Hall coefficient of dilute Cu-Au(Fe) alloys. I. Experiment* †

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We have measured the Hall coefficient of a series of Cu-Au alloys containing dilute amounts of Fe, where both the host Cu-Au composition and the Fe-impurity concentration were varied. We find that the Hall coefficient due to the Fe impurity is strongly field and temperature dependent. The dependence on impurity concentration is predominantly linear, contrary to expectations of most previous theoretical calculations based on the free-electron model. Our results can be explained in terms of a theory which includes a multiple-carrier host, and which is presented in the following paper. As a function of host composition, the temperature and field dependence are found to be consistent with the existence of a low-temperature spin-compensated state.

I. INTRODUCTION

Extensive studies have been made on the behavior of metals and alloys containing dilute amounts of magnetic impurities which exhibit the Kondo effect. Various properties[1,2] have been investigated in some detail and are reasonably well understood. Among these are measurements of susceptibility, resistivity, specific heat, thermoelectric power, Mössbauer studies, nuclear-magnetic resonance, neutron scattering, and others. The purpose of the present investigation was to find manifestations of the Kondo effect in the Hall coefficient of dilute magnetic alloys, to compare experimental behavior with theory, and to find evidence for the existence of the low-temperature spin-compensated state.

Previous theoretical studies on the Hall effect in Kondo systems, all based on the free-electron model, have been made by More,[3] Béal-Monod and Weiner[4] (BMW), Fert and Jaoul,[5] and by Bloomfield, Hecht, and Sievert (BHS).[6] It is well-known that magnetic impurities give rise to a spin-dependent scattering and a potential scattering, which is additional to the potential scattering associated with the host. These additional contributions to the scattering rate give rise to an increase in resistivity as the temperature is decreased, causing the resistance minimum observed in many such materials. There is field dependence in the resistivity (magnetoresistance) and in the Hall coefficient which derives from the fact that the spin-coupling of conduction electrons with the magnetic impurities is modified in the presence of an external magnetic field. In particular, More[3] and BHS[6] found that the resistivity depends on the sum of the conduction-electron spin-up and spin-down scattering rates, while the anomalous part of the Hall coefficient depends on their difference. Since an external magnetic field breaks the symmetry in the occupation of the spin states of both the conduction and impurity electrons, an investigation of the Hall coefficient should yield direct information on the field dependence and hence the spin dependence of the conduction-electron scattering rate.

Measurements of the Hall coefficient have been performed on a variety of dilute alloys.[4,7-9] Recent measurements include those of P. Monod (cited in Ref. 4) on Cu(Mn) and Alderson and Hurd[7] on Cu(Fe), Au(Fe), and Cu(Mn). Monod took data only well above the Kondo temperature T_K, and therefore these measurements do not encompass the temperature range of greatest interest. Alderson and Hurd concerned themselves with relatively pure alloys with long electronic mean free paths. Their results are dominated almost entirely by a low-field to high-field transition in the magnetic field range of interest, and by fairly large effects attributed to the existence of superparamagnetic clusters.

The alloy system chosen for the present investigation[10] is structurally disordered Cu-Au containing small amounts of Fe. To ensure dilute Fe concentrations, C, we have used the standard guide $C < 100T_K$ ppm/°K to choose the various Fe concentrations appropriate to a particular Cu-Au host. Due to the very short mean free paths in the Cu-Au hosts, the low-field to high-field transition is eliminated and the effects of superparamagnetic clusters are minimized. Further, resistivity studies by Loram, Whall, and Ford[11] have shown that T_K varies continuously over a wide range of temperatures (0.3 to 30 °K) as a function of Cu-Au host composition.[12] Thus it was possible to study the Hall coefficient as T_K was varied, and T_K could be chosen at some intermediate value such that the available temperature and magnetic fields effected a transition from the (partially) spin-compensated state (below T_K) to the magnetic state (above T_K).

Our measurements for the Hall coefficient of the host materials without Fe impurities show considerable structure as a function of Cu-Au composition. Some of these features have been previously observed,[13,14] and in the following paper (hereafter referred to as Hall Effect II)[15] we account for this behavior in terms of anisotropic scattering rates associated with various types of electrons in Cu-Au, and relative changes in these rates as the Cu-Au composition is varied. When magnetic impurities are introduced into this system, the behavior of the extra term in the Hall coefficient associated with the impurity shows a dependence on Cu-Au host composition which is consistent with previous measurements on other properties which showed the existence of a low-temperature spin-compensated state. The behavior of this term as a function of temperature, magnetic field, and concentration does not agree with theoretical predictions of More,[3] BMW,[4] and BHS[6] based on a single-carrier model. However, we find that qualitative agreement between theory and experiment can be obtained by taking into account the existence of several carriers in the Cu-Au host material.[16] In Hall Effect II we develop formulas for the anomalous resistivity and Hall coefficient of a polycrystalline metallic host containing a dilute concentration of randomly distributed magnetic impurities.

II. EXPERIMENTAL PROCEDURE

Hall measurements were effected in a superconducting magnet as a function of magnetic fields to 60 kG at 4.2 °K and at approximately 1.5 °K using standard dc techniques. A constant current of 1.9 A was used to produce a Hall voltage which was measured with a resolution on the order of nanovolts on a null detector. The error in Hall measurements is estimated to be 3.5%, stemming mainly from errors in sample dimensions, magnetic-field values, and random thermal fluctuations in the Hall voltage. Sample compositions and homogeneity are also a major factor. The major portion of the error was systematic, however, and changes in Hall voltage could be observed to better than 1% within a given run.

The samples were prepared from pure (99.999%) starting materials by melting the constituent elements in an argon-arc furnace and quenching. The ingots were cut into many thin wafers with projecting "ears" near the center, and then handlapped to the desired thickness (about 0.10 in.). Platinum current leads were spot welded to the ends, and voltage leads were spot welded to the "ears" of the samples. A detailed description of sample preparation, sample geometry, apparatus, and measuring procedure appears elsewhere.[17]

Chemical and spectroscopic analysis confirmed the existence of Fe in concentrations comparable to the nominal concentrations calculated from the weights of the starting materials. However, the nominal concentrations gave more consistent and reasonable results, and were therefore used throughout this work.

The absolute resistivity and the residual-resistivity ratio were measured for the Cu-Au and Cu-Au(Fe) alloys. The absolute resistivity of the Cu-Au alloys followed the classical $x(1-x)$ behavior (where x is the concentration of one of the constituents) for disordered alloys. The residual-resistivity ratios were used to give a measure of the amount of structural ordering. A few isolated samples were found to have anomalously large residual-resistivity ratios, indicating the presence of an ordered phase, and the Hall data for these alloys are therefore not included in the results. The degree of ordering present was comparable for all remaining alloys within a particular series and the measured effects are thus predominantly due to the addition of Fe and not due to differing amounts of ordered phase.

In order to investigate the effect of annealing on the measured Hall coefficients, some of the ingots were cold worked before being cut to shape, and then annealed for 10 days under vacuum at 830 °C and quenched in a brine solution. It was found that this procedure shifted the Hall coefficient for a given Cu-Au host and all its corresponding Cu-Au(Fe) alloys by the same amount, so that the contribution due to the Fe remained unaffected. All data are therefore presented for alloys as obtained from the furnace, with no further treatment.

The resistivity was measured as a function of temperature for several Cu-Au(Fe) samples. The characteristic Kondo contribution proportional to $\ln T$ was found in all cases and the resistivity due to the Fe impurity was found to be linear in impurity concentration within experimental error. This indicates that the Fe is in solution, that single-Fe-impurity effects predominate (the dilute limit), and that errors in the nominal Fe concentrations are at worst systematic.

In order to interpret the Hall-coefficient data obtained for Cu-Au(Fe) alloys, it was necessary to obtain measurements for the host Cu-Au system. The Hall coefficient at 4.2 °K is plotted as a function of at.% Au in Cu in Fig. 1. For comparison data of Dugdale and Firth[13] and Barnard *et al.*[14] on disordered Cu-Au alloys are included on the plot. The agreement is very good qualitatively, and quantitative agreement is excellent at the Cu-rich end. The value of $(-6.55 \pm 0.2) \times 10^{-13}$ V cm/AG obtained for Cu in the present experiment agrees very well with previous results. These data serve as a further check on the reliability both of the samples and the measurements. The behavior of the Hall coefficient shown in Fig. 1 can be understood in terms of the variation of Fermi-surface

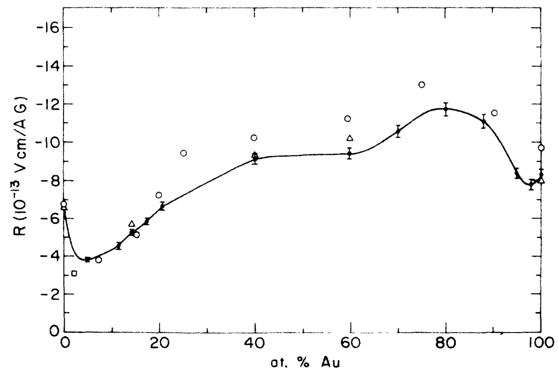

FIG. 1. Hall coefficient of host Cu-Au alloys as a function of composition. The data points refer to: Φ—untreated samples; △—samples which were cold worked and annealed; ○—data of Barnard *et al.* (Ref. 12); □—data of Dugdale and Firth (Ref. 11).

parameters as a function of composition, and will be discussed in Hall Effect II.

III. RESULTS AND DISCUSSION

The Hall coefficient (at 1.5 and 4.2 °K) as a function of magnetic field from 0 to 60 kG appears in Fig. 2 for ten different Cu-Au hosts containing varying amounts of Fe impurity. The effect of an equivalent nonmagnetic impurity was investigated by substituting the isoelectronic element Ru for the Fe in several Cu-Au(Fe) alloys. The contribution due to Ru was found to be small and field independent, whereas Fe gives rise to relatively large field-dependent effects, which are thus apparently magnetic in origin.

The data exhibit several major features: (a) To first order, the effect due to Fe is linear in Fe concentration C, with the possible admixture of a small C^2 term; (b) upon alloying Fe into Cu-Au, there is a strong reduction[18] in magnitude of the Hall coefficient for small amounts of Fe (of the order of 100 ppm), and this reduction is strongly field and temperature dependent; and (c) the dependence on temperature and field is much greater for the Cu-rich alloys than for the Au-rich alloys. This is consistent with the existence of a spin-compensated state. Since T_K is of the order of degrees for Cu-rich alloys, we span the Kondo state in energy for the available temperatures and fields, and thus see a large effect. For Au-rich alloys T_K is a fraction of a degree, so that we are well above

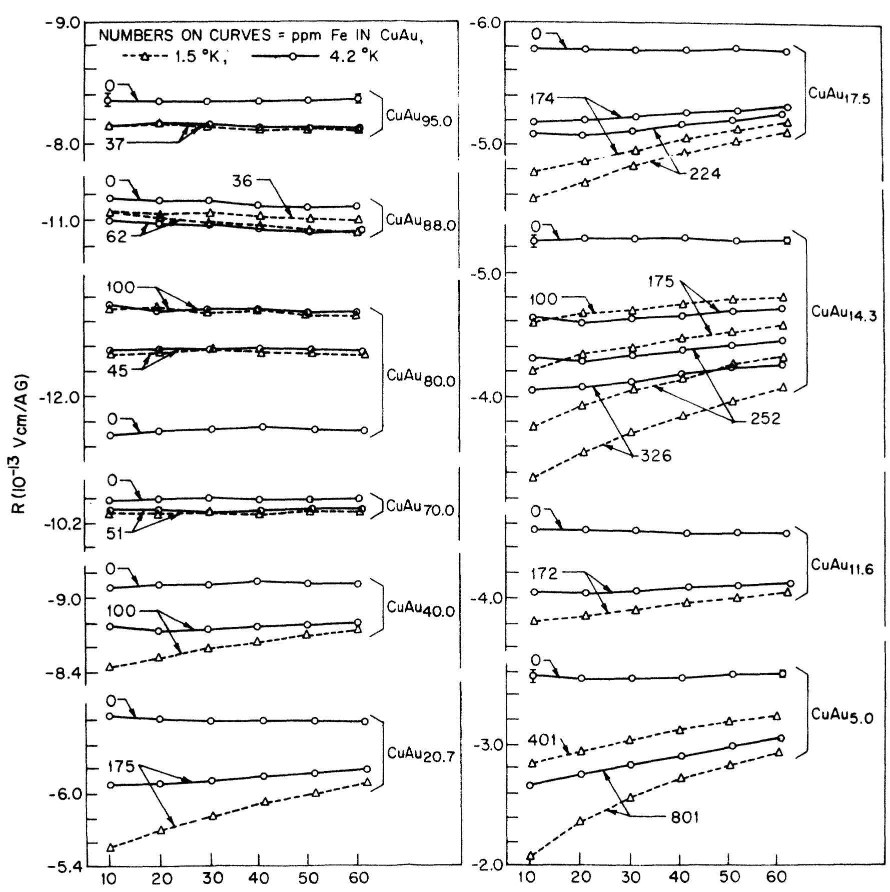

FIG. 2. Hall coefficient of Cu-Au(Fe) alloys as a function of magnetic field. Data are presented for ten different Cu-Au host compositions containing varying amounts of Fe as labeled. Solid lines and dashed lines are for 4.2 and 1.5 °K, respectively. The error bars show random error only.

the Kondo state in temperature, and increasing temperatures and fields have little effect on the spin-compensated state. A more detailed discussion of the data follows.

A. Dependence on Fe concentration

One of the most striking features of the data is the concentration dependence, which is predominantly linear. To first order, the data for each host can be fitted to the expression $|R| = |R_h| - a(H,T)C$, where R_h is the Hall coefficient of the host alloy without Fe, and $a(H,T)$ is a phenomenological parameter derived from the data which depends on host composition, on field and temperature, but not on concentration. The most extensive data for a single host (i.e., largest number of different Fe concentrations) were obtained for the alloy Cu-$Au_{14.3}$, for which the Hall coefficient is presented in Fig. 3 as a function of concentration.

A term linear in concentration is not expected on the basis of previous theories by More,[3] BMW,[4] and BHS,[6] contrary to our present findings. On the other hand, Fert and Jaoul[5] and Giovannini[19] obtain a linear term by introducing an extra (skew scattering) spin-orbit term into their Hamiltonian. These theories all assume a single-carrier host. However, using the ordinary *s-d* Hamiltonian only, we show in Hall Effect II that one can account for the observed behavior by invoking several carriers which are known to exist in Cu-Au (and, in fact, in most realistic materials).

We also examined the data to determine whether there are terms in C^2 (and higher-order terms). The large size of the error bars in Fig. 3 makes it impossible to deduce directly any small deviation from linearity. The major portion of this error is systematic, however, and can be eliminated using the following two-step procedure. By plotting $(|R_h| - |R|)/|R_h| C = a(H,T)/|R_h|$, we eliminate systematic errors deriving from current, voltage, and field measurements. The quantity $a(H,T)/|R_h|$ still contains rather large errors due to uncertainties in thickness determinations and impurity concentration, so that a comparison of absolute values has no meaning. However, for any given pair of samples for which R_h and R were measured as a function of field, these errors in thickness and concentration are again systematic, so that a comparison of relative values at different fields is meaningful. In order to examine the behavior of $a(H,T)/|R_h|$ for various samples as a function of field, we therefore shift the values of $a(H,T)/|R_h|$ for various concentrations so that they coincide at an arbitrarily chosen field and temperature. We chose 60 kG and 1.5 °K, and the resulting shifted values

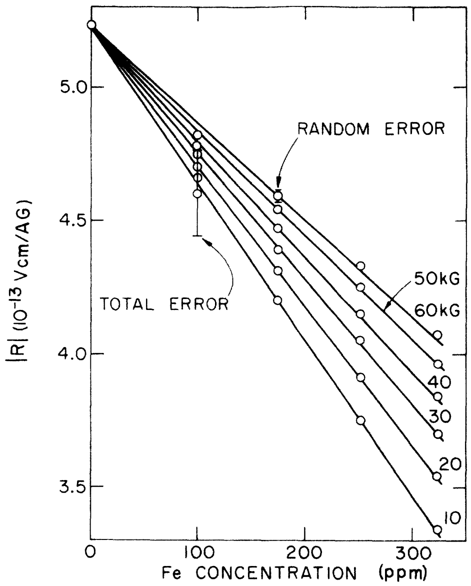

FIG. 3. Hall coefficient at 1.5 °K as a function of Fe concentration for $Cu_{85.7}Au_{14.3}$(Fe) alloys. The larger error bars show the total error, while the smaller error bars denote the random part of the error only.

$a'(H,T)/|R_h|$ are shown in Fig. 4. The error bars include random errors, but no systematic errors as discussed above. The curves clearly do not superimpose, indicating the presence of nonlinear contributions. Note that in all cases the additional contribution increases $a'/|R_h|$ for increasing C.

Note that the percentage change for the $CuAu_5$ host is particularly large. Since the Fe concentrations in this host are greater by approximately a factor of 2 than in other hosts, this might indicate that nonlinear contributions arise from interaction effects between impurities. However, T_K is a good deal higher for the $CuAu_5$ host, and it is well known that larger impurity-concentration levels are allowed in higher-T_K systems before interaction effects occur. We believe that these nonlinear contributions arise from a different source. In Hall Effect II we predict quadratic and higher-order corrections to the predominantly linear behavior of the excess magnetoresistance and Hall coefficient.

B. Dependence on temperature and field

The qualitative behavior of the Hall coefficient as a function of temperature and field can be compared with the calculation by BHS.[6] It is shown in Hall Effect II that if the phenomenological parameter $a(H,T)$ is concentration independent (i.e., R is strictly linear in C), then $a(H,T)$ should vary directly as the magnetoresistance calculated by BHS and shown in Fig. 5. A plot of $a(H,T)/|R_h|$ vs H, for one carefully measured sample including addi-

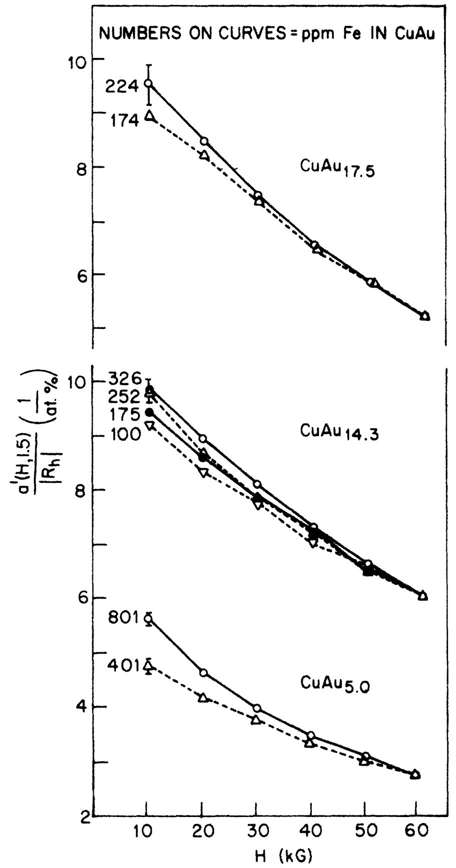

FIG. 4. Shifted parameter a' $(H,\ 1.5)/|R_h|$ (see text) as a function of magnetic field for three Cu-Au hosts containing Fe. All values are derived from data taken at 1.5 °K.

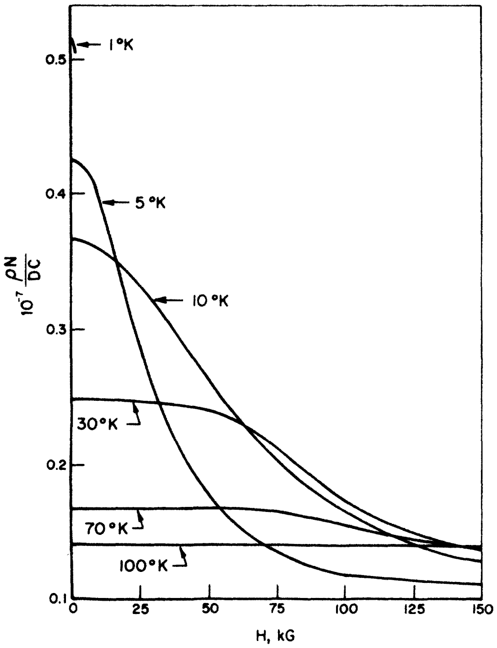

FIG. 5. Resistivity as a function of magnetic field, calculated by BHS (Ref. 6) for $T_K = 16$ °K. Here ρ is the resistivity, N is the number of unit cells in the lattice, D is the conduction-electron bandwidth, and C is the impurity concentration.

tional low-field points, appears in Fig. 6 for $T = 1.5$ and 4.2 °K. The qualitative agreement between these data and the calculated magnetoresistance is very good. We do not expect quantitative agreement because the calculation of Fig. 5 is based on the free-electron model, while the measured materials have a complicated band structure and the Kondo parameters are not well known.

The effect of nonlinear terms in C can be seen by examining the 5-at.%-Au data in detail. Figure 7 shows the parameter $a(H,T)/|R_h|$ from Hall-coefficient data (solid line) and $\Delta\rho/\rho(0)$ from magnetoresistance data (dashed line). Neither the Hall-coefficient data nor the magnetoresistance have the expected qualitative behavior shown in Fig. 5 and found for our more dilute Fe-doped samples. In particular, the curvature of $\Delta\rho$ does not change sign at higher fields, and the curvature of the R vs H data is of the wrong sign. The existence of nonlinear terms could explain this behavior. Assuming that the largest terms in R are linear and quadratic in C, we can effect a separation of these two terms using data for two Fe concentrations by solving two simultaneous equations. The resulting coefficient of the linear term is shown in Fig. 7 (dot-dash line) and does behave as expected, indicating that the predominant nonlinear contribution is in fact quadratic.

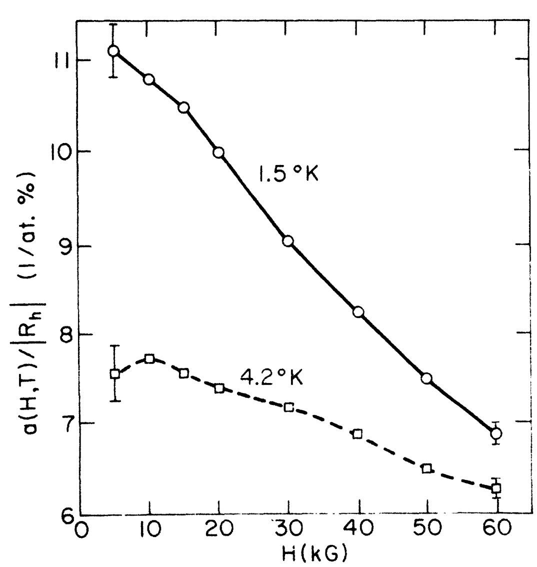

FIG. 6. The parameter $a(H,T)/|R_h|$ as a function of magnetic field for 252-ppm Fe in $Cu_{85.7}Au_{14.3}$. The error bars show random error only.

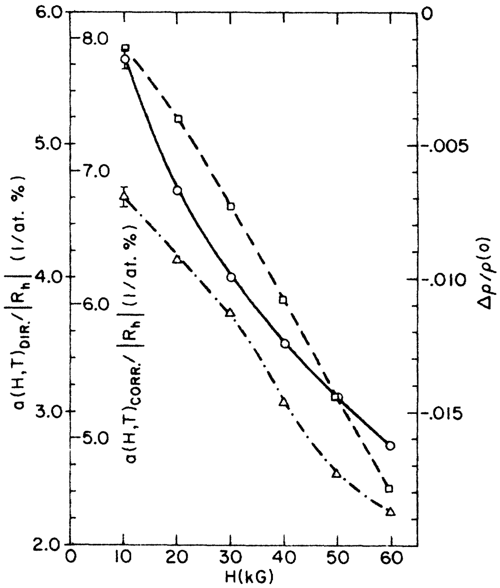

FIG. 7. Magnetoresistance $\Delta\rho/\rho(0)$ (dashed line) and $a(H, T)_{DIR}/|R_h|$ (solid line) at 1.5 °K as a function of magnetic field for 801-ppm Fe in $Cu_{95}Au_5$. Here $\Delta\rho = \rho(H) - \rho(0)$. The dot-dashed line represents $a(H, T)_{CORR}/|R_h|$, the coefficient of the linear term as discussed in the text. The total error for the $\Delta\rho/\rho(0)$ data is smaller than the symbols. The random error is shown on the low-field points for $a(H, T)_{DIR}/|R_h|$ and $a(H, T)_{CORR}/|R_h|$, and this error decreases continuously to a value smaller than the symbols at high fields.

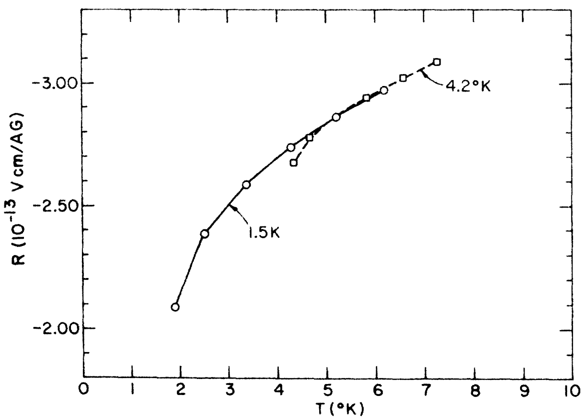

FIG. 8. Hall coefficient as a function of $[T^2 + (sg\mu_B H/k_B)^2]^{1/2}$ for 801-ppm Fe in $Cu_{95}Au_5$, assuming a value $g = 2$, and scaling parameter $s = 0.75$ (see text and Table I). Note that the abscissa appears in units of temperature. The random error is approximately the size of the symbols or smaller.

In order to show the equivalence of thermal ($k_B T$) and magnetic-field energies ($g\mu_B H$) in breaking up the spin-compensated state, the Hall data obtained at both temperatures (1.5 and 4.2 °K) were plotted as a function of these energies. The best results were obtained by treating the thermal and field energies as orthogonal vectors, thus plotting R as a function of the square root of the sum of the squares of the energies, and assuming a scaling factor s, such that $k_B T = sg\mu_B H$. The 5-at.%-Au data are plotted in this manner in Fig. 8. Also, the values of s required to get the best fit between the two temperature runs appear in Table I for various Cu-Au(Fe) alloys.

C. Dependence on host composition

We now examine the bahavior of the data as a function of host composition. The quantity chosen to represent a measure of the overall field effect is $(R_{60} - R_{20})/R_h C$, where R_{60} and R_{20} are the values of the Hall coefficient at 60 and 20 kG. The low value was not chosen at 0 or 10 kG, because R_0 can be deduced only by an unreliable extrapolation, and R_{10} has a large error. The difference, $R_{60} - R_{20}$, was normalized to concentration and to the host value R_h, as is suggested by the theory in Hall Effect II. The variation of $(R_{60} - R_{20})/R_h C$ (for $T = 1.5$ and 4.2 °K) as a function of at.% Au appears in Fig. 9. The most prominent features of these data are the maximum around 20-at.%Au for the 1.5 °K data and the sign reversal for Au-rich alloys. It should be noted that the error was much larger for the Au-rich data because the lower Kondo temperatures dictated lower Fe concentrations. However, the sign reversal does appear to be real.

The behavior of the Hall coefficient as a function of host composition for the Cu-rich alloys can be understood in terms of the Kondo state as follows. For high Kondo-temperature alloys to the left of the maximum, the available fields are not sufficient in energy to produce a large effect on the spin-compensated state. As more Au is added and T_K decreases, the field energies become more effective in breaking up the low-temperature state, the largest effect occurring at 20-at.% Au. As more Au is further added (alloys to the right), T_K is re-

TABLE I. Scaling parameter s ($k_B T = sg\mu_B H$), deduced to give the best equivalence between thermal and field energies, for various Cu-Au(Fe) alloys.

at.% Au	at. ppm Fe	s
5.0	801	0.75
11.6	172	0.56
14.4	175	0.52
14.2	252	0.55
17.5	174	0.51
17.5	224	0.55
20.7	175	0.52
40.0	100	0.56

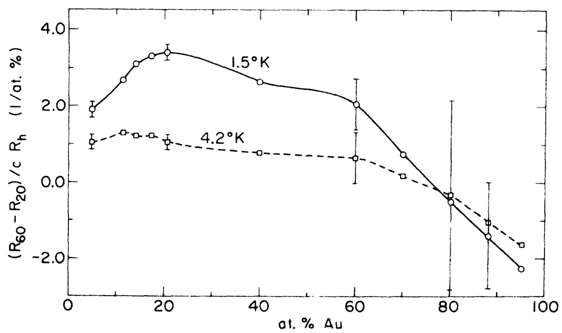

FIG. 9. Normalized change in Hall coefficient due to Fe impurity as a function of Cu-Au host composition. The error bars shown random error only, which in this case is the major contribution.

duced further, so that the ambient temperature of 1.5 °K becomes comparable with T_K, and eventually higher than T_K. For these alloys, the thermal energy is sufficient to break up the spin-compensated state, and the effect of fields is progressively reduced. The data at 4.2 °K fit with this explanation because the peak shifts to the left (or higher T_K) for our higher measuring temperature. More quantitatively, one can estimate T_K for the host composition at which the peak value occurs (i.e., 20-at.% Au for the 1.5 °K data), by assuming that for this alloy T_K is centered in the range of field energies. The measurements were taken at 1.5 °K, and the center of the field range is 40 kG or 4 °K (using 10 kG as roughly equivalent to 1 °K). Following the procedure in the last paragraph of Sec. III B, we can calculate $T_K = [(1.5)^2 + (4)^2]^{1/2} = 4.3$ °K for the Cu-Au_{20} host. This agrees quite well with the estimate of 3 °K by Loram, Whall, and Ford[11] for this composition, considering that it is only an order-of-magnitude calculation.

IV. CONCLUSION

We have measured the Hall coefficient of a series of Cu-Au alloys containing dilute amounts of Fe, where we varied both the host Cu-Au composition and the Fe-impurity concentration. We find that the Hall coefficient due to the Fe impurity is strongly field and temperature dependent, and that these effects are magnetic in origin. The dependence on impurity concentration is predominantly linear, contrary to expectations based on some previous work[3,4,6] which used the free-electron model. Our experimental results concerning the temperature, field, and concentration dependence can be explained in terms of a theory which includes the effects of a multiple-carrier host, and which is presented in the following paper, Hall Effect II.

By varying the Cu-Au host composition, we were able to vary T_K (and thus the energy kT_K associated with the Kondo state) relative to the available temperature and field energies. The temperature and field dependence as a function of host composition are found to be consistent with the existence of a low-temperature spin-compensated state.

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