Transition from the Magnetic to the Nonmagnetic Transitional Impurity State in Copper-Aluminum Alloys: The Nature of the Nonmagnetic State

O. F. Gruber
Physik Department der Technischen Hochschule, Munich, Germany

and

J. A. Gardner
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania

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The static susceptibility of Mn and Fe impurities has been measured in several liquid copper-aluminum alloys, ranging in concentration from 80 at.% copper to 80 at.% aluminum. The impurity susceptibility in the copper-rich alloys is well described by Kondo perturbation theory. The parametric fit indicates that the zero-order state is the same as in pure copper and that T_K rises rapidly with aluminum concentration. In the aluminum-rich alloys the susceptibility of both impurities increases rapidly with temperature, in sharp contrast to the constant susceptibility found for the low-temperature "nonmagnetic" impurity and in contrast to the predictions of both the Kondo bound-state model and the weak-coupling–spin-fluctuation model which have been suggested for this impurity state. The latter model cannot be made consistent with the data, but it is speculated that the Kondo model may display anomalies similar to those found experimentally if the bound state is disrupted by thermal scattering.

INTRODUCTION

It is well known[1] that the high-temperature magnetic properties of Mn and Fe in noble metals are qualitatively similar to those of free paramagnetic ions. The impurity susceptibility has a Curie-like temperature dependence with a Curie constant approximately that expected for a free ion. Transitional impurities in trivalent metals do not exhibit free-ion magnetism on the other hand but display a large paramagnetic susceptibility which is approximately constant below room temperature. This experimental investigation was undertaken in order to study continuously the transition from the "magnetic" to the "nonmagnetic" state of Mn and Fe impurities in host alloys of variable electron per atom ($\mathfrak{z}$) ratio. The impurity susceptibilities in liquid Cu-Al alloys of 20, 40, 60, and 80 at.% Al have been measured and are given in this paper. Determination of the host nuclear resonance perturbation by impurities in this same alloy system is presently being completed and will be published later. Some preliminary results are given in this paper.

We chose to study liquid alloys primarily for experimental reasons. Copper and aluminum are completely miscible in the liquid state, and several percent of either impurity may be dissolved easily. The susceptibility per impurity in the liquid state is found experimentally to be independent of concentration for as much as 5% of impurity, and it can consequently be measured accurately. Some difficulty may be anticipated in comparison of these experimental results with present model calculations for an impurity interacting with the conduction band of a low-temperature solid. The lack of long-range order in liquids is of no consequence since the model is not sufficiently detailed to take band structure into account. In fact since the conduction-band density of states is approximated by a constant, a liquid alloy corresponds more closely to the model than does a low-temperature solid alloy in which the impurity environment is subject to statistical variation. The simple Anderson model which we discuss is probably as applicable to liquid alloys as to pure metals, but calculations of the physical properties of this model may need to be altered at very high temperature. Little change is necessary for mean-field calculations other than the inclusion of thermal averaging which may affect any fine structure on a scale of the thermal energy. This kind of model temperature dependence is also important for the solid and has been considered in detail already. Many-body calculations which incorporate spatial and temporal correlations between the impurity and the conduction electrons may need more serious revision to be applicable to a high-temperature experiment in which these correlations are thermally restricted. To our knowledge such thermal effects have not yet been considered in any detail, and we can only speculate on what changes may occur. In the following discussion it is suggested that the anomalous temperature dependence observed for the susceptibility of transitional impurities in liquid aluminum and the liquid Cu-Al alloys may result from thermal disruption of a many-body impurity–conduction-electron state. Although this suggestion requires theoretical justification, it does provide a possible basis for distinguishing two different descriptions of the non-

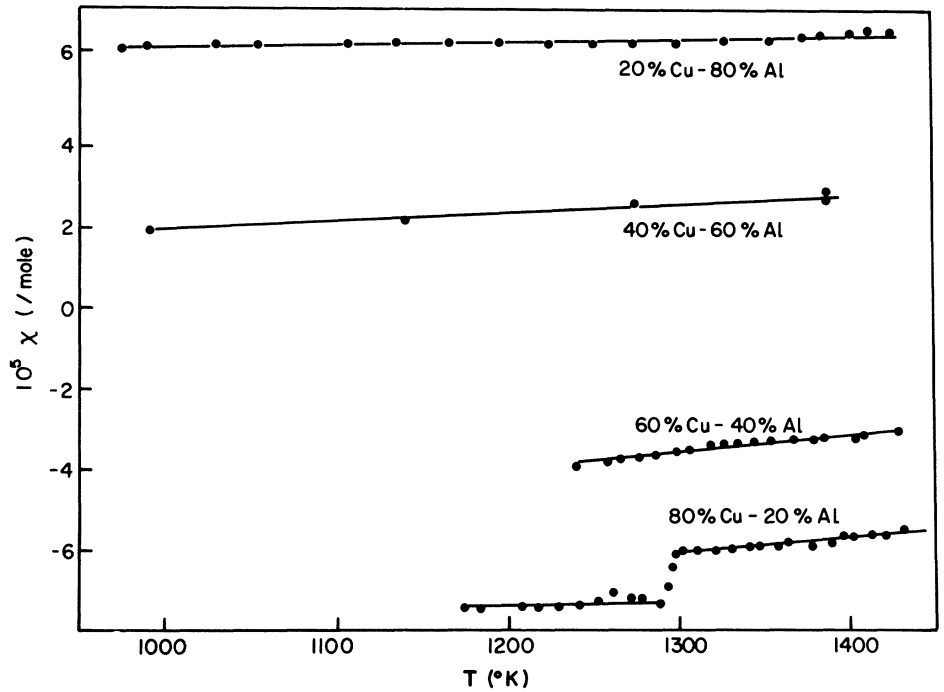

FIG. 1. Molar susceptibility of the liquid Cu-Al host alloys. The alloy concentrations shown are atomic percentages. Since the 80 at.% Cu-20 At.% Al alloy is also a solid solution, the susceptibility of this alloy is shown below the liquidus. Experimental inaccuracy for χ is 0.5×10^{-5} cgs/mole.

magnetic state which otherwise have qualitatively similar features.

EXPERIMENTAL RESULTS

The susceptibilities of the Cu-Al host alloys are shown vs temperature in Fig. 1. The impurity susceptibility χ_I at 1100 °C in each host alloy, in pure Cu,[2] and (for Mn) in pure Al[3] is given in Table I. χ_I is defined by

$$\chi_I = (1/c)[\chi_A - (1-c)\chi_H] , \quad (1)$$

where χ_H and χ_A are the susceptibilities of the host and the host with concentration c of impurity, respectively. The relative temperature dependence of χ_I in all these hosts is shown in Figs. 2 and 3. Qualitatively the magnitude of χ_I is found to decrease smoothly with increasing Al concentration, and its temperature dependence changes from a Curie $1/T$ behavior in pure Cu to a nonlinear increasing function of temperature in pure Al. The susceptibility of Mn and Fe in all the copper-rich liquid hosts is qualitatively similar to that in pure liquid copper, with the Curie behavior being replaced by a more and more pronounced Curie-Weiss-like temperature dependence as aluminum is added. The impurity susceptibilities in the aluminum-rich alloys display an equally marked similarity with that of Mn in pure liquid Al. There is apparently a well-defined transition from a magnetic impurity state to a nonmagnetic state in the vicinity of the 50-50 at.% concentration point for both Mn and Fe.

In order to facilitate the discussion of these results and gain some perspective on the nature of the impurity state in liquid metals, it is helpful to compare the known high- and low-temperature susceptibilities of Mn and Fe in pure copper and aluminum. The impurity susceptibility of *Cu*Fe has been measured in quenched metastable solution from a few millidegrees to room temperature[4,5] and in true solid solution from 900 °C through the melting point.[2] Although the magnetic moment is somewhat larger at high temperature, all data are roughly consistent with a free spin susceptibility proportional to $1/T$ above the Kondo temperature ($T_K \sim 16$ °K) with a magnetic moment corresponding to a spin between $\frac{3}{2}$ to 2. On melting χ_I increases by about 5% and continues to follow a $1/T$ dependence in the liquid state. At low temperature the susceptibility departs markedly from a Curie law and for moderate fields may be fit by a form[1]

$$\chi_I = \mu^2/3k(T+T_K) , \quad (2)$$

where μ is approximately the high-temperature magnetic moment. Since Mn is soluble to a considerable degree in copper, the susceptibility of *Cu*Mn has been measured from a few degrees through the melting transition.[2,6,7] A Curie susceptibility is observed with a magnetic moment slightly smaller

TABLE I. The impurity susceptibility for Fe and Mn in liquid Cu-Al alloys. T_K and μ are found by fitting the data to Eq. (6) of the text. For pure Cu, T_K cannot be determined in this way and the known value for the solid is used instead. Experimental uncertainty for χ_I is approximately $\pm 0.10 \times 10^{-3}$ cgs/mole.

Host	Impurity	χ_I(1100 °C) (cgs/mole)	T_K (°K)	μ/μ_B
Pure Cu	Mn	2.55[a]	0.06[b]	5.57
	Fe	1.85[a]	16[c]	5.14
80 at.% Cu-20 at.% Al	Mn	2.38	62	6.22
	Fe	1.57	38	4.89
60 at.% Cu-40 at.% Al	Mn	1.91	160	6.27
	Fe	1.02	237	5.10
40 at.% Cu-60 at.% Al	Mn	1.51	...	...
	Fe	0.58	...	...
20 at.% Cu-80 at.% Al	Mn	1.27	...	...
	Fe	0.46	...	...
Pure Al	Mn	1.09[d]	...	...

[a]Reference 2. [c]Reference 4.
[b]Reference 8. [d]Reference 3.

than that of a free spin of $\frac{5}{2}$. Careful measurement has shown that the Curie "constant" is actually increasing slightly with temperature between 20 °C and the melting point.[6] As in *Cu*Fe a 5% discontinuity is observed at the melting point, and the $1/T$ dependence continues in the molten state.[2] The very low Kondo temperature of ~60 mdeg and strong impurity interactions preclude normal susceptibility measurement below T_K, but nuclear orientation studies[8] are consistent with a form similar to Eq. (2).

Since the electronic properties of simple metals change little on melting, the impurity state should be very similar in the high-temperature solid and the liquid state. The small change of the Mn and Fe susceptibility on melting and their similar temperature dependence in the two phases of copper confirm this supposition for *Cu*Mn and *Cu*Fe. Small changes on melting are also found for the susceptibility of other transitional impurities in copper.[2] Because the 80-20 at.% Cu-Al alloy is the only one of the host alloys which is also a solid solution, the impurity susceptibility was measured across the melting transition only in this alloy, and it also exhibits a small increase in magnitude and little change in slope on melting.

The *Al*Mn system has not been as well studied as the two Kondo systems described above, and because of the limited solubility of Fe in Al, very little at all is known of *Al*Fe. The impurity susceptibility of Mn in Al has been measured only below room temperature[9] and in the liquid state,[3] and unlike the magnetic case previously discussed, there is little similarity between the high- and low-temperature susceptibility. At low temperature χ_I is approximately constant at 1.4×10^{-3} cgs/mole, while at the liquid melting point it is 0.8×10^{-3} cgs/mole and increasing sharply with temperature. The reason for the different temperature dependence of the susceptibility at low and high temperature is not known.

DISCUSSION

Most models for the transitional impurity state are special cases of the Anderson model[10] of an impurity with orbital d states $|d, s\rangle$ having energy ϵ_{ds}, interorbital exchange energy U_1, and an exchange energy U between spin states of the same orbital. An interaction energy V_{kd} is assumed between $|d, s\rangle$ and the conduction-electron state of momentum k. For the purposes of our qualitative discussion it is sufficient to ignore U_1, or equivalently assume a single nondegenerate orbital. We also neglect interactions between impurities. The Anderson model has been treated most extensively in the strong coupling or magnetic limit of U/Δ large and in the weak coupling or nonmagnetic limit of Δ/U large. Here Δ is the "level width" and is given by

$$\Delta = \pi \rho \left| V_{kd} \right|^2 , \tag{3}$$

where ρ is the conduction-electron density of states. Although a few difficult theoretical problems remain unsolved, physical properties of the model in these two limits are fairly well understood. There has been notable progress in solving the Anderson model in the intermediate-coupling range between the two limits,[11-14] but the approximations which are presently necessary are difficult to assess quantitatively. We shall discuss only the "spin-fluctuation" extension of the weak-coupling limit for which some semiquantitative results are available.[15-17] Since the model parameters are in general not directly accessible experimentally, the appropriate approximation for any system must be determined by the fit to experiment. Unfortunately this procedure is not unambiguous, and there are serious questions about which limit if either is appropriate in many impurity systems. Because of the experimental observation of a Curie susceptibility for Mn and Fe in copper it is generally agreed that these impurity states should be treated in the strong-coupling limit, and we consider this case first.

Schrieffer and Wolff[18] demonstrated that in the magnetic limit the Anderson interaction Hamiltonian may be approximated by the Kondo interaction $H = J\, \vec{s} \cdot \vec{S}$ between the conduction-electron spin $\vec{s}$ and the local spin $\vec{S}$, provided the energy ϵ_d of the occupied orbital and the energy $\epsilon_d + U$ of the unoccupied orbitals are not too close to the Fermi level. These energies have been determined from optical properties of several magnetic impurity systems

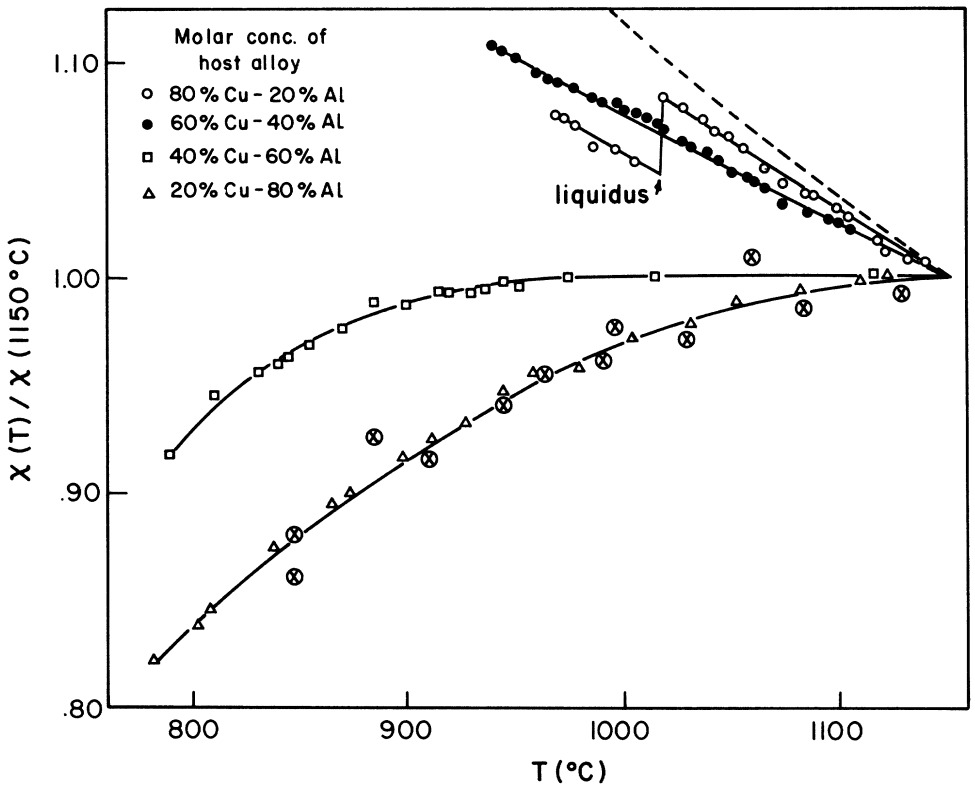

FIG. 2. Susceptibility of Mn in liquid Cu-Al alloys relative to its value at 1150 °C. The susceptibility in solid 80 at.% Cu-20 at.% Al is shown also. The circled x's are the susceptibility of Mn in liquid Al from Flynn *et al.* (Ref. 3), and the dashed line represents a $1/T$ dependence which is observed for the susceptibility of Mn in liquid copper (Ref. 2).

and found to be well removed (2 or 3 eV) from the Fermi level.[1,19] If energy is referenced with respect to E_F, the coupling energy J is given by

$$J = 2\,|\,V_{kd}|^2\, U/\epsilon_d(\epsilon_d + U)\ , \tag{4}$$

and the condition for the validity of the transformation is that $|\rho J| \ll 1$. It should be noted that J is an intrinsically negative energy. Kondo[20] showed that perturbative expressions for the physical properties of a magnetic impurity interacting with the conduction-electron gas by this mechanism are well behaved at high temperature but become unphysical below a characteristic temperature

$$T_K = D/k\ e^{1/\rho J}\ , \tag{5}$$

where D is a cutoff energy usually taken to be of order ϵ_d. This characteristic temperature is identified with that at which the experimental properties are found to have similar anomalous behavior (and for which we have used the same symbol). The susceptibility above T_K for an impurity having unperturbed magnetic moment μ is given by[21,22]

$$\chi = \frac{\mu^2}{3kT}\left(1 + (\rho J) + (\rho J)^2 \ln\frac{kT}{D} + \cdots\right)$$

$$= \frac{\mu^2}{3k\,T}\left(1 - \frac{1}{\ln(T/T_K)}\right) \tag{6}$$

on summing all orders to logarithmic accuracy. Although the high-temperature susceptibility in most clearly magnetic impurity systems is qualitatively well described by the above relation, the strong inverse dependence on T masks the perturbation, and the applicability of the Kondo model is demonstrated much more dramatically by resistance, specific heat, and thermopower anomalies. A solution of the Kondo problem at low temperatures has not as yet been found despite massive efforts,[23] and no approximation has proved to be completely satisfactory. It is generally believed, however, that at low temperature the impurity and conduction electrons combine into a many-body state having zero net spin and finite susceptibility at $T = 0$. This expectation is qualitatively consistent with most experimental data.

If μ is chosen for the best fit, the effective Curie constant $C(T) = \chi_I\, T$ for Mn and Fe in pure solid copper is qualitatively well described by Eq. (6) over a broad temperature range. Above the melting point Gardner[24] found that χ_I decreased somewhat less rapidly than inversely with temperature, but

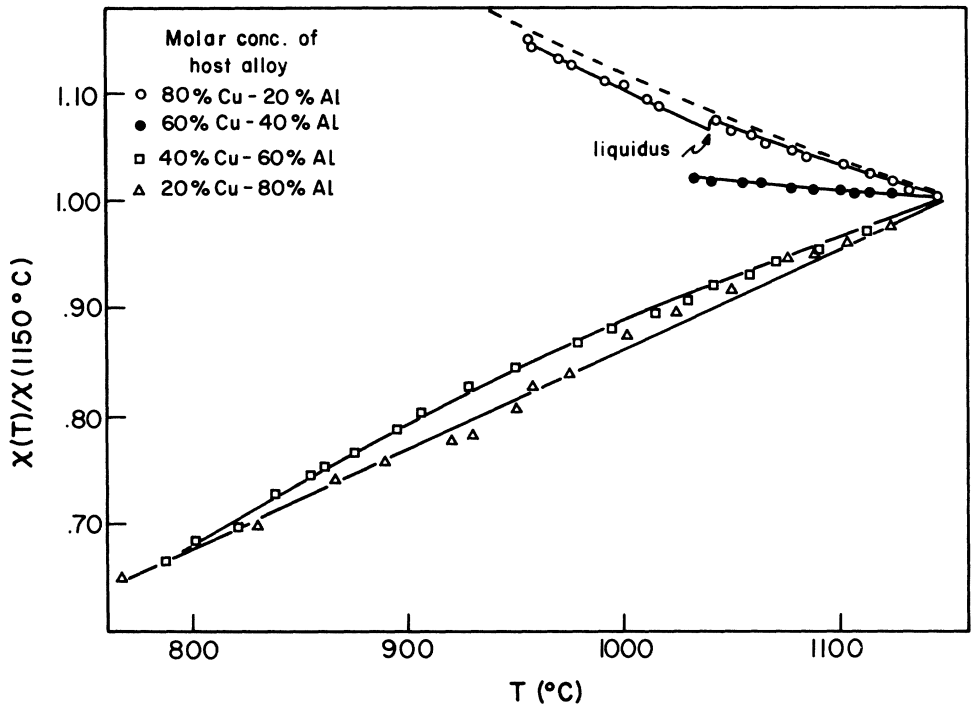

FIG. 3. Susceptibility of Fe in liquid Cu-Al alloys relative to its value at 1150 °C. The susceptibility in solid 80 at.% Cu-20 at.% Al is shown also. The dashed line represents a $1/T$ dependence which is observed for the susceptibility of Fe in liquid copper (Ref. 2).

the deviation is within the experimental precision, and one may conclude only that the data are not inconsistent with a Kondo interaction. The susceptibility change on melting may be attributed to a small change in the model parameters due to volume expansion or band-structure differences. Since the volume expansion on melting should cause ρ to decrease, the Kondo temperature in the liquid should be somewhat smaller and the susceptibility consequently larger than in the solid. Although this suggestion agrees qualitatively with experiment, it cannot be made quantitative, and we will take the Kondo temperature in the two phases to be the same. In the copper-rich Cu-Al hosts, the deviation of χ_I from a Curie law is pronounced, and one may determine both T_K and μ by fitting the data to Eq. (6). These parameters are given in Table I. The Kondo temperature increases with addition of Al to the host metal, while the magnetic moments correspond roughly to an unperturbed spin of 2 ($\mu = 4.9\ \mu_B$) for Fe and $\frac{5}{2}$ ($\mu = 5.9\ \mu_B$) for Mn in all cases. The approximately constant value of μ indicates that the zeroth-order impurity state in all copper-rich alloys is the same as in pure copper. The good fit of the susceptibility data with Eq. (6) does not of itself justify the Kondo model, because the data can be fit equally well by a variety of other curves including a Curie-Weiss form. The intuitively reasonable dependence of the model parameter on aluminum concentration is impressive, however, and must be taken as strong evidence for the validity of the perturbative Kondo formula. It should be emphasized as well that the constant value of μ over more than an order-of-magnitude range of T_K is a significant result, since it indicates that the impurity spin is not renormalized to any great extent by the Schrieffer-Wolff transformation. Consequently if the value of the impurity spin may somehow be inferred (as is frequently possible), μ is fixed, and it should not be regarded as a continuously variable fitting parameter.

It is clear from the rapid increase in T_K as aluminum is added to the host and from the qualitative change in the temperature dependence of χ_I near 50-50 at.% Cu-Al concentration that the same type of Kondo perturbation theory can no longer be used for the impurity state in the aluminum-rich host alloys. Since the qualitative similarity among all the susceptibility data in the aluminum-rich alloys shown in Figs. 2 and 3 leads us to believe that the impurity states in all these hosts and in pure aluminum are described by the same model, we shall discuss the nonmagnetic models for *Al*Mn and then extend them to the liquid alloys.

Historically the constant low-temperature susceptibility of transitional impurities in aluminum has been taken as evidence that the impurity electrons become a part of the conduction band, and

Friedel[25] proposed a model of a localized "virtual bound state" which overlaps the Fermi level and contributes to the density of states. The nonmagnetic limit of the Anderson model is a quantitative extension of this model, for which the impurity contribution (per orbital) to the density of states is given by

$$\rho_{\mathrm{loc}}=\frac{2}{\pi}\frac{\Delta}{\epsilon_d^2+\Delta^2}\ . \tag{7}$$

Because of the Coulomb repulsion at the impurity site, the susceptibility is enhanced above the normal Pauli value by a factor η, where

$$\eta=\frac{1}{1-\frac{1}{2}U\rho_{\mathrm{loc}}}\ . \tag{8}$$

While this model is qualitatively consistent with all experimental data, Schrieffer[26] has shown that the data are also entirely consistent with a Kondo model state having such a high T_K that only the many-body ground state is observed. He pointed out that if the susceptibility is given by Eq. (2) and if T_K is large, the system would appear to be nonmagnetic. Although in both limits a constant zero-order susceptibility is predicted, some temperature dependence is expected in either case. A Curie-Weiss temperature dependence is found for low-temperature Kondo systems, while a small decrease proportional to T^2 is expected in the nonmagnetic limit because of thermal averaging over the impurity density of states.[27] The susceptibility of *Al*Mn has been observed to decrease as T^2 over a small temperature range, and the data are in agreement with the nonmagnetic model provided a level width of a few tenths of an eV and an enhancement factor of order 5 are postulated.[9] On the other hand, a nuclear resonance frequency shift closely related to the impurity susceptibility but which is not subject to the subtraction errors inherent in determination of χ_I has been found to be well described by the temperature dependence of Eq. (2) with $T_K \sim 2000\ ^\circ\mathrm{K}$.[28] This frequency shift is observed for an Al near neighbor to the Mn. It is proportional to the conduction-electron spin-density disturbance around the impurity and should be approximately proportional to the impurity susceptibility. From Eq. (2), the low-temperature susceptibility of a Kondo state having $T_K = 2000\ ^\circ\mathrm{K}$ and $\mu = 5.9\ \mu_B$ is 2×10^{-3} cgs/mole, in satisfactory agreement with the experimental value of 1.4×10^{-3} cgs/mole. Consequently there is some semiquantitative agreement with both models, and there are no low-temperature data which clearly discriminate in favor of either.

In a quantitative sense, however, the fitting parameters are not internally consistent in either case. The Kondo model is a good approximation only when $|\rho J| \ll 1$, and a Kondo temperature of several thousand degrees cannot be attained with this restriction. If the cutoff energy in Eq. (5) is taken to be a few eV as suggested by experimental values of ϵ_d, $|\rho J|$ must be of order 0.5 if T_K is several thousand degrees. On the other hand, the small level widths which are necessary to fit the data to the weak-coupling model susceptibility are much too small to be consistent with the comparable or larger values found for the magnetic state of the same impurity, and an enhancement factor of 5 is clearly inconsistent with the weak-coupling limit of $\eta \sim 1$. Obviously neither limit is entirely appropriate to the nonmagnetic transitional impurity state without some additional intermediate-coupling corrections. The difficulties associated with Kondo ground-state theory have prevented any extension beyond the Kondo approximation which is valid at low temperature. Corrections to the weak-coupling limit lead to dynamic spin fluctuations and a renormalization of the enhancement factor.[15,16] It has been suggested[15] that the latter may cause a reduction of the susceptibility which is initially proportional to T^2 and which goes over into a Curie form when the thermal time $\hbar/kT$ becomes of the order of the spin-fluctuation time. The intermediate-coupling corrections do not change qualitatively the model susceptibility and may resolve the inconsistency which we noted. We conclude that either model provides an acceptable qualitative description of the low-temperature experimental properties of the nonmagnetic impurity state, and a quantitative description may be obtained if intermediate-coupling corrections are included. Unfortunately even though the models are very different in principle, the qualitative properties of the two are the same, and the quantitative differences are probably too uncertain to allow a distinction to be made on purely quantitative grounds.

Since the low-temperature properties of *Al*Mn and other nonmagnetic transition-metal impurity systems are qualitatively consistent with both the Kondo and weak-coupling model it is somewhat surprising to find that the high-temperature susceptibility is apparently inconsistent with both. Rather than decreasing, the susceptibility of Mn in liquid Al and both Mn and Fe in the aluminum-rich Cu-Al liquid hosts is found to increase sharply with temperature. The most obvious possible cause of the anomaly is that the model parameters may change with temperature, either because of lattice expansion, vibrational averaging, or some explicit temperature dependence such as that responsible for the T^2 dependence of χ_I. Flynn *et al.*[3] estimated that lattice expansion alone could cause a large enough increase in the weak-coupling model density of states to explain the susceptibility anomaly. Ignoring the T^2 dependence of χ_I it is straightforward to verify that a free-electron volume dependence for ρ implies that the susceptibility of a half-filled level with an enhancement factor of 5 will increase

twice as rapidly as the volume even if V_{kd} and U do not change. This increase is considerably smaller than that found experimentally, but it is possible that ρ and V_{kd} may decrease rapidly with volume expansion, causing the susceptibility to increase even when the T^2 term is subtracted. A similar volume dependence for ρ and V_{kd} in the Kondo limit would cause T_K to decrease as a function of temperature, and if the decrease is very rapid, the susceptibility may increase, as observed experimentally. There are probably many kinds of parametric temperature dependence which could cause the susceptibility of either model to increase with temperature, and despite a natural skepticism for attributing anomalous behavior to *ad hoc* parametric changes, such possibilities should not be summarily ruled out. Fortunately however, this explanation of the susceptibility anomaly can be criticized on more substantial grounds.

We have remarked that the conduction-electron spin polarization near the impurity is expected to have approximately the same temperature dependence as the impurity susceptibility. The spin polarization can be calculated for the weak intermediate-coupling model and the Kondo model at $T \gg T_K$. The radial dependence of the polarization is sensitive to the detailed energy dependence of the parameters and is probably not very reliable, but it does not change with temperature, and the magnitude at any given point is proportional to the susceptibility. Experimental observation of resonance line broadening by magnetic impurities has shown that the spin polarization distant from the impurity is proportional to the susceptibility at $T \gg T_K$ as expected, but that it is not exactly proportional at lower temperature.[1] The temperature dependence of the two are qualitatively similar, however. Both are constant at very low temperature, and both decrease monotonically as the temperature rises. In liquid alloys containing magnetic impurities the resonance line is not appreciably broadened but is shifted in proportion to the average of the impurity-induced conduction-electron spin polarization over host nuclei. The average is dominated by the near-neighbor positions to the impurities, because the spin polarization decreases rapidly and oscillates in sign far from the impurity. In pure copper and all Cu-Al alloys the sign of the liquid host frequency shift corresponds to a negative magnetization near either Mn or Fe impurities.[2,29] In *Al*Mn a negative magnetization is found both in the liquid[3] and low-temperature solid,[28] and the magnitudes of the average over host nuclei in the two cases differ by less than a factor of 2. A negative magnetization is not necessarily inconsistent with either model, and we shall restrict our attention to the temperature dependence of the magnitude of the liquid host resonant frequency shift.

In pure copper the host shift is roughly proportional to the susceptibility as expected for a Kondo state of $T \gg T_K$, and it has a negative slope with temperature in all the Cu-Al alloys and in pure Al, whereas the impurity susceptibility has a negative slope only in the copper-rich alloys. In the aluminum-rich alloys the magnitude of the host frequency shift decreases smoothly (as does the susceptibility) with increasing aluminum concentration. The host frequency shift in liquid *Al*Mn decreases with temperature even more rapidly than would be expected from an extrapolation of low-temperature data. It is clear that a parametric temperature dependence cannot be accepted as the cause of the unexpected positive slope of χ_I unless the same parametric change also results in a sharp decrease in the magnitude of the spin polarization near the impurity. Since we do not know the spin polarization near an impurity in a Kondo bound state, and since the calculated parametric dependence of this quantity is probably unreliable in any case, we must turn to experiment to find the parametric dependence.

Although there are several parameters in each case, the physical properties are sensitive to only one combination, (ρJ) for the Kondo model, and $(\frac{1}{2} U \rho_{1oc})$ for the weak intermediate-coupling model. To the extent that other changes may be neglected, a parametric dependence on temperature would be equivalent to changing the $\mathfrak{z}$ ratio of the host and should consequently cause a change of the same sign in the susceptibility and host frequency shift. Since the explicit temperature dependence of the two properties also apparently has the same sign, even if the model parameters do change with temperature it seems very unlikely that the susceptibility and host frequency shift could be changed in opposite directions as is found experimentally. We should point out that the decrease of the host frequency shift cannot be attributed either to high-temperature damping of the extended spin-polarization cloud which is negligible near the impurity or to a simple change in the average over host nuclei as the lattice expands. The radial dependence of the polarization in *Al*Mn can be estimated from the low-temperature resonance shifts, and the changes of their average as the lattice expands should be negligible.

We have discussed in detail how thermal averaging, lattice expansion, and possible parametric changes with temperature can affect the physical properties of systems which are described by either model. It seems unlikely that any of these particular mechanisms can be responsible for the experimentally observed temperature dependence of the impurity susceptibility and host resonance shift in liquid aluminum and the aluminum-rich alloys, but we have not yet considered the possibility of a restriction of many-body correlations

at high temperature. Many-body correlations are very important for the Kondo bound state, and it could be disrupted by any restriction of this sort. Other than a possible reduction of the spin-fluctuation time, however, the weak intermediate-coupling calculations are not changed by any considerations of many-body restrictions. A decrease of the spin-fluctuation time would cause the susceptibility to decrease rather than increase with temperature as found experimentally. Before discussing the possibility of thermal disruption of the Kondo bound state, we point out that we have now considered every simple way by which the susceptibility and host resonance shift data in the liquid state might be reconciled with the weak intermediate-coupling limit of the Anderson model, and we have rejected every one of them. We therefore conclude that the weak-coupling limit is not a proper model for the nonmagnetic transitional impurity state even with the inclusion of all straightforward spin-fluctuation corrections. This model has long been regarded as almost synonymous with the nonmagnetic transition-metal impurity state, and it goes without saying that it may not be dismissed casually. We emphasize that the high-temperature anomalies which we have discussed are not inconsequential. There is a strong, qualitative, and apparently irreconcilable difference between experiment and this model, and while it is never impossible that differences of this kind may be reconciled in some way which has been overlooked, we feel that the most reasonable possibilities have been examined carefully and rejected for sound reasons. Of course, one may object that even if the model is inconsistent with high-temperature liquid-state experimental data, it may be quite acceptable at low temperature. The model parameters of the impurity state in pure copper and the highest copper concentration alloy apparently do not change greatly on melting, however, and it is unlikely that the parameters change greatly at the aluminum melting point either. If the weak-coupling model is valid for low-temperature solid aluminum, the very minor changes in the aluminum electronic properties on melting can hardly drive the model unrecognizably far into the intermediate- or strong-coupling range. At best the case for this model is very weak.

The Kondo model fares somewhat better. It has been shown that a severe reduction of spin memory time via the spin-orbit interaction of nearby impurities can destroy the Kondo bound state, [30] and it is not improbable that strong thermal scattering can have a similar effect. Since the many-body interactions at low temperature decrease the effective spin of the impurity state, any suppression of these interactions should restore the impurity spin to a larger fraction of its unperturbed value and increase the susceptibility. We point out that an increase of χ_I is a natural consequence of thermal disruption of the many-body interaction, and no further assumptions are necessary to understand the positive slope of χ_I with temperature. Furthermore, any disruption of the bound state must be accompanied by a change in the conduction-electron-polarization cloud, which is not necessarily proportional to the accompanying change in susceptibility. It is possible that the conduction-electron polarization near the impurity can decrease as found experimentally, even though the susceptibility increases with temperature. We may draw several additional inferences about the nonmagnetic state from the nature of the transition which we observe in the liquid alloys. The impurity state of both Mn and Fe undergoes a distinct transition near 50-50 at. % Cu-Al concentration, and there is no indication of any other transition. The magnitude of the susceptibility exhibits no striking discontinuity as ϑ changes from 1 to 3, but the temperature dependence changes markedly at $\vartheta = 2$. Although the anomalous high-temperature susceptibility overemphasizes the difference in the temperature dependence, this is nonetheless characteristic of the Kondo transition observed near $T = T_K$. We have remarked that the Kondo approximation is rigorously valid only for $|\rho J| \ll 1$, and we may expect it to become progressively less applicable as this dimensionless coupling constant approaches unity. At present we do not know at what point the approximation becomes invalid, and it may be a reasonable model for all $|\rho J| < 1$ corresponding to $T_K < 10\,000\,^{\circ}\mathrm{K}$. In this case, and provided no catastrophic change in the impurity energy level occurs as ϑ changes, the impurity state in the liquid alloys should undergo a transition into a Kondo bound state when a ϑ ratio corresponding to a Kondo temperature equal to the temperature of measurement is reached. If this is the transition seen experimentally, we presume that since no other transition is seen, the Kondo model remains valid for all the alloys and for pure aluminum.

We have indulged in a good bit of reasonable but relatively naive speculation about the Kondo model in order to demonstrate that it is not necessarily inconsistent with high-temperature experimental observations. In the absence of calculations which may justify our speculation we cannot rule out the possibility of intermediate coupling for the impurity state near $\vartheta = 3$, but we probably can rule out the usual spin-fluctuation–weak-coupling model. If the Kondo model is not strictly applicable to this nonmagnetic state, a proper picture probably must include spin fluctuations which are strongly related to the Kondo bound-state interactions. Since

this type of fluctuation is not included in any of the spin-fluctuation or other intermediate-coupling pictures at this time, we believe that the Kondo model is presently the most defensible approximation to the nonmagnetic state of Mn and Fe. If the inclusion of thermal disruption into many-body calculations does not prove to be prohibitively difficult, high-temperature experiments of this type may provide a means for determining finally what degree of intermediate coupling is required to describe these states properly. In addition, high-temperature experiments may become a very useful way to study other many-body properties which are not easily accessible at low temperature.

EXPERIMENTAL PROCEDURE

The susceptibilities were measured by the Faraday method. A liquid sample in a covered alumina crucible was suspended by a thin quartz rod into the field of a conventional iron magnet. The sample was carefully positioned at the maximum of $H\,dH/dz$, and its weight recorded with the magnet off and on. The susceptibility was independent of field and all measurements were done at the maximum field of 15 kG. In order to inhibit oxidation and evaporation of the liquid, the sample chamber and balance housing were maintained at a pressure of 40 Torr of purified argon. The sample chamber was heated by a molybdenum-wound water-cooled furnace placed between the magnet pole caps.

The copper, aluminum, and iron (obtained from American Smelting and Refining Co., United Mineral and Chemical Corp., and Johnson, Matthey Ltd., respectively) used for making the samples were all of 99.999% purity, while the Mn (from Carmant Gesellschaft für Technik und Industrie) was 99.9% pure. Some of the samples were made by melting the constituents in an alumina crucible sealed in quartz, agitating the molten metal for approximately 1 h, and then quenching in cold water. Others were made *in situ* by loading the constituents into a sample holder, taking the temperature above the melting points of the host metals, and allowing the sample to homogenize for 1 h or more before beginning the measurement. In the latter case the susceptibility reached an equilibrium value within 20 min and was indistinguishable from that of an alloy made by the first method.

Because the metals homogenized most rapidly at high temperature, the susceptibility was usually measured at 1150 °C first, and then the temperature was slowly decreased with the force being measured periodically over a few hours until the liquid temperature was reached. When the temperature was raised and the high-temperature susceptibility remeasured, the second value was consistently slightly smaller than the first in all alloys containing Mn and Fe. The discrepancy, which was attributed to slow oxidation of the impurity by residual oxygen in the chamber, was negligible provided the measurements were completed within 5 h. Consequently no attempt was made to attain thermal equilibrium at each data point, and the measurements were customarily made as the temperature was drifting slowly. The differing thermal response of the thermocouple and sample to the nonequilibrium situation caused an error of as much as 10 °C in the recorded sample temperature. This is the largest uncertainty in the relative temperature dependence of the copper-rich impurity susceptibilities shown in Figs. 2 and 3.

The volume of the liquid sample was approximately 1 cm^3, and the magnetic force was typically 50 mg for the pure host alloys and 10 times larger with a few percent of Mn or Fe added. The force could be measured with sufficient reproducibility (0.4 mg) that the experimental accuracy is determined by other factors. The predominant uncertainty in the host alloy susceptibility is caused by errors inherent in measuring and subtracting the susceptibility of the crucible and suspension system, while the magnitude of the impurity susceptibility is also sensitive to uncertainty in concentration. We estimate that the precision of the relative impurity susceptibility shown in Figs. 2 and 3 is 2% for the aluminum-rich alloys and becomes negligible in comparison to the temperature uncertainty in the 80-20 at.% Cu-Al alloy. These estimates do not include an over-all uncertainty of about 2% in the calibration of the magnetic field derivative. Since consistency with the previously published results for copper and aluminum hosts is necessary, the same calibration method was used in all three measurements, and systematic differences between these data and those of Refs. 2 and 3 are negligible.

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Resistivity and Magnetoresistance of Dilute Solutions of Mn in Cu-Ni Alloys*

A. R. Harvey† and S. Legvold
Department of Physics and Institute for Atomic Research, Iowa State University, Ames, Iowa 50010

and

D. T. Peterson
Department of Metallurgy and Institute for Atomic Research, Iowa State University, Ames, Iowa 50010

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The electrical resistivity from 2 to 100 K and the longitudinal magnetoresistance from 0 to 85 kOe at 4.2 K have been measured on $Cu_{1-x}Ni_x$ alloys ($x = 0.06$, 0.12, 0.23) containing 0 to 1175 ppm Mn as magnetic impurities. All Mn-bearing samples exhibited resistivity minima, and the difference in resistivity between each $Cu_{1-x}Ni_x$(Mn) alloy and its Mn-free equivalent depended linearly on $\log_{10}T$ for nearly an order of magnitude in T. These phenomena are characteristic of dilute magnetic alloys and suggest that the results can be interpreted in terms of the Kondo effect. This picture is supported by the magnetoresistance of the alloys, which was negative for all Mn-bearing samples. The magnetic contributions to the resistivity and magnetoresistance were also proportional to the Mn concentration and essentially independent of Ni concentration. The former result is interpreted as an indication that interaction effects among the Mn ions were negligible, and the latter result suggests that the Ni had very little effect on the local-moment character of the Mn.

I. INTRODUCTION

The resistivity minimum of dilute magnetic alloys was explained theoretically by Kondo.[1] He based his theory on a model in which it was assumed that localized magnetic moments form at the impurity sites and subsequently interact with the conduction electrons via the s-d exchange interaction. His finding stimulated a considerable amount of theoretical and experimental interest in the properties of dilute magnetic alloys. (Excellent reviews of the theoretical and experimental situations up to 1969 have been given by Kondo[2] and Heeger,[3] respectively.) One of the metals which has been used quite extensively as the host in the experimental work on this problem is Cu. A wealth of evidence[3,4] indicates that Fe, Mn, and Cr exhibit local-moment character in Cu, and of