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Hall Coefficients of Cu, Ag, and Au in the Range 4.2–300°K

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The Hall coefficient R of high-purity polycrystalline group-IB metals and some single-crystal Cu samples has been determined with high precision in the approximate temperature range 4.2–300°K and in a magnetic field of 15 kG. The general temperature dependence of R for each IB metal can be explained for temperatures down to about 50°K in terms of what is known about the electronic relaxation times associated with different electron scattering processes. But at lower temperatures these data show a new behavior: The $|R|$-versus-temperature curve for each metal shows an apparent maximum centered at about 40°K. Experiments are described which show this is not a sample-size effect, not an effect of trace impurities, but probably a result of a phonon-drag contribution to R. The work has involved similar measurements of some very dilute *Ag*Au, *Ag*Zn, and *Ag*Cd alloys.

I. INTRODUCTION

THERE has been considerable recent interest in the interpretation of the Hall coefficient R of α-phase alloys of group-IB metals with nontransitional solutes. Although there is not yet a quantitatively successful theory of R, there has been some progress in the interpretation of the variation of R with either solute concentration or with temperature[1] for these alloy systems. This progress has been from the viewpoint, suggested some time ago,[2] that R is probably determined by two principal influences: that arising from the electronic structure of the alloy, and that arising from the anisotropic electron relaxation time over the Fermi surface. From this progress one would therefore expect that the interpretation of the temperature dependence of R for the pure solvent metals will be a simpler problem and will probably only involve electronic scattering processes.

In fact, there appears to have been relatively little interest in the temperature dependence of R for the group-IB metals. From the existing data (which will be reviewed in Sec. II) it is found that those available for temperatures below about 77°K are from the earliest work and often have a precision which is well below that possible with current instrumentation. For temperatures above 77°K, however, there exist data from recent, relatively high-precision measurements which extend to approximately 800°K. These data show a minimum in the $|R|$-versus-temperature T curve at about 200°K for both polycrystalline and single-crystal samples, and that R is very strongly temperature-dependent for temperatures below the minimum. It would clearly be desirable both to extend the range of high-precision data to lower temperatures and to offer some interpretation of the observed temperature dependence of R. These are the purposes of this paper.

In Sec. IV we give results of measurements of R for pure group-IB metals in the approximate temperature range 4.2–300°K and at a fixed field of approximately 15 kG. These data are in good agreement with the previous high-precision work which exists for temperatures above 77°K, and for lower temperatures they show that $|R|$ does not continue to monotonically increase with decreasing temperature, but shows an apparent maximum in the $|R|$-versus-T curve which is centered at about 40°K. We find that there is possibly corroborating evidence for this behaviour from early work, although this has not always been referred to by the authors.

In Sec. V we have proposed several plausible explanations for the observed apparent maximum in the temperature dependence of $|R|$ for these metals and, through a choice of suitable experiments referred to in Sec. IV, we have provided strong evidence to eliminate many of the proposed explanations. We are left with at least one possible explanation which we favor, which is that the temperature gradient set up in the sample by the phonon-drag heat flow may make a contribution to R through the Ettingshausen-Nernst effect. We have not been able to devise an experiment to conclusively prove or disprove this suggestion, although the results of measurements upon certain very dilute alloys which we have made do support this suggested explanation. We wish to emphasize, however, that it is by no means firmly established that our favored interpretation of the low-temperature behavior of R is correct.

II. SUMMARY OF PREVIOUS SIMILAR MEASUREMENTS

Advances in the purity of available materials and in instrumentation have led to steady improvements in the precision and reliability of available values of R for the solid group IB metals and their related alloys. In view of this, and since a comprehensive review of work prior to about 1955 exists,[3] it is convenient here to consider only measurements made after 1955, and to divide the published data into the following categories: (1) Measurements made upon single crystals at fixed, low temperatures with a view to their interpretation in terms of the Fermi surface. Such measurements have

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* National Research Council of Canada Postdoctoral Fellow.

[1] V. Heine, Phil. Mag. 12, 53 (1965); C. M. Hurd, *ibid.* 14, 647 (1966); R. D. Barnard, *ibid.* 14, 1097 (1966).

[2] B. R. Coles, Phys. Rev. 101, 1254 (1956); J. R. Cooper and S. Raines, Phil. Mag. 4, 145 (1959).

[3] J.-P. Jan, Solid State Phys. 5, 1 (1957).

been made upon Cu,[4–6] Ag,[6] and Au.[6] (2) Measurements upon very thin films. These have been reported for various group I*B* metals.[7] (3) Measurements of the temperature dependence of *R* for polycrystalline samples. Data available in this category are presented in the order: author(s), approximate temperature range of measurement, material(s) studied. Fukuroi and Ikeda,[8] 1–20°K, Cu, Ag, Au; Frank,[9] 80–800°K, Cu, Ag, Au; Gaidukov,[10] 0.75–295°K, Au; Berlincourt,[11] 4–300°K, Cu; Blue,[12] 77 and 300°K, Cu; Blue,[12] 4–300°K, Au; Köster *et al.*,[13] 90–800°K, Cu, Ag, Au; Hurd,[14] 77–300°K, Cu; Plate,[15] 50–300°K, Ag. (4) Measurements of the temperature dependence of *R* in single-crystal samples [order as in (3)]. Love,[16] 4–300°K, Cu; Köster *et al.*,[13] 90–400°K, Cu, Ag.

The conclusions from the above are that *R* is known for the polycrystalline, solid group I*B* with relatively high precision in the range 77–800°K from several recent measurements.[13–15] In this temperature range the temperature dependence of *R* is qualitatively the same for each metal and qualitatively independent of whether the sample is polycrystalline or single crystal.[13] Starting from the highest temperature for which data exist, it is found that $|R|$ for each group-I*B* metal decreases with decreasing temperature until at approximately 200°K the $|R|$-versus-T curve passes through a minimum and thereafter $|R|$ increases rapidly with reducing temperature. In the temperature region below 77°K, the available data are less precise than for the higher temperatures, but there is evidence of an apparent maximum in the $|R|$ versus T curve centered at about 40°K in polycrystalline Cu[11] and Au.[12] There is also evidence of a magnetic field dependence of *R* at low temperatures which has been attributed to sample size effects.[11]

III. EXPERIMENTAL METHOD

The sample holder, of which an exploded view is shown in Fig. 1, is a development of a design described in an earlier paper[14] where the effects of various possible sources of error in such measurements were considered. Referring to Fig. 1, the sample *A* is sandwiched between mica insulators *C* and held in position on the brass body of the apparatus by the brass plate *G*. The current through the sample is supplied via the terminal clamps *B*. The sample's temperature is measured with a Chromel-AuCo (Au+2.1 at. % Co) thermocouple in thermal contact with the sample at *F*. The Hall potential leads *D*, which are of the same material as the sample as far as the binding post *E*,[14] are soldered with a low-thermal solder to the extremities of the sample's electrodes. The whole apparatus is enclosed in a stainless steel can (not shown in Fig. 1) which can be evacuated and which contains helium thermal exchange gas during measurement. Measurements of the Hall voltage were accomplished at different temperatures during the slow warming of the apparatus and in a fixed magnetic field of 15.155 kG (as determined by a proton resonance unit) provided by an electromagnet with 12-in.-diam pole faces. The field variation over the sample was less than about 1 part in 10^5.

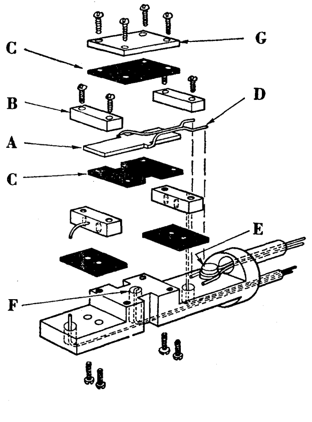

FIG. 1. Exploded view of sample holder. See text for details.

The samples, both polycrystalline and single crystal, were cut from prepared sheet by means of a Servomet spark cutter and a fixed template. This procedure ensures identical sample shapes and accurate opposition of the Hall electrodes for each sample. The sample is basically a rectangle (see Fig. 1) with dimensions 1×5.7 cm and cut with two protruding, rectangular Hall electrodes of dimensions 0.5×0.2 cm. These dimensions are chosen to avoid significant disturbance of the current flow through the sample[14] by the soldered connections at their extremities (such can arise from the presence of excessive amounts of solder[14] or from the superconducting transition of the low-thermal solder[6]). The thickness of the sample in the region of the Hall electrodes was determined by a Van Leuven light-wave micrometer with a resolution of 2.5×10^{-5} cm and a suitable anvil diameter[14] and operated at an anvil pressure of about 1 oz cm^{-2}. The thickness was determined after the Hall measurements were completed to avoid errors from possible work hardening of the samples by the micrometer.

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[4] J. E. Kunzler and J. R. Klauder, Phil. Mag. **6**, 1045 (1961).

[5] S. G. Lipson, Proc. Roy. Soc. (London) **A293**, 275 (1966).

[6] R. G. Chambers, Proc. Roy. Soc. (London) **A238**, 344 (1956); N. E. Alekseevskii and Yu. P. Gaidukov, Zh. Eksperim. i Teor. Fiz **42**, 69 (1962) [English transl.: Soviet Phys.—JETP **15**, 49 (1962)].

[7] K. L. Chopra and S. K. Bahl, J. Appl. Phys. **38**, 3607 (1967); M. A. Jeppesen, *ibid.* **37**, 1940 (1966).

[8] T. Fukuroi and T. Ikeda, Sci. Rept. Tohoku Univ. **8**, 205 (1956).

[9] V. Frank, Appl. Sci. Res. **B6**, 379 (1957).

[10] I. P. Gaidukov, Zh. Eksperim. i Teor. Fiz. **34**, 836 (1958) [English transl.: Soviet Phys.—JETP **34**, 577 (1958)].

[11] T. G. Berlincourt, Phys. Rev. **112**, 381 (1958).

[12] M. D. Blue, J. Phys. Chem. Solids **11**, 31 (1959); J. Appl. Phys. **33**, 3060 (1962).

[13] W. Köster, D. Hagmann, and K. E. Saeger, Z. Metallk. **54**, 619 (1963).

[14] C. M. Hurd, J. Sci. Instr. **42**, 465 (1965).

[15] H. Plate, Physik Kondensierten Materie **4**, 355 (1966).

[16] W. F. Love, J. Phys. Chem. Solids **9**, 281 (1959).

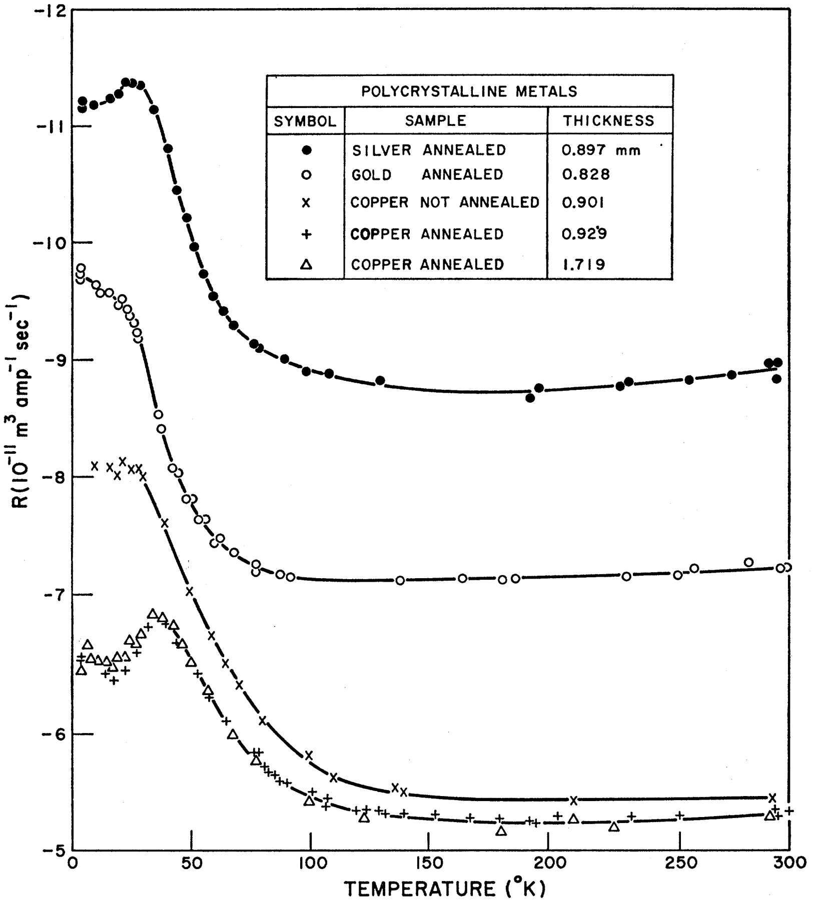

FIG. 2. Temperature dependence of the Hall coefficient for polycrystalline group-I*B* metals.

Sample thicknesses were of the order 0.9 mm (see Sec. IV).

The samples were prepared from 99.9999% (6*N*) pure starting material[17] of which some trace analyses have been carried out and published elsewhere.[18] The polycrystalline samples were cut from rolled sheet and, after heavy chemical cleaning to remove possible surface contamination, were either measured directly (unannealed state) or after annealing in vacuum for 24 h at 550°C (annealed state). Since the grain size may have an effect upon the low-temperature values of R,[11] it is worth recording that the annealed samples generally showed rolling texture with elongated grains of approximate average dimensions of 1.5×0.2 cm. The single-crystal sheets were grown by the Bridgman method in high-purity graphite molds from specially prepared seed crystals. The alloy casting techniques have previously been described.[18]

A dc measurement technique was employed. A stabilized, primary current density in the sample of about 100 A cm^{-2} was maintained and the corresponding Hall voltage (typically approximately 1×10^{-6}V) was measured with a Guildline Instruments[19] type 9176G potentiometer, which has a resolution of 1×10^{-9}V, together with a type-9460 photocell galvanometer amplifier and indicating galvanometer. This combination has an over-all sensitivity of 1×10^{-9}V/mm and a range of 1×10^{-3}V. The Hall voltage was determined from the difference between the measured voltage with and without the applied magnetic field (in this way the inevitable, spurious thermal voltages in the measuring circuit were eliminated; some other necessary experimental precautions have been described previously[14]), and R was calculated from the mean Hall voltage obtained for all four permutations of the applied magnetic and electric field directions. We estimate the accuracy of R at any temperature to be approximately $\pm0.04\times10^{-11}$ m^3 A^{-1} sec^{-1}.

IV. EXPERIMENTAL RESULTS

In this section we amplify the information presented in Figs. 2–4, and in Sec. V we shall consider some of the implications of the results. Values of R versus T for polycrystalline, annealed samples of the group-I*B* met-

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[17] Cu supplied by Gallard-Schlessinger Chemical Corporation; Ag and Au supplied by Consolidated Mining and Smelting Co.

[18] C. M. Hurd, Cryogenics **6**, 264 (1966); J. Phys. Chem. Solids **27**, 1371 (1966); **28**, 1345 (1967).

[19] Smiths Falls, Ontario, Canada.

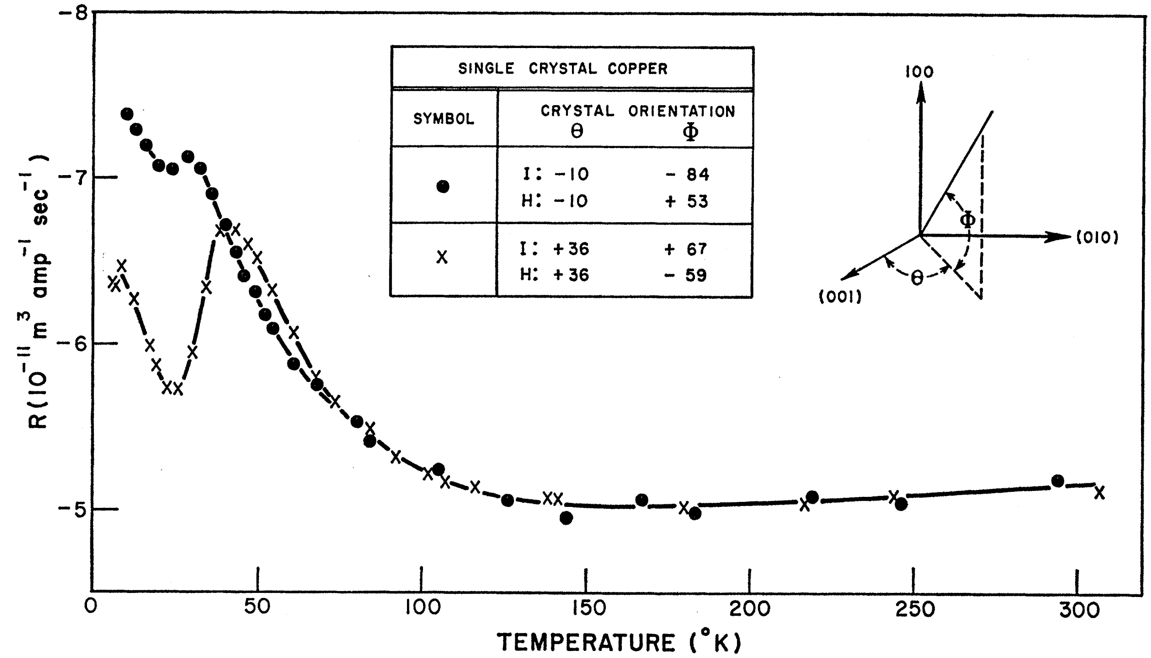

FIG. 3. Temperature dependence of the Hall coefficient for two single-crystal Cu samples. *H* represents the direction of the applied magnetic field, and *I* that of the primary electric current.

als are shown in Fig. 2. (We choose to present our data graphically. The tabulated results are available upon request.) They are in good agreement with the earlier results which exist in the approximate range 77–800°K,[13–15] while in the temperature region below 77°K (for which there are no previous, relatively high-precision data) the results show an apparent maximum in the $|R|$-versus-T curve which is roughly centered at 40°K. This effect appears to be least pronounced in Au.

The effect of work hardening of the sample upon R is known from previous work in the range 77–800°K[13,14] to lead to a general increase in $|R|$ which is most pronounced at low temperatures. Measurements made on an unannealed Cu sample (Fig. 2) confirm this, and also show that the low-temperature behavior of R is markedly affected. This is possibly in conflict with some earlier results[11] where an unannealed sample showed some evidence of the apparent maximum in $|R|$ versus T at about 40°K to which we referred above. There is also previous evidence[11] that R in pure Cu is influenced by sample size effects at low temperatures. To test this for our sample thickness range we have made measurements upon two Cu samples with differing thicknesses (Fig. 2) and we find no apparent size effects.

A systematic study of the Hall effect in Cu single crystals is presently under way, but to illustrate a point made in Sec. V we show in Fig. 3 some preliminary results for two such samples. The direction of the measuring current (I) and the magnetic field (H) with respect to the crystalline axes are shown in the insert to Fig. 3. To within experimental error these samples give the same results in the approximate temperature range 70–300°K, but below 70°K the temperature dependence of R differs considerably between the two and it appears that the apparent maximum in the $|R|$-versus-T curve is dependent upon the crystallographic directions of the externally applied fields.

It will be seen from arguments presented in Sec. V that a study of the effect upon the low-temperature behavior of R of certain types of substitutional impurities could be informative—particularly for a homovalent impurity, where the scattering potential will be relatively short-range, and for different alloys of equal concentrations of charged impurities which have similar electronic structures in the solvent metal but differing atomic masses. Accordingly, we show in Fig. 4 the results for annealed, polycrystalline, α-phase alloys of *Ag*Au, *Ag*Zn and *Ag*Cd, where the solute concentration is nominally 500 ppm, and one *Ag*Au alloy of nomial concentration 5000 ppm. Values of the solute concentration determined by chemical methods[20] are given in Fig. 4.

V. DISCUSSION OF THE RESULTS AND CONCLUSIONS

We show in Fig. 5 (curve A) a schematic diagram of the qualitative temperature dependence of $|R|$ versus T for a polycrystalline sample of a pure group IB metal. Curve B represents the behavior for a substitutional alloy containing about 500-ppm monovalent or polyvalent solute (e.g., *Ag*Au or *Ag*Cd), and curve C the behavior of a similar alloy of higher concentration

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[20] Carried out by the Analysis Section of this Division.

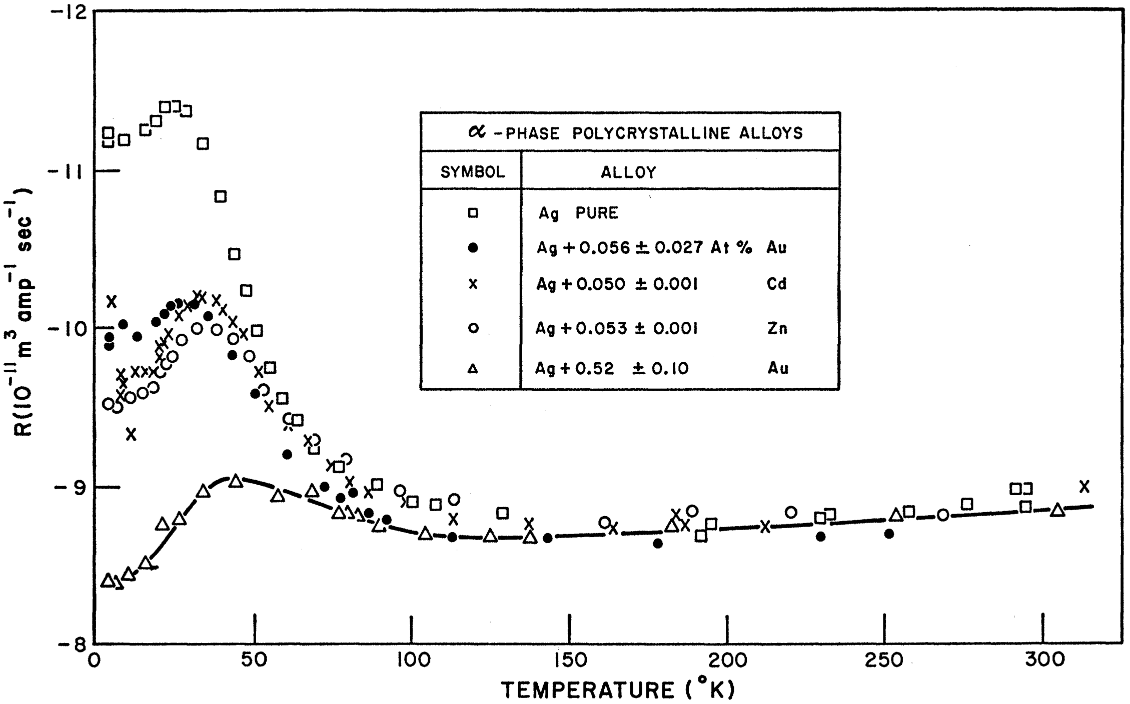

FIG. 4. Temperature dependence of the Hall coefficient of Ag showing the effect of small additions of Au, Cd, and Zn, in α-phase.

(e.g., Ag+$\frac{1}{2}$ at.% Au). Figure 5 is based upon our own results together with those published for the higher temperature range.[13] It is seen that for solute concentrations up to at least 5000 ppm there is a temperature above which R is unaffected by the addition of solute. In the discussion of these alloys we shall refer to the regions on either side of this temperature as the phonon-dominated and impurity-dominated regions.

Our qualitative interpretation of the behavior shown in Fig. 5 is based upon the following two considerations. Firstly, it is known[21] that for the group-IB metals the conduction electrons with p-like symmetry occupy momentum states on the neck of the Fermi surface, have therefore some negative component in their effective-mass tensor and physically tend to move along the channels between the ions in the solid, while electrons with s-type symmetry occupy states on the belly of the Fermi surface, have essentially the character of free electrons and their wave functions have their greatest amplitude at the ion sites. Secondly, we expect the Hall coefficient to be determined by the balance between the s- and p-type electrons free to contribute to the conduction process; i.e., we expect R to be a function of the densities, relaxation times, and velocities of the s- and p-type conduction electrons.

There is now much detailed information about the electronic structure of the noble metals, including information about their electronic velocities at various parts of the Fermi surface.[22] Much less is known, however, about the variation of the electronic relaxation $\tau(\mathbf{k})$ over the Fermi surface. Ziman[21] has given a theoretical treatment which leads to some estimates of the anisotropy of τ for both phonon and impurity scattering in a noble metal, and he showed how some features of the temperature dependence of R in Cu support his conclusions. Recently this work received further indirect support from its application to a qualitative interpretation of the electrical resistivity of certain noble metal alloys.[23] We shall show that our Hall data are also consistent with Ziman's results, which will form the basis of our interpretation.

In the pure metals the electron scattering is by phonons. The behavior of $|R|$ versus T (Fig. 5, curve A; or see Fig. 2) shows, for increasing temperature from 4.2°K, initially an apparent maximum. We shall discuss this in later paragraphs. For increasing temperatures above this maximum R becomes increasingly positive up to a temperature where $dR/dT=0$. We believe (following Ziman[21]) that R becomes increasingly positive because of the relatively rapid increase with temperature in the number of umklapp processes for electron states on the belly. This will result directly in a decrease with increasing temperature in the relaxation time for belly electrons, τ_B. For neck electrons, however, since there is no cutoff frequency for umklapp processes,[21,23] such are probably effective down to the lowest temperatures and we do not expect the relaxation time on the neck, τ_N, to decrease as rapidly with increasing temperature as that on the belly. The net re-

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[21] J. M. Ziman, Phys. Rev. **121**, 1320 (1961).

[22] D. Schoenberg, Phil. Trans. Roy. Soc. London **255**, 85 (1962).

[23] J. S. Dugdale and Z. S. Basinski, Phys. Rev. **157**, 552 (1967).

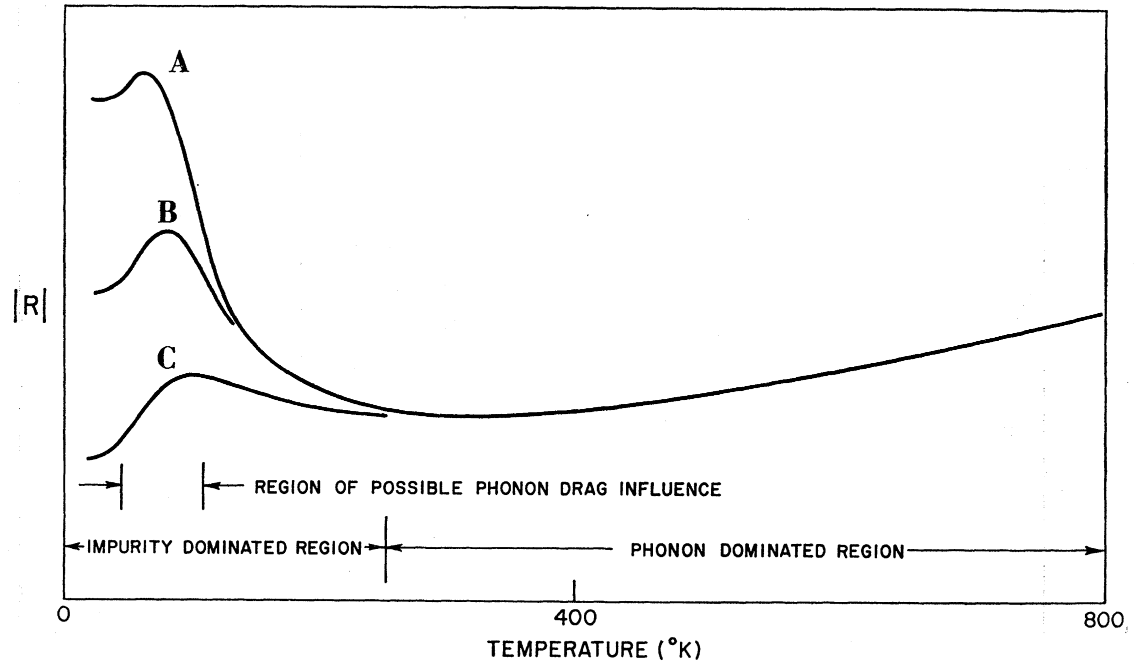

FIG. 5. Schematic representation of the temperature dependence of the Hall coefficient of a group-I*B* metal. The sketch is based upon our own results together with those available[13] for the higher temperature region. Curve *A* is for the pure metal. Curves *B* and *C* represent the effect of increasing additions of either a homovalent or polyvalent solute in the α-phase and with a concentration of up to $\sim$0.5 at. %. It is proposed in the text that in the interpretation of the temperature dependence of *R* the temperature range can be divided into the indicated regions.

sult is that for increasing temperature there is a relative decrease in the contribution of *s*-type electrons to the conduction process, at least up to the temperature where $dR/dT=0$. At a sufficiently high temperature, however, there will be sufficient phonons with large wave number to saturate the possible umklapp processes of belly states, and then it is expected[21,23] that $\tau_N \approx \tau_B$. We believe that in the I*B* metals this situation is reached where $dR/dT=0$, i.e., at about 150°K. Above this temperature our results show that *R* is practically independent of *T*, although the data at higher temperatures[13] suggest that *R* becomes roughly linearly dependent[24] upon *T* (as indicated in Fig. 5). In the region where $\tau_N \approx \tau_B$, a temperature independent *R* is to be expected[25] since it is known[26] that it is only the anisotropy of τ which appears in the general expression for *R* and not the absolute value. In the temperature region where the electrical resistance increases linearly with *T*, we expect no change in the anisotropy of the phonon scattering, only in its amplitude. Thus experiment is in agreement with this qualitative theory, except at the higher temperatures where *R* shows a slight temperature dependence. It has been suggested[25] that strong anharmonic effects in the phonon scattering at high temperatures could change the anisotropy of τ and produce this temperature dependence of *R*.

We now turn to the apparent maximum in $|R|$ versus *T* for the pure group-I*B* metals which occurs at approximately 40°K (Figs. 5 and 2). We know of no previous reference to this behavior although there is possible evidence of it in earlier work for Cu [11] and Au.[12] We have proposed three possible explanations, which we shall enumerate and discuss separately.

(1) The behavior arises from sample size effects. There is some support for this proposal from previous work by Berlincourt[11] which showed a size effect for *R* at 4.2°K in Cu strips of thickness up to about 0.79 mm. This is orders of magnitude greater than that expected from free electron theory which gave an electronic mean free path at 4.2°K ($l_{4.2}$) in Berlincourt's samples of 0.019 mm. The conclusion from that work was that for Cu, and presumably for the other I*B* metals, *R* at low temperatures is far more susceptible to sample size effects than free-electron theory would suggest. Our measurements of an unannealed Cu sample (Fig. 2), in which l_T will be much reduced by dislocation scattering, could be taken as supporting evidence for the present proposal since the apparent maximum in $|R|$ does not exist for this sample. However, Berlincourt's work gave evidence that samples of thickness greater than about 0.79 mm showed no size effects and probably had characteristics of the bulk material. Since our pure metal samples were thicker than this, we would not expect size effects to be

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[24] The data of Köster *et al.* have not been corrected for changes in the thickness of the sample with temperature. This correction amounts to approximately a 1% reduction in $|R|$ at 800°K and hence reduces the apparent temperature dependence of *R*.

[25] V. Heine, cited in Ref. 1.

[26] J. M. Ziman, Advan. Phys. 10, 1 (1961).

evident. To check this we have determined R for two annealed Cu samples, which were identical except for thicknesses of 0.929 and 1.719 mm, and we find (Fig. 2) no size effect (as expected from the above work) and yet both show the low-temperature behavior of R which is under discussion. We feel that this convincingly demonstrates that this behavior does not arise from a sample size effect. (We have not investigated any possible field dependence of R at low temperatures, but neither would we expect any since Berlincourt[11] showed that for an applied field of 15 kG there is no field dependence of R at 4.2°K for Cu samples thicker than 0.79 mm.) There is also other evidence which contradicts the present proposal, and this is shown in Fig. 4. Substitutional alloys based on Ag with solute concentrations up to 0.5 at. % also show the apparent maximum in $|R|$ versus T.

(2) The behavior arises from the effect of electron scattering by trace impurities, which become the most significant scattering source at low temperatures. (In other words, the apparent maximum in $|R|$ versus T is really the effect of a reduction in $|R|$ as T is reduced from about 30°K.) At a sufficiently low temperature in an annealed, pure metal sample it is expected that the trace impurities will become the predominant scattering source and their influence will therefore be evident in the observed value of R. The observed behavior of R with reducing temperature (Fig. 2) requires this influence to first become evident at about 30°K in group-IB metals having a starting purity of 6N. This is entirely reasonable, since it is known from the electrical resistivity that the residual resistance region extends to about 25°K,[27] and furthermore our results for the very dilute polycrystalline alloys do confirm that either a homovalent or polyvalent impurity does reduce $|R|$ at the lowest temperatures (Fig. 4). This proposal could also explain, in terms of slight differences of purity, the observation that the apparent maximum in $|R|$ versus T is least pronounced in Au (Fig. 2).

We have, however, one result which we feel is inconsistent with the validity of proposal (2), and this is illustrated in Fig. 3. From a study of two single-crystal Cu samples, we find that the low-temperature behavior of R under discussion is dependent upon the crystallographic directions of the applied external fields. For one sample the $|R|$-versus-T curve shows a maximum *and* a minimum at low temperatures. We would not expect impurity scattering to exhibit such effects and we feel that Fig. 3 presents conclusive evidence that proposal (2) is incorrect, although it seems sure that at sufficiently low temperatures the impurity scattering will become an important contributor to R.

(3) The behavior arises from the influence of the phonon-drag effect. The occurrence of a phonon-drag component in the thermoelectric power (S_g) of a noble metal is a well-known[28] effect arising from the interaction between the phonon current present with a temperature gradient and the electronic system. The phonon drag can also influence the electrical resistivity[29,30] and (we believe) the Hall coefficient. In the appropriate temperature range there will be associated with the primary electronic current a phonon-drag heat current which will cause a thermoelectric voltage to be set up between the ends of the sample. The direction of this voltage is independent of the sign of S_g,[30] and is always such as to give an apparent reduction in the electrical resistance of the sample. Thus in effect the phonon drag introduces a secondary electric current which is in the same direction as the primary current. This secondary current will be subjected to the same interactions as the primary current and will contribute to the Hall field in the same manner. From our previous arguments, and knowing the approximate temperature region in which the phonon drag exists,[28] it follows that the secondary current flows in a temperature region where τ_B is several times larger than τ_N and therefore the effect of phonon drag will be to make R more negative (whatever the sign of S_g).

The pure metals in fact show such a behavior and therefore the above prediction, together with the experimental results (Fig. 2), stands as support for the present proposal. Furthermore, a qualitative comparison between the phonon-drag contribution to the thermoelectric power and the presumed contribution to R (obtained by assuming that the R values unaffected by phonon drag lie on a linear interpolation between R at 4.2°K and that at about 75°K) shows that they have very similar temperature distributions.

There is also support for proposal (3) from our measurements of unannealed samples and of single crystal Cu samples. Consider firstly the effect upon R expected from a high dislocation density in the sample. The phonon-drag heat flow (and hence the presumed phonon-drag contribution to R) will be quenched. Furthermore, it is expected from the results of Dugdale and Basinski[23] that in the temperature region where the dislocation scattering is the dominant mechanism the ratio τ_N/τ_B is smaller, by an order of magnitude, than for scattering by either a charged or an uncharged impurity. Therefore, in addition to the quenching of the presumed phonon-drag peak referred to above, R is expected to exhibit a tendency to more negative values in this temperature region. The results given in Fig. 2 show that both these expectations are fulfilled. In single crystals, on the other hand, it is believed[31] that the phonon-drag effect in Cu is significantly dependent upon the crystallographic direction (although there appears to be no published, direct evidence of this). Therefore, in terms

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[27] W. B. Pearson, Phil. Mag. **46**, 911 (1955).

[28] D. K. C. MacDonald, *Thermoelectricity* (John Wiley & Sons, Inc., New York, 1962).

[29] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960).

[30] R. P. Huebener, Phys. Rev. **146**, 502 (1966).

[31] M. Bailyn, Phys. Rev. **157**, 480 (1967); J. S. Dugdale and M. Bailyn, *ibid.* **157**, 485 (1967).

of this belief the results of Fig. 3 again provide support for proposal (3).

An ideal test for the proposal (3) would be a study of the effect upon R for a noble metal of a solute which is known to affect only the phonon system (and hence the phonon-drag effect) without influencing the electronic scattering processes. Unfortunately, such is not possible, but we believe that comparative studies of certain alloy systems could be an informative alternative. Ag was chosen as the solvent metal, and we studied the effects upon R of small concentrations of Au, Zn, and Cd. The extra phonon-impurity scattering in an alloy produced by the solute will reduce the phonon-drag effect. The size of this reduction will depend upon the strength of the phonon-impurity interaction. Au was initially chosen as solute because of its large atomic mass difference from the solvent. Figure 4 shows that the apparent peak in R at about 40°K is certainly reduced by 500-ppm Au, and reduced further (but not completely extinguished) by the addition of 5000-ppm Au. This agrees with the results of thermoelectric power measurements,[32] which show evidence of phonon drag at 9000 ppm, but it is not clear from the results of Fig. 4 whether proposal (2) or (3) is correct. More conclusive evidence to support proposal (3) comes from the comparison of the results for the *Ag*Cd and *Ag*Zn alloys. From the consideration of the atomic masses, we expect the Zn ions to scatter the phonons more strongly than the Cd ions, while there is strong evidence[33] that Zn and Cd in Ag have practically identical solute structures and scattering potentials for both *s*- and *p*-type electrons. Therefore, from the point of view of electron scattering, we expect equal concentrations of these solutes in Ag to have practically identical effects upon R in the impurity dominated region. Any difference in the temperature dependence of R for the two alloys would presumably be in the phonon-drag region where the stronger phonon-impurity scattering in the AgZn system would reduce $|R|$ relative to that for the AgCd system.

The tests referred to in the above paragraph cannot conclusively establish proposal (3), but any discrepancy between the above predictions and observation would throw doubt upon the proposal. We do not find any such discrepancy; a comparison of the results for the *Ag*Zn and *Ag*Cd alloys shows (Fig. 4) that they have identical R values (to within experimental precision) for temperatures down to about 50°K, and below this the presumed phonon-drag contribution to R is largest for *Ag*Cd. Our conclusion is, therefore, that the apparent maximum in $|R|$ versus T for the group I*B* metals at low temperatures probably arises from a phonon-drag contribution to R.

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