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Significance of Hall-Effect Measurements in Very Dilute Alloys

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The Hall coefficients of some samples of high-purity polycrystalline I*B* metals are found to be field-independent when measured in the high-field condition. This is contrary to expectations expressed in the literature. It is shown that the presence of trace impurities can cause an apparent field dependence of the Hall coefficient, which is presumably what previous workers have observed, but which is not a fundamental property of the pure metal; it is caused by the transition between the high- and low-field conditions during the experiment. The work has involved measurements of the Hall coefficients at 4.2°K of alloys of the I*B* metals with controlled trace amounts of Zn, Mn, or Fe impurities. From measurements on doped-Cu single crystals, an empirical criterion for the low-field–high-field transition in the *Cu*-Zn system at 4.2°K is established which can presumably be extended to analogous systems. It is shown, using this criterion, that the anomalous temperature dependence of the Hall coefficients of the pure I*B* metals seen at about 50°K is definitely not the result of a low-field–high-field transition. The proposed explanations of this anomaly are reexamined in the light of these results.

I. INTRODUCTION

Several studies of the Hall coefficients of the pure group-I*B* metals and of dilute, polycrystalline alloys based upon them have recently been published.[1–5] These measurements have been made from the point of view that when the correct low-field conditions are satisfied in the sample then the interpretation of the results can give information about the anisotropy of the relaxation time of the conduction electrons under the influence of the different scattering mechanisms. For a metal having a multiply connected Fermi surface, the values of the Hall voltage obtained for a polycrystalline sample which is not in the low-field condition (i.e., one for which $\omega_c\tau \gg 1$, where ω_c is the cyclotron frequency corresponding to the applied magnetic field and τ is the average relaxation time of an electron in a cyclotron orbit) are essentially uninterpretable in terms of any anisotropic property of the electronic system. The measured Hall voltage is simply a result of an averaging of the individual Hall voltages of the (presumably) randomly oriented crystallites, and for each crystallite the Hall voltage—and its dependence upon temperature and magnetic field—is dependent upon the crystallographic orientation. How such an average should be calculated is not known *a priori* and, although some simplifying approximations have been made,[6] the formal mathematical problem for a metal with a multiply connected Fermi surface is formidable. Thus Hall voltages obtained from polycrystalline samples in a high-field condition remain of little value to the study of the anisotropic properties of a metal's electronic structure.

Providing that measurements are made in the low-field condition (i.e., where the lifetime of an electron between collisions remains short enough that the topological features of the Fermi surface are not manifested in the electronic motion), the problem of how the individual Hall voltages of the crystallites are averaged to form the observed voltage does not arise; the Hall voltage of each crystallite is independent of the crystallographic orientation and is determined essentially by the ratio of the effective numbers of electrons of different symmetry properties which are available for the conduction process. This does not imply that the anisotropy of the electronic structure of a metal cannot influence a low-field Hall voltage in a polycrystal. On the contrary, if a change in some anisotropic parameter alters the effective numbers of electrons of different symmetries, then it will appear directly as a change in the observed Hall voltage of the polycrystal. (An example of such an effect is Ziman's suggestion[7] that umklapp processes from "belly" states are progressively frozen out with reducing temperature, thereby directly affecting the temperature dependence of the Hall coefficients of the I*B* metals.) It is this approach to the study of changes in anisotropic electron scattering which is the basis of the recent work referred to above.

In the interpretation of the results of this type of measurement it is clearly vital to know whether a sample is in a low-field condition. It is one purpose of this paper to examine a remark made previously in this context,[3] namely, that for a polycrystalline sample in the high-field condition the Hall coefficient is expected to be dependent upon the applied magnetic field. We show from results described in Sec. III that this expectation is apparently incorrect, and that the field dependence which is sometimes observed in the pure

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* National Research Council of Canada Postdoctoral Fellow.

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[2] R. D. Barnard and L. Sumner, Phil. Mag. **20**, 399 (1969).

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[4] W. Huppmann and F. Stangler, Phys. Status Solidi **31**, K107 (1969); Oesterr. Akad. Wiss. Math. Naturw. Kl. Sitzber. Abt. II **105**, 217 (1968).

[5] T. Matsuda, J. Phys. Chem. Solids **30**, 859 (1969).

[6] J. M. Ziman, Phil. Mag. **3**, 1117 (1958).

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group-I*B* metals is very probably due to the effect of trace impurities.

In Sec. IV we establish empirically, from measurements on doped-Cu single crystals, a criterion for the low-field condition in the *Cu*-Zn system. This system was chosen as representative of the set of alloys which are based upon the I*B* metals and have polyvalent solutes. Our empirical criterion can presumably be extended to apply to other members of the set.

In Sec. V we examine the temperature dependence of the Hall coefficient of some polycrystalline alloys which are known, from the results of Sec. IV, to have been obtained in the low-field condition. We find that the anomalous temperature dependence of the Hall coefficients of the pure I*B* metals, whose absolute values show a maximum at about 50°K,[1–4] is definitely a property of the low-field condition and does not entirely arise as a result of the transition between the two conditions. This leads us to reexamine some of the proposed explanations of this anomaly and to correct what we feel are some misconceptions among them.

II. EXPERIMENTAL

The polycrystalline samples were prepared as described previously[1] from starting material of 99.9999% purity.[8] Some analyses of the starting material are given in Table I, and the residual-resistance-ratio (RRR) values of typical samples after preparation are given in Fig. 1. The determination of the impurity concentration was carried out by members of the Analytical Section of the National Research Council of Canada. For concentrations $<\sim 20$ ppm the method of carrier distillation spectroscopy was used, while for alloys of higher concentration either the method of atomic absorption or a conventional wet chemical method was used. The RRR values for each alloy are given in Fig. 1 and their linear variation with impurity concentration was verified for each alloy system as a check that none of the samples showed metallurgical peculiarities. This linear variation having been established with precision for the alloy system from RRR values obtained for more concentrated alloys. Before measurement, the samples were annealed in vacuum at 550°C for a minimum of 24 h before slowly cooling to ambient temperature.

The single-crystal samples were grown by the Bridgman method in high-purity graphite molds from a previously prepared polycrystalline alloy of the desired concentration. Specially oriented pure Cu seed crystals were used. The method was conducive to some zone refining with a consequent resultant concentration gradient in the sample. Analysis showed that this could amount to about 10% variation over the length of a sample. The RRR values for these samples are given in the caption to Fig. 3. Other details of the sample preparation are as previously described.[1] The instrumentation and the techniques used to determine the Hall voltage are identical to those described previously.[1]

TABLE I. Typical analyses of starting materials.

Material	Impurity[a] (ppm weight)
Cu[b]	Fe (0.10) Mn (not visible <0.01) Co (not visible <0.01), Mg (0.01) Si (0.1)
Ag[c]	Fe (0.3), Si (0.2), Mg (0.06) Cu (0.02)
Au[c]	Fe (0.06), Ag (0.3), Mg (<0.1) Cu (0.1)

[a] The results are from spectrographic analysis by halide carrier distillation. The impurities are not necessarily in solid solution (cf. the RRR values given in Fig. 1).
[b] Supplied by American Smelting and Refining Co.
[c] Supplied by Consolidated Mining and Smelting Co.

III. MAGNETIC FIELD DEPENDENCE

Dugdale and Firth[3] have stated that for a polycrystalline sample in the high-field condition it is expected that its Hall coefficient will be field dependent, and further that the appearance of a field dependence as $\omega_c\tau$ is increased (through a combination of either increasing field strength or decreasing temperature) can be used as a test for the onset of the high-field condition. Such a point of view is perhaps based upon the known behavior of the Hall effect in single crystals of the I*B* metals. In the high-field condition the Hall coefficient, and its dependence upon field, varies strongly with the crystallographic orientation. Therefore in a polycrystalline sample in the high-field condition, although the observed Hall effect is formed by some averaging of all the individual contributions of the crystallites which is not understood in detail, it might be guessed *a priori* that the Hall coefficient would, in general, show a resultant field dependence which would not exist in the low-field condition. Dugdale and Firth[3] have observed such a behavior at 4.2°K for a nominally pure polycrystalline sample of Ag (although not, significantly, for an even purer sample of Cu), and a similar field dependence has been reported for the I*B* metals in other work including that by Gaidukov,[9] by Franken and Van den Berg,[10] and by Chambers.[11]

However, the above argument has neglected one possibility: It may happen that the contributions to the Hall effect from the crystallites in a polycrystal are combined in such a way that their individual field dependences effectively cancel. The Hall coefficient would then show no net field dependence in the high-field condition. (It would in any case not show any in

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[8] Cu supplied either by Gallard-Schlessinger Chemical Corp. or by American Smelting and Refining Co. Ag and Au supplied by Consolidated Mining and Smelting Co.

[9] I. P. Gaidukov, Zh. Eksperim. i Teor. Fiz. **34**, 836 (1958) [Soviet Phys. JETP **34**, 577 (1958)].

[10] B. Franken and G. J. Van den Berg, Physica **26**, 1030 (1960).

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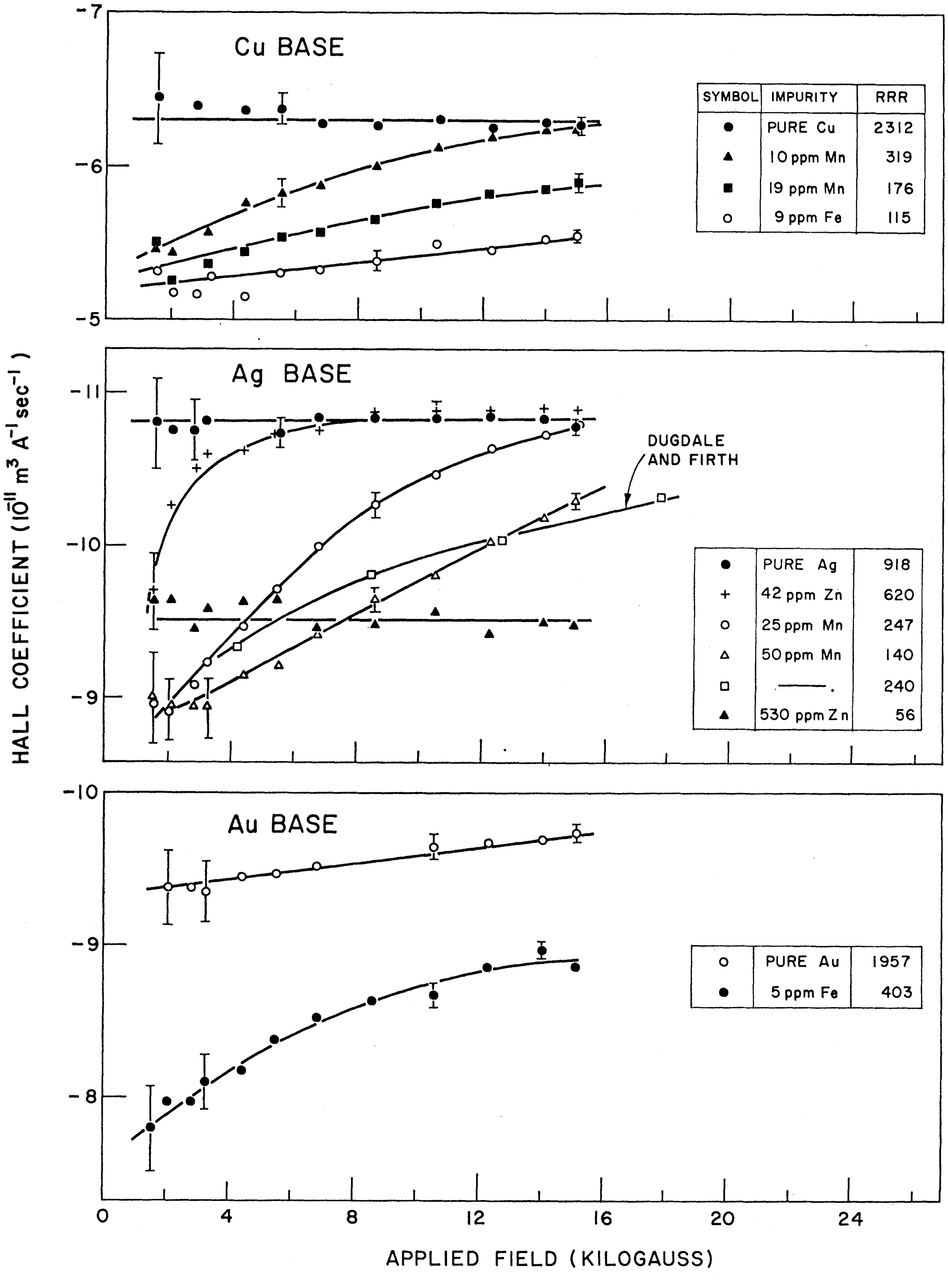

FIG. 1. Field dependence of the Hall coefficient of polycrystalline samples at 4.2°K. The impurity, its concentration in atomic ppm, and the residual resistance ratio ($\text{RRR}=R_{273°\text{K}}/R_{4.2°\text{K}}$) are given for each sample. The error bars illustrate the accuracy estimated for a result at a given applied field; the precision of a result (i.e., neglecting the error in the sample's thickness) is about 30% better.

the low-field condition, as we pointed out in Sec. I.) We shall show from data presented in Fig. 1 that this appears to be the case for the I*B* metals, and further that an apparent field dependence can be produced in a sample which, as a result of trace impurities, passes from the low-field to the high-field condition as the applied magnetic field is increased. We think that this apparent field dependence is what has been observed by some previous workers for samples of nominally pure I*B* metals.

Figure 1 shows the field dependence of the Hall coefficient obtained at 4.2°K for some polycrystalline pure I*B* metals and for some very dilute alloys based upon them. Before discussing the relevance of these results to the above argument, we would like to make the following observation: Values of the Hall coefficient at a given field B', $R_{B'}$, were calculated from the usual formula for the field-independent case

$$R_{B'}=V_{B'}t/IB', \tag{1}$$

where $V_{B'}$ is the Hall voltage observed for a total current I in a sample of thickness t. This procedure is only valid if V varies linearly with B, since Eq. (1) is a special case of a general definition

$$R_{B'}=\left(\frac{\partial V}{\partial B}\right)_{B=B'}\frac{t}{I}. \tag{2}$$

When V does not vary linearly with B, then Eqs. (1) and (2) can give appreciably different results for the apparent field dependence of R and, of the alloy systems referred to in Fig. 1, we find that this difference is most pronounced for the *Ag*-Mn system. Since the data of Dugdale and Firth were apparently obtained using Eq. (1), and since we particularly wish to make a comparison with these data, we have chosen in Fig. 1 to present our results as calculated from Eq. (1). We shall leave aside any discussion of the choice between Eqs. (1) and (2) since it is incidental to our present argument.[12] Here we simply wish to show that the Hall effect observed in polycrystalline samples of some of the pure I*B* metals is effectively field independent and it can become field dependent when a trace of impurity is present. The results calculated from Eq. (1) are adequate for this.

First, consider the behavior found for the Hall coefficient of the pure I*B* metals (Fig. 1). It will be shown from the results given in Sec. IV for a Cu single crystal that samples of equivalent purity to those under consideration are in a high-field condition when in an applied field of 15 kG and at a temperature of 4.2°K, yet we find that the Hall coefficients of polycrystalline Cu and Ag show no field dependence in the range of fields studied. On the other hand the Hall coefficient of pure Au does show a field dependence which is just detectable within our limits of precision. Judging from the results for the Au+5 ppm Fe sample, this observed field dependence could arise from an impurity concentration equivalent to about 1 ppm Fe. This is, however, approximately a factor of 10 greater than the value obtained from chemical analysis (Table I). Thus we do not have a certain explication of the behavior of the Hall effect seen in Au, but it is clear that Fe is a troublesome impurity, although proportionately less so in Cu than in Au. (Compare the change in the Hall coefficient produced by 9 ppm Fe in Cu with that produced by 5 ppm Fe in Au.) Since Fe is not soluble in Ag, we shall concentrate the argument upon the Ag-based alloys.

The addition of 530 ppm Zn to Ag produces no detectable field dependence of the Hall coefficient in the range of fields studied. This is as would be expected since it will be shown, from the results given in Sec. IV for the analogous *Cu*-Zn system, that such an alloy at 4.2°K is almost certainly in the low-field condition in a field of 15 kG. Therefore the results for the 530 ppm *Ag*-Zn alloy shown in Fig. 1 are for the low-field condition and no field dependence is expected. The absolute value of the Hall coefficient of this alloy at 4.2°K is -9.62×10^{-11} m^3 A^{-1} sec^{-1}, having been reduced from that of pure Ag by the effect of the anisotropic impurity scattering. The addition of 42 ppm Zn to Ag, on the other hand, is seen to produce an apparent field dependence at the lower fields which has disappeared at about 7 kG. This we believe represents the transition between the low- and high-field conditions. Above about 7 kG the high-field condition exists and the details of the anisotropy of the predominant scattering process are irrelevant to the observed Hall effect; it is the topological details of the Fermi surface which determine the Hall voltage of each crystallite and hence the Hall voltage of the polycrystal. (Evidently any change in the shape of the Fermi surface of Ag produced by the addition of 42 ppm Zn which would affect the relative numbers of carries of different symmetries is not detectable in these measurements since the high-field Hall coefficient observed for the alloy is the same as that of pure Ag.) As the field is reduced below 7 kG we see the onset of the low-field condition, and the Hall coefficient tends toward its low-field value. This value being determined by the detailed anisotropy of the predominant scattering process.

We can now look at the results for the alloys containing magnetic impurities from this point of view (Fig. 1). An alloy of Ag+50 ppm Mn would apparently require a field of approximately 19 kG before the high-field condition was reached. When compared with the results for the Ag+42 ppm Zn alloy, this behavior reflects the relative efficiencies of Mn and Zn as electronic scattering centers in Ag; for roughly an equivalent amount of each solute it requires a proportionately higher field to bring about the high-field condition in the presence of the Mn impurity.

We can put this argument on a slightly more quantitative basis by plotting the estimated minimum applied field at which the high-field is observed, H_{crit}, against the RRR of the alloy. (In these very dilute alloys the RRR varies essentially as the inverse of the

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[12] It is worth noting that the general problem of the choice between Eqs. (1) and (2) could be avoided if authors would quote values of the Hall resistivity rather than the Hall coefficient, such as is done, for example, in the case of ferromagnetic samples.

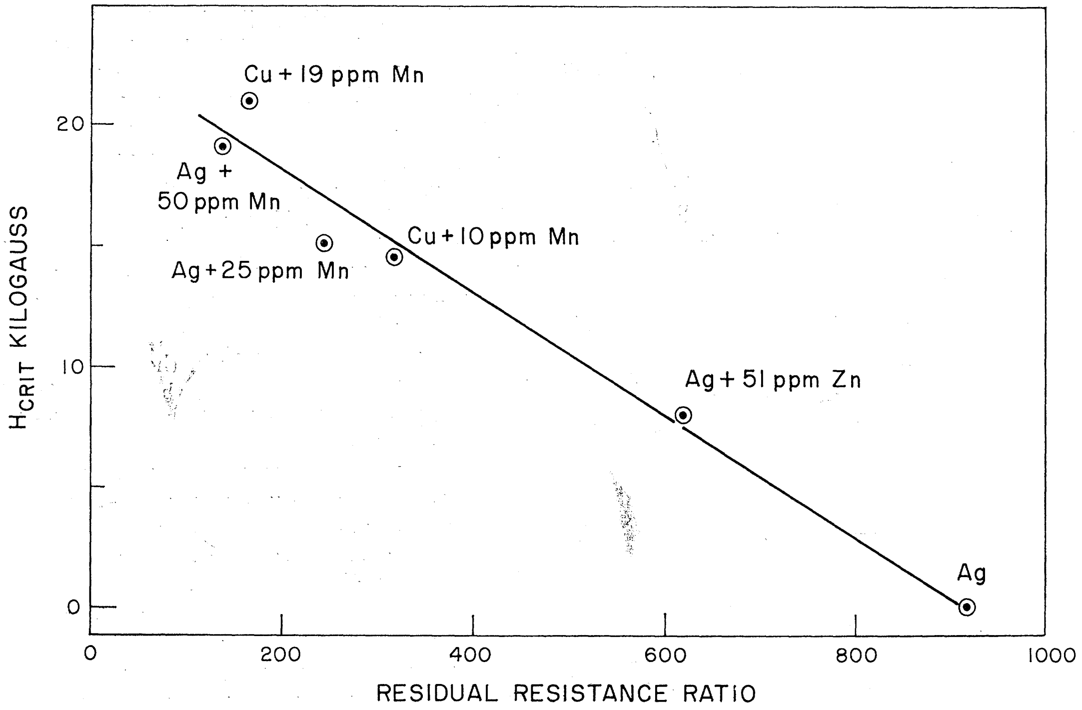

FIG. 2. Minimum field at which the high-field condition is observed ($H_{\rm crit}$) at 4.2°K versus the residual resistance ratio for the samples of Fig. 1.

electronic mean free path at 4.2°K.) This is shown in Fig. 2. We emphasize that there is considerable uncertainty in the extrapolated values of $H_{\rm crit}$ estimated for some of the alloys, and the numerical values shown in Fig. 2 should not be treated with great seriousness, but the figure is useful in two respects. It illustrates a general relationship between RRR and $H_{\rm crit}$, which adds weight to our interpretation of the data of Fig. 1, and it will provide a useful indicator of the high-field condition at 4.2°K in other studies of alloys based upon the I*B* metals.

We conclude from the results presented in this section that the Hall coefficients of pure polycrystalline samples of the I*B* metals at 4.2°K are in practice always measured in the high-field condition and are field independent. An apparent field dependence which is sometimes observed is due to the presence of trace impurities. The results of Dugdale and Firth[3] for nominally pure Ag suggest from the data shown in Fig. 1 that the impurity content of their sample was equivalent to about 30 ppm Mn (this being the most probable impurity). This estimate is confirmed by comparing the known RRR value of this sample with those for the *Ag*-Mn system. Therein lies the explanation of why a field dependence was seen for the Hall coefficient of this sample, but no comparable effect was seen for a purer sample of Cu.[3] Hence the test suggested by Dugdale and Firth to determine whether a Hall coefficient has a true low-field value cannot be valid, and in Sec. IV we consider the establishment of an alternative empirical criterion.

IV. CRITERION FOR LOW-FIELD CONDITION

It is clear from the remarks made in Sec. I that for the interpretation of Hall-effect measurements in very dilute alloys it is essential to know whether the data refer to the high- or low-field condition. The most reliable criterion would be an empirical one rather than, for example, a calculated estimate of $\omega_c\tau$ (which becomes particularly approximate for a metal with a multiply-connected Fermi surface). To show that the low-field condition exists in an experiment it would be preferable to show by direct measurement of some electronic transport property that the topological details of the Fermi surface were indeed not manifested. It is impractical to go to this limit for each Hall-effect measurement, but we have done it for the *Cu*-Zn system at 4.2°K. Our idea being that this system is probably representative of the whole class of alloys based upon the I*B* metals and having polyvalent solutes. Using the known scattering cross sections for these solutes, the results for the *Cu*-Zn system should provide at least a guide for the whole of that class.

We are concerned here only with using the anisotropy of the high-field Hall coefficient, and its dependence upon solute concentration, as an indicator of the high-field–low-field transition. We shall therefore not go

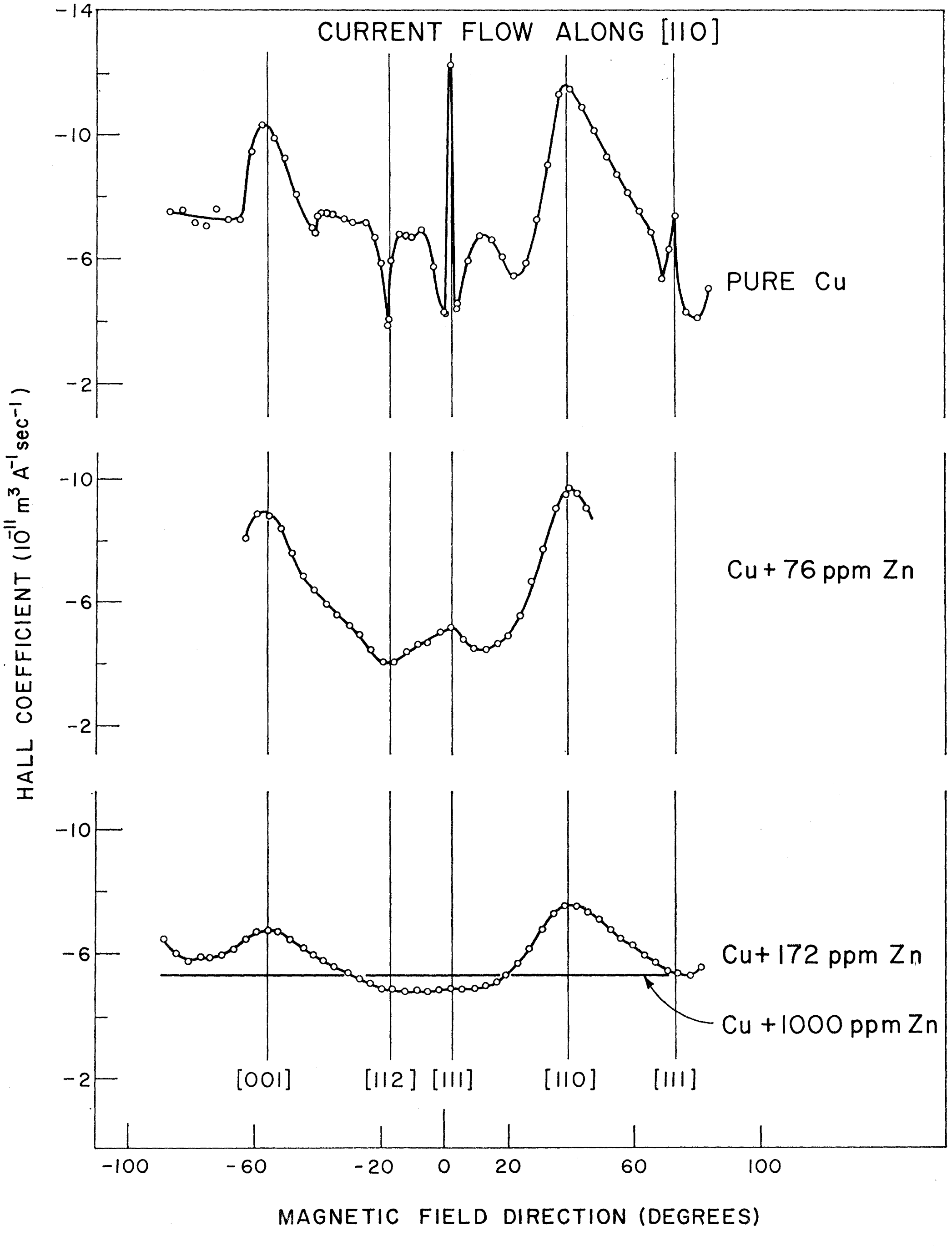

FIG. 3. Variation of the Hall coefficient with magnetic field direction for some doped Cu single crystals. Temperature is 4.2°K and the applied field is 15.17 kG. The RRR values of the samples are (in order of decreasing purity) 2312, 544, 260, and 53. The corresponding Hall coefficient of polycrystalline Cu at this temperature and field is -6.45×10^{-11} m^3 A^{-1} sec^{-1}.

into a detailed description of the influence of the various topological features of the Fermi surface upon the high-field Hall effect (see, for example, the review by Fawcett[13]). A study is being made of the influence upon this anisotropy of different, dissolved foreign elements in Cu, and will probably be the subject of a subsequent publication.

The Hall coefficients of single crystals of Cu of a fixed orientation (see Fig. 3) have been measured at 4.2°K as a function both of Zn concentration and of the direction of the applied magnetic field of 15.17 kG. The influence of the topology of the Fermi surface is

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[13] E. Fawcett, Advan. Phys. 13, 139 (1964).

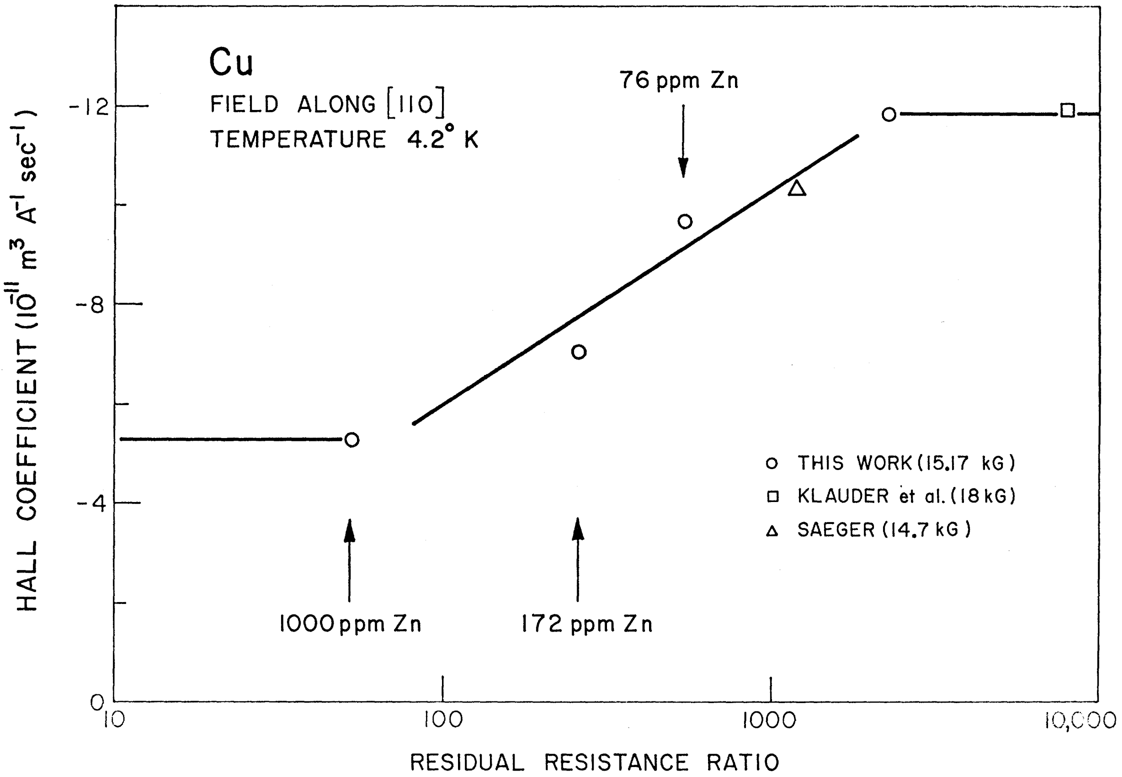

FIG. 4. Hall coefficient at 4.2°K for an applied field of 15.17 kG along [110] in Cu samples plotted against the RRR. The low-field condition exists for RRR$<\sim$50 and the high-field condition for RRR$>\sim$2000. Results obtained for different values of the applied field are included. This is possible since for this orientation the Hall coefficient becomes effectively field independent above about 14 kG. [See Fig. 4(b) of Ref. 14.]

progressively reduced as Zn is added until the low-field condition is reached somewhere between 172 and 1000 ppm. As in Fig. 2, we can represent this behavior in a slightly more quantitative way by plotting the Hall coefficient for a given direction of applied magnetic field against the RRR value. This is shown in Fig. 4, where the data are for the applied field along [110]. We have chosen this direction partly because it allows us to incorporate the comparable results from the works of Klauder *et al.*[14] and of Saeger,[15] partly because it remains distinguishable even with appreciable solute concentrations, and partly because for this orientation the Hall coefficient is less sensitive to a slight misalignment of the sample than it would be, for example, with the field along [111]. Because of such experimental difficulties, the Hall-coefficient values plotted in Fig. 4 are less accurate than those obtained for polycrystalline samples. However, their accuracy is sufficient to show in Fig. 4 (to within at least half an order of magnitude) at what value of RRR the low-field condition begins and to show that, at least for this particular direction of applied field, the Hall coefficient between the high- and low-field conditions varies roughly as the logarithm of the RRR.

V. TEMPERATURE DEPENDENCE IN LOW-FIELD CONDITION

The absolute value of the Hall coefficients of the pure I*B* metals shows an anomalous maximum in its temperature dependence. This is centered at about 50°K and has been the subject of recent interest.[1–4,15] Among the suggested possible explanations current in the literature are that it is due to: (a) the influence of residual impurity,[3] (b) a freezing out of umklapp processes from "neck" regions of the Fermi surface,[2,4] (c) the phonon-drag effect.[1] We shall first consider some recent criticisms of (c) in the light of our results in Sec. III and correct what we think is a misconception on the part of Barnard and Sumner of the physical origin of the effect.

As Dugdale and Firth[3] have pointed out, the Hall-coefficient values quoted by Alderson *et al.*[1] for the pure polycrystalline I*B* metals at the lowest temperatures are not for the true low-field condition (this we have confirmed in Sec. III). It can be argued from this that the anomalous temperature dependence in question

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[14] J. R. Klauder, W. A. Reed, G. F. Brennet, and J. E. Kunzler, Phys. Rev. **141**, 592 (1966).

[15] K. E. Saeger, Phys. Status Solidi **28**, 589 (1968).

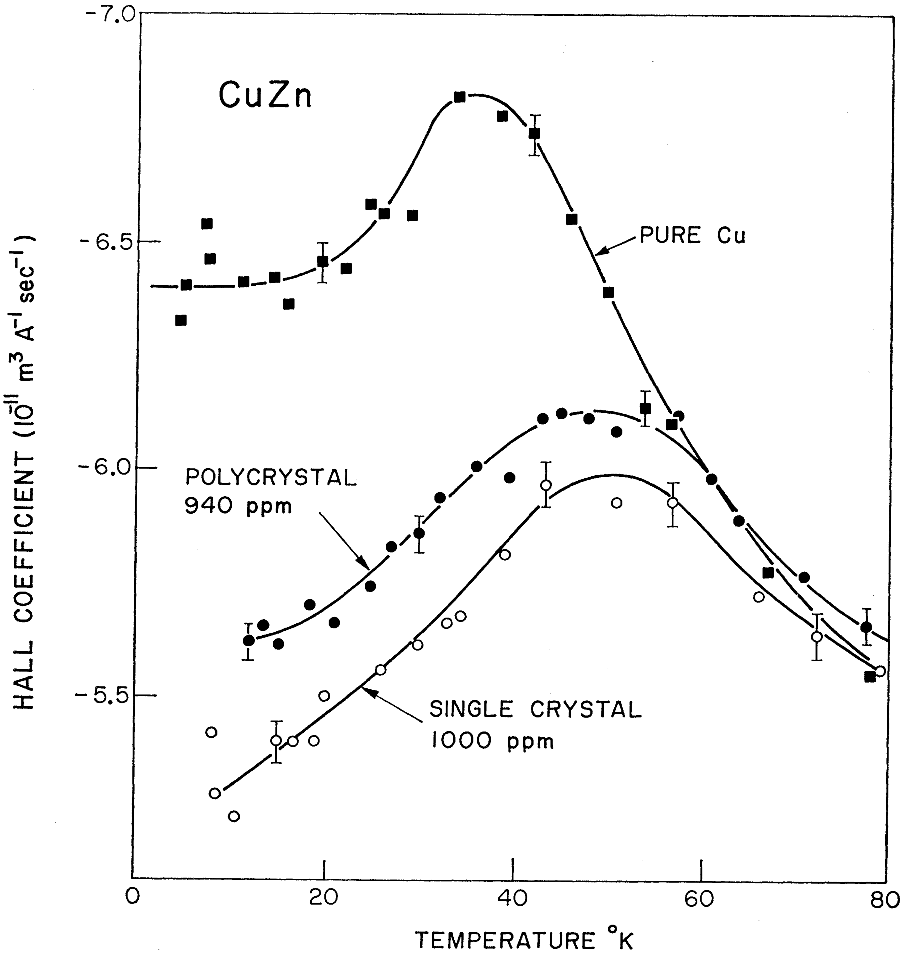

FIG. 5. Temperature dependence of the Hall coefficients of polycrystalline Cu+940 atomic ppm Zn and single-crystal Cu +1000 ppm samples compared with that for pure Cu. The alloys are known from Sec. IV to be in the low-field condition throughout the experiment.

may be simply associated with the transition from the low-field to the high-field condition as the temperature is raised and the electronic mean free path is reduced by the phonon scattering. If this is the case, then a sample which is in the low-field condition throughout the experiment (i.e., in the whole of the temperature range 4.2–300°K) should show no anomaly in its temperature dependence. In Fig. 5 we show the variation of the Hall coefficient with temperature for a polycrystalline sample of Cu+940 ppm Zn. This is known from the results of Sec. IV to be in the low-field condition throughout the experiment, and yet the anomaly is observed. Furthermore, Barnard and Sumner[2] show that the anomaly exists even in an alloy of Cu+0.4-at.% Zn. These results thus eliminate the possibility that the anomaly observed for the I*B* metals arises entirely from a transition between the low- and high-field conditions. Saeger's results for a Cu single-crystal sample[15] support this view since they show that the temperature at which the anomaly occurs does not scale with $\omega_c\tau$ when the applied magnetic field is varied, but remains fixed. Saeger concludes that the anomalous effect can only be caused by a direct temperature-dependent mechanism.

Barnard and Sumner[2] have criticized suggestion (c) involving a phonon-drag contribution as being unlikely in view of their rough estimates of its magnitude, and have proposed an alternative possible explanation involving the Ettingshausen-Nernst effect. There appear to us to be some misconceptions in that work, and we show in the following why we feel their estimates are not reliable. We shall consider the problem from a simple kinetic point of view.

Let a primary electronic flux J_x be established in the x direction by an external electric field. In the phonon-drag temperature region this flux will set up a "dragged" heat flow U_x in the phonon system which is given by $U_x = \Pi_g J_x$, where Π_g is the phonon-drag component of the Peltier heat. The heat flux in the phonon system will set up an internal temperature gradient in the *electronic* system. The fact that the electronic system cannot come into thermal equilibrium with the lattice is the fundamental cause of the phonon-drag effect, and the temperature difference between electrons at opposite ends of the sample ΔT_x will be given by

$$\Delta T_x = U_x l / k_L A \,, \qquad (3)$$

where l is the sample's length in the x direction and A

its cross-sectional area. The lattice thermal conductivity k_L is the appropriate parameter in Eq. (3), since it is through the *phonon* system that the "dragged" energy has been transported.

The internal temperature gradient in the electronic system will cause a net diffusion of the more energetic electrons away from the "hotter" regions and this, for a sample in an open circuit and in equilibrium, would establish a concentration gradient of electrons along the x direction, thereby giving rise to the so-called phonon-drag thermoelectric field. When the sample is part of a closed circuit, such as we are considering in this case, Huebener[16] has shown that the additional diffusion current along the x direction effectively changes the electrical resistivity and, in fact, always reduces it, whatever the sign of the phonon-drag thermopower. If we now consider the consequences for the Hall effect, it is seen that the additional current density along the x direction will contribute its own Hall field to that given by J_x; i.e., there will be an Ettingshausen-Nernst field due to the "dragged" heat flow U_x. There is thus no distinction, such as Barnard and Sumner have proposed, between the apparent reduction in the resistivity and the appearance of an additional Hall field; they are manifestations of the same effect but viewed under different experimental conditions.

Furthermore, if one choses to calculate the additional Hall voltage due to the Ettingshausen-Nernst effect, ΔV^{EN}, from an expression such as[2]

$$\Delta V_y^{\mathrm{EN}} = Q\Delta T_x B_z w/l\,, \tag{4}$$

where w is the width of the sample and B the applied magnetic field, then the following implication of Eq. (4) should be noted: The equation implies, by analogy with the case when the electronic system is in equilibrium, that ΔV_y^{EN} varies simply with the product of ΔT_x and B. It is by no means clear that this would be so under the nonequilibrium conditions which prevail, and furthermore Q is *not* the Ettingshausen-Nernst coefficient of the equilibrium case. It is a special coefficient relevant only to the *electronic* system thermally isolated from the lattice. What its value should be is not clear *a priori* and is not available from experiment. It is for these reasons that we feel that at the present time no useful estimate can be made for ΔV_y^{EN}.

VI. CONCLUSION

We have already summarized at the end of Sec. III the conclusions which can be drawn from the principal, new data of this paper, which are shown in Fig. 1. To these conclusions we add one remark: The anomaly reported in the field dependence of the Hall coefficient of Au,[9] which has been cited as possible evidence of the formation of a compensated spin state around the Fe impurity,[17] is probably simply a result of the transition between the low- and high-field conditions, of which examples are shown in Fig. 1.

In the light of Sec. V we feel that of the possible explanations listed there for the anomalous temperature dependence of the Hall coefficients of the IB metals, (a) and (c) remain the most probable, even though experimental evidence can be found which is apparently in disagreement with both. Saeger[15] finds that the anomalous maxima occur at the same temperature in single crystals of Cu with different impurity concentrations, which would not be expected from (a), while Barnard and Sumner[2] show that for an alloy system where the phonon-drag thermopower appears to resurge at high concentrations, there is no comparable resurgence of the anomaly in question. This apparently contradicts (c). We feel, however, that (b) is still the least probable of the proposed explanations, for it is known[7] that there is no cutoff frequency for umklapp processes from "neck" states on the Fermi surface. It is the ratio of the relaxation times for electrons in neck and belly states τ_n/τ_b which determines the Hall coefficient, and since at the lowest temperatures both τ_n and τ_b will be simultaneously limited by the same spectrum of low-momentum phonons, it is difficult to see how τ_n/τ_b could decrease and then increase again at the lowest temperatures[2] as required by (b).

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Note added in proof. We have stated above that the anomalous temperature dependence of R is definitely not entirely the result of a low-field–high-field transition. Recent work by us suggests that a more guarded position should be taken. In particular, the lack of anisotropy in R observed in Fig. 3 for Cu+1000 ppm Zn is not necessarily an indicator of the low-field condition: If the effect of the solute is to eliminate contributions to R from open orbits, the Fermi surface becomes effectively closed and an isotropic R is then possible—even in a predominantly high-field condition. A more detailed discussion will be given by Hurd and Alderson in J. Phys. Chem. Solids (to be published).

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