})/\text{length}$. Small errors in this factor can lead to serious errors in the determination of $\delta\rho$ from the measured resistance values. If we call the error in f for an alloy specimen Δf , and the corresponding quantities for the pure specimen f_p and Δf_p , it can readily be shown that the fractional error introduced into the calculation of $\delta\rho$ is

$$\frac{\Delta f}{f} + \frac{\rho_{id}}{\delta\rho} \left(\frac{\Delta f}{f} - \frac{\Delta f_p}{f_p} \right).$$

Since for $T > 200^\circ\text{K}$, $\rho_{id} \gg \delta\rho$, we see that the errors introduced into $\delta\rho$ can indeed be very large. Moreover, since ρ_{id} is temperature dependent, errors in geometry can give rise to a fictitious temperature dependence of the calculated values of $\delta\rho$ which may not be present in the data.

For the tin specimens the ratio method eliminated another experimental difficulty arising from the anisotropy in their electrical resistivity. In tin, the electrical conductivity⁵ perpendicular to the fourfold symmetry axis of the crystal is 1.44 times the conductivity parallel to this axis. Since our specimens were in general composed of a few large crystals, it would have been necessary to know quite accurately the crystalline orientation with respect to the specimen rod axes if we were to compare the absolute resistivities of the alloy and pure specimens. Fortunately, we found that the resistance

ratio $r_p(T)$ was the same function of T within experimental error for all of our pure tin specimens, independent of the orientation of their fourfold axes with respect to the cylinder axes. In these measurements the angle between the axes varied between 58° and 86°. Thus the ratio method also eliminates errors arising from this source.

Equation (3) does not define $Z(273)$, but for this temperature merely gives an identity, since $r(273) = r_p(273) = 1$. We, therefore, used the scheme which we now describe to calculate this quantity. If it is assumed that $Z(T)$ does not vary rapidly with temperature, it will approximately equal $Z(273)$ for temperatures near 273°K, and Eq. (3) may be written

$$Z(T) \simeq Z(273) \simeq [r(T) - r_p(T)]/[1 - r_p(T)].$$

Thus, values of r and r_p at room temperature were used to calculate an approximate value of $Z(273)$. We found that when this initial estimate was too small, the values of $Z(T)$ calculated from (3) with this value of $Z(273)$ increased with decreasing temperature down to 198°K. The value of Z at the liquid nitrogen point, however, would be smaller than the value at 198°K. That is to say, $Z(T)$ would pass through a maximum. Since this type of temperature dependence seems unreasonable, such an estimate of $Z(273)$ was taken to be incorrect. If the value of $Z(273)$ on the initial estimate was too high, then $Z(T)$ would increase uniformly with temperature. Such behavior is possible. However, a value of $Z(273)$ could always be found which led to an essentially constant value of $Z(T)$ in the temperature interval $198^\circ\text{K} \leq T \leq 348^\circ\text{K}$. If any trend in $Z(T)$ remained, it corresponded to a very small positive temperature coefficient. Under these circumstances $Z(77)$ was equal to or slightly less than $Z(198)$. Moreover, the value of $Z(77)$ is quite insensitive to the choice of $Z(273)$ over a wide range of values. Thus the criterion used in choosing $Z(273)$ was to take that value which gave an essentially constant value of $Z(T)$ in the range $198^\circ\text{K} \leq T \leq 348^\circ\text{K}$. This is in keeping with theory (see Sec. 4) which indicates that $\delta\rho$ should be constant in this temperature range. Furthermore, the experiments of Gerritsen and Van der Aa⁶ and Linde⁷ on other metals have shown that the temperature coefficient of $\delta\rho$ is quite small, usually an order of magnitude less than the temperature coefficient of resistivity of the pure metal.

As a check on this criterion, we performed a model calculation in which we assumed an exact expression for $\rho(T)$ with parameters comparable in magnitude to the measured values, and treated these model data as outlined in the previous paragraph. For constant $\delta\rho$, incorrect choices of $Z(273)$ led to behaviors of $Z(T)$ identical to those described. When $\delta\rho$ was assumed to depend on temperature, we found that unless $(1/Z)dZ/$

⁵ See, e.g., A. N. Gerritsen, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 158.

⁶ A. N. Gerritsen and J. M. L. C. Van der Aa, *Appl. Sci. Research* **A6**, 191 (1956).

⁷ J. O. Linde, *Ann. Phys.* **15**, 219 (1932).

$dT < 10^{-3}$ ($^{\circ}\text{K}$) $^{-1}$, it was not possible to find a $Z(273)$ giving a constant $Z(T)$ in the high-temperature region. For temperature coefficients of about 10^{-3} , the value $Z(273)$ resulting in an apparently constant $Z(T)$ was somewhat smaller than the true value, although the difference was comparable to our experimental error in the actual determination of $Z(273)$. From this analysis we conclude that the values of $Z(273)$ we obtain using our criterion are at worst slightly too small and any temperature coefficient of $Z(T)$ is no larger than 10^{-3} ($^{\circ}\text{K}$) $^{-1}$.

4. RESULTS AND DISCUSSION

The values of $\bar{Z}(T)$ [see Eq. (4)] at 4.2°K , 77°K , and 273°K as calculated from our resistance measurements of all the specimens are shown in Table I. As has already been stated, \bar{Z} is constant within experimental error between 198°K and 378°K . Resistance measurements were also made on several of the dilute alloy specimens in the temperature range between 1.9°K and 4.2°K . In all cases the resistance was independent of temperature, indicating that $\bar{Z}(4.2)$ is the true residual resistance ratio of the specimens. The accuracy of the determination of \bar{Z} varied somewhat among the specimens. We estimate the uncertainty of its value to be between ± 0.002 and ± 0.003 for the aluminum specimens, ± 0.005 and ± 0.010 for the tin alloy and ± 0.002 for copper.

It is to be noted in Table I that for each specimen the values of \bar{Z} at the higher temperatures are greater than $\bar{Z}(4.2)$. Furthermore, for any given alloy series \bar{Z} is proportional to $\bar{Z}(4.2)$. This is illustrated in Fig. 1, where the data for tin are plotted. It is to be further noted that this behavior is independent of the solute.

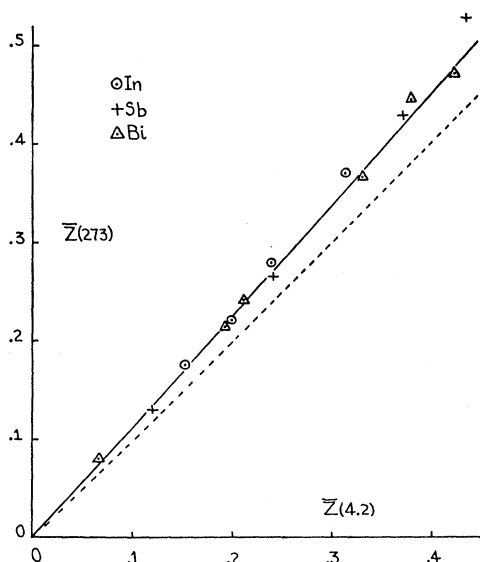


FIG. 1. The impurity resistance ratios at 273°K of the tin specimens are shown as a function of their residual resistance ratios. The specimens had the concentrations of indium, antimony, or bismuth listed in Table I. The dashed line has slope unity.

TABLE II. The values of α in Eq. (2) are given at 77°K and 273°K for the three solvents.

Solvent	$\alpha(77)$	$\alpha(273)$
Al	1.11	1.12
Sn	1.08	1.12
Cu	1.05	1.05

The same characteristics are evident in the aluminum alloys. The data for copper, although meager, are consistent with those for aluminum and tin.

It can be seen from Fig. 1 and Table I that the data are described by Eq. 2 with the values of α listed in Table II. The α values for aluminum and tin were obtained by fitting the data by the method of least squares.

We believe that this is the first detailed comparison between the high-temperature impurity resistivity and the residual resistivity of alloys. Gerritsen and Linde⁸ observed qualitatively similar effects in some copper and gold alloys, but it is not clear from their work if $\delta\rho$ depends on the nature of the solute. Pippard⁹ observed a value of $\alpha(273) = 1.12$ for tin alloys containing only indium, in agreement with the value given in Table II. In view of the fact that our model calculation showed that an incorrect choice of $Z(273)$ could give rise to an apparent maximum in $Z(T)$, we are somewhat dubious about the reality of the maxima reported by Krautz and Schultz² for a gold and a silver alloy. Since they do not discuss in detail how they treated their data, we cannot comment further. However, we do not believe there is any evidence for maxima in our data.¹⁰ The observations in alloys of a temperature coefficient of $\delta\rho$ about 0.1 of that of the pure metal have previously been mentioned. As we said, we are not sure if such a temperature coefficient is present in our data, but its presence would not affect our conclusions in any essential way.

The other investigations of which we are aware dealt with cold-worked metals, the work of Krautz and Schultz¹ on tungsten having been described in Sec. 1. Rutter and Reekie¹¹ made similar measurements on cold-worked copper and aluminum. Their absolute resistivity measurements on aluminum seemed to show a very large temperature dependence of $\delta\rho$. Berghout,¹² however, found no appreciable deviations from Matthiessen's rule in cold-worked copper and aluminum, but he did seem to observe them in silver and gold. If the changes in resistivity produced by cold work can

⁸ A. N. Gerritsen and J. O. Linde, *Physica* **18**, 877 (1952).

⁹ A. B. Pippard, *Phil. Trans. Roy. Soc. London* **A248**, 97 (1955).

¹⁰ If all the maxima occurred between 77°K and 198°K we might have missed them. However, Krautz and Schultz state that the maximum occurs at the temperature for which $\rho_{\text{id}} \approx \delta\rho$. In our more impure specimens this criterion is satisfied at temperatures appreciably greater than 198°K , and we find no more evidence of a maximum in $Z(T)$ for these specimens than in the others.

¹¹ J. W. Rutter and J. Reekie, *Phys. Rev.* **78**, 70 (1950).

¹² C. W. Berghout, *Physica* **18**, 978 (1952).

be compared with those produced by impurities, our measurements on aluminum support those of Berghout.

As a last experimental fact, we mention that the values we obtain for the rate of increase of $\delta\rho(273)$ with impurity concentration in the aluminum alloys are in reasonable agreement with those reported by Robinson and Dorn¹³ from determinations of absolute resistivities at 293°K.

It would seem that the temperature dependence of $\delta\rho$ observed in this investigation is the rule for most metals. If particular metals or alloys exhibit quite different properties, these most probably arise from special characteristics of the atoms, as occur, for example, in magnetic materials. That is to say, when deviations from Matthiessen's rule occur, we should expect the primary change in impurity resistivity with temperature to be an increase of several percent independently of the solute.

Several theoretical investigations have predicted the qualitative features of $\delta\rho$ that are observed. Kohler¹⁴ has proved that, in general, one expects deviations from Matthiessen's rule to be positive. Moreover, by assuming a particular form for the electronic distribution function for free electrons in the presence of lattice and impurity scattering, he showed that $\delta\rho$ would be expected to change with temperature according to the equation

$$\delta\rho = \rho_r \{ 1 + [\beta\gamma\rho_{id}/(\beta\rho_r + \gamma\rho_{id})] \}. \quad (6)$$

At high temperatures, $\rho_{id} \gg \rho_r$, so that $\delta\rho = (1 + \beta)\rho_r = \alpha\rho_r$, in agreement with the results collected in Table II. At low temperatures, $\rho_{id} \ll \rho_r$, so that $\delta\rho = \rho_r + \gamma\rho_{id}$, and the data of Krautz and Schultz¹ on tungsten are in reasonable agreement with this expression. However, Sondheimer and Wilson,¹⁵ using a different model, in

which there is two-band conduction in the metal, obtain an expression quite similar to Eq. (6). In particular, the low- and high-temperature limits of their expression are identical with those of (6). Furthermore, MacDonald¹⁶ has shown formally that if the relaxation time for lattice scattering is dependent on electronic wave number, whereas the impurity scattering is independent of this number, one derives deviations from Matthiessen's rule which again have the same limits. The case considered by Bross and Seeger¹⁷ in which part of the electronic scattering is anisotropic seems to be a special form of MacDonald's treatment. Finally, we mention that Sondheimer¹⁸ has shown that for a free electron gas one can get deviations from Matthiessen's rule because it is not possible to define relaxation times for scattering in the intermediate temperature range. These deviations are zero at low and high temperatures and do rise to a maximum in between; but the assumptions made in this calculation are so idealized as probably to make it inapplicable to actual metals.

There appears to be a surfeit of models which seem qualitatively to explain the experimental data. Unfortunately, none of these have been put into quantitative form, so that it is not possible to say which of the models most appropriately describes the data.

5. ACKNOWLEDGMENTS

We are indebted to the Aluminum Corporation of America for the pure aluminum we used in making the alloys and to Mr. G. Chanin for help in their preparation. C. Potter and A. R. Riccardo of the American Smelting and Refining Company kindly furnished us with the copper alloys. It is also a pleasure to acknowledge numerous conversations with Dr. E. A. Lynton.

¹³ A. T. Robinson and J. E. Dorn, *J. Metals* **3**, 457 (1951).

¹⁴ M. Kohler, *Z. Physik* **126**, 495 (1949).

¹⁵ E. H. Sondheimer and A. H. Wilson, *Proc. Roy. Soc. (London)* **A190**, 435 (1947).

¹⁶ D. K. C. MacDonald, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, pp. 146-7.

¹⁷ H. Bross and A. Seeger, *J. Phys. Chem. Solids* **4**, 161 (1958).

¹⁸ E. H. Sondheimer, *Proc. Roy. Soc. (London)* **A203**, 75 (1950).