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Conduction-Electron Spin Polarization near Mn and Fe Impurities in Copper and Copper-Aluminum Alloys

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We have measured the perturbation of the two host-metal Knight shifts by Mn and Fe impurities in liquid copper-aluminum alloys. A simple approximation for the liquid-metal radial distribution function allows the conduction-electron spin polarization near the first-neighbor site to be calculated. The impurities are "magnetic" in the high-copper-concentration host alloys, and the spin polarization is found to have its first node just beyond the first-neighbor position. From the width of the negative-spin-polarization region near the impurity, we show that the cutoff of the spin-spin interaction energy $J(q)$ must be smaller than $2k_F$, and we estimate very roughly that the cutoff should be about $1.2k_F$.

I. INTRODUCTION

It is well known that Mn and Fe impurities are "magnetic" in noble metals but "nonmagnetic" in polyvalent metals. In noble metals at high temperature the impurity magnetic susceptibility has a Curie-like temperature dependence and a Curie constant approximately that of a free ion. In trivalent metals, on the other hand, the impurity susceptibility is paramagnetic and fairly large in comparison to normal Pauli paramagnetism, but it is relatively independent of temperature in most cases. This experimental investigation was undertaken in order to study continuously the transition from the "magnetic" to the "nonmagnetic" impurity state of Mn and Fe impurities in host alloys of variable electron-to-atom ratio. In a previous paper,[1] hereafter referred to as I, the static sus-

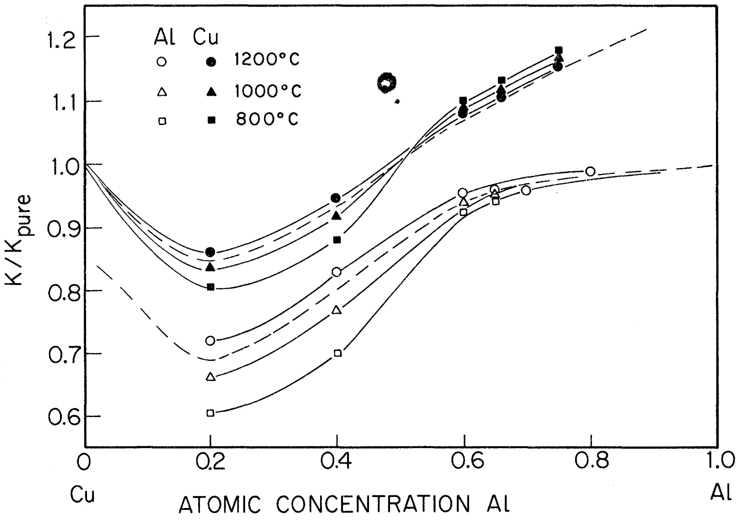

FIG. 1. Knight shifts of copper and aluminum in liquid Cu-Al alloys. The dashed lines are the Knight shifts given in Ref. 2 for a temperature of 1100 °C. All data are normalized to $K(1100\,^{\circ}\mathrm{C})$ in the pure liquid.

ceptibility of Mn and Fe in liquid Cu-Al alloys was reported. In this paper we give the results of NMR measurement of the conduction-electron spin-density perturbation in the Cu-Al host by these impurities.

We chose to study liquid alloys primarily because the mutual solubility of the various metals in the solid state is too limited to allow a broad range of host-electron-to-atom ratios to be studied. Of course, the temperature of measurement is of necessity rather high, but since it is two orders of magnitude smaller than the host Fermi temperature, there is no reason to believe that finite-temperature theory should not be quite as applicable to these liquid systems as to solids. There are some reasons to believe that a liquid host may be preferable to a solid from a theoretical point of view as well. In a solid-host alloy each impurity is subject to statistical variation in its static surroundings, but in a liquid such variations rapidly average (on a time scale of 10^{-12} sec). Consequently, the usual average-band-theoretical model for the host is more reasonable for liquids than solids. In addition, a free-electron model is a better representation of a liquid band structure than a solid. A single plane wave (suitably orthogonalized to the atomic cores) is a fairly good representation of the conduction-electron states in most liquid metals, even for momenta near that of the zone boundaries in the solid. Since a free-electron model is always assumed for the host conduction states, the liquid is a better subject for study on these grounds as well. A final and very important consideration is that nuclear resonance in liquids measures an average, rather than a distribution, of nuclear hyperfine field because of the very rapid diffusion in the liquid state. The perturbation of this average by an impurity is weighted strongly by the conduction-electron spin perturbation near the impurity, a region which is difficult to investigate in the solid state.

II. EXPERIMENTAL RESULTS

In this experimental work we measured the change ΔK of the Knight shift K of each host-metal nuclear-resonance position when impurities were added. In simple metals the Knight shift is primarily due to the contact interaction between the nuclear spin and the conduction-electron spin density at the nucleus. The observed change ΔK is proportional to the average change in the electron spin density at the particular nucleus under consideration. Within experimental error, ΔK was found to depend linearly on the impurity concentration, an indication that impurity-impurity interactions are negligible. We used impurity concentrations in the range of 1–5 at.%, and no evidence of impurity interactions was found even at maximum concentration levels.

The Knight shifts K_{Al} and K_{Cu} depend on the composition of host alloy and are slightly temperature dependent as well. These Knight shifts are shown versus host alloy composition in Fig. 1. The data are in good agreement with previously published results.[2] It is convenient to define a dimensionless quantity Γ_{ij} which is independent of impurity concentration:

$$\Gamma_{ij} = (1/c_i)(\Delta K_j / K_j) , \qquad (1)$$

where ΔK_j is the change in the Knight shift K_j of the jth host-metal resonant frequency when concentration c_i of impurity i is added. $\Gamma_{\mathrm{Mn\text{-}Cu}}$ and $\Gamma_{\mathrm{Mn\text{-}Al}}$ are shown versus host alloy composition in Fig. 2, and $\Gamma_{\mathrm{Fe\text{-}Cu}}$ and $\Gamma_{\mathrm{Fe\text{-}Al}}$ are shown in Fig. 3.

Experimental inaccuracy in determination of the temperature dependence of Γ_{ij} was too large to

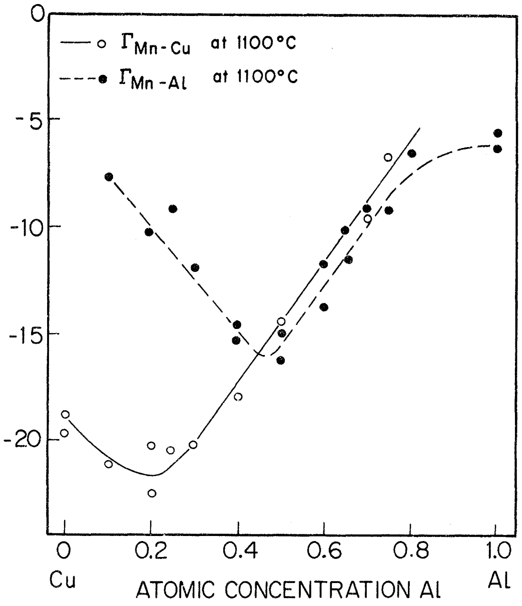

FIG. 2. Normalized Knight-shift perturbation by Mn impurities in liquid Cu-Al alloys. Γ_{ij} is defined by Eq. (1) of the text.

justify anything other than a straight-line fit to the data in the rather limited liquid-state temperature range. The derivative of Γ_{ij} with respect to temperature is shown in Figs. 4 and 5. The derivative is normalized in such a way that it is -1 if Γ_{ij} follows a Curie temperature dependence, as would be expected if the impurity were "magnetic" and interacting weakly with the conduction electrons of the host.

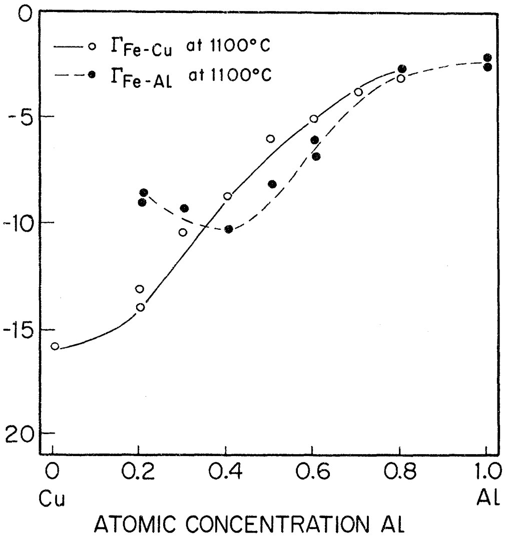

FIG. 3. Normalized Knight-shift perturbation by Fe impurities in liquid Cu-Al alloys. Γ_{ij} is defined by Eq. (1) of the text.

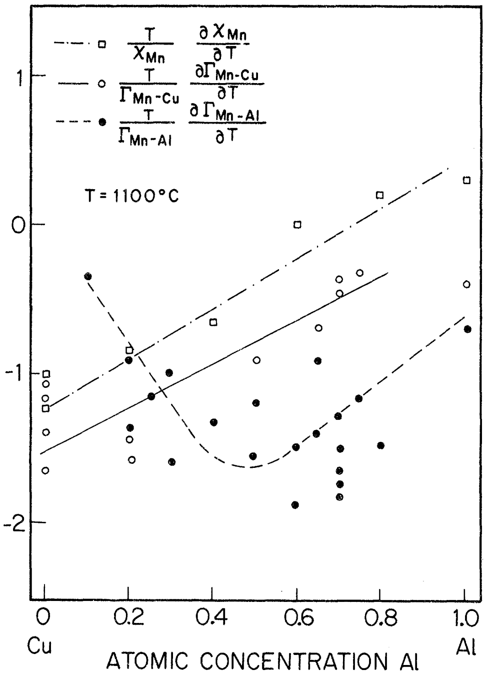

FIG. 4. Temperature derivative at 1100 °C of the Mn impurity susceptibility and host-Knight-shift perturbation in liquid Cu-Al alloys. Susceptibility data are taken from Ref. 1. The derivative in each case is normalized to be equal to -1 if the temperature dependence is a Curie law. The lines are intended only to show the trend of the data.

III. RADIAL DEPENDENCE OF SPIN PERTURBATION

With the assumption that only the contact interaction need be considered, ΔK may be used to find directly the average conduction-electron spin-density polarization at the nucleus j. It is more convenient, however, to discuss the spin polarization of the smooth pseudo-wave-function, which we have approximated by a plane wave in the absence of impurities. In the single orthogonalized-plane-wave (OPW) approximation, it has been shown[3] that in a given host the experimentally measured resonance shift may be taken as directly proportional to the pseudo-wave-function spin density at the nucleus. In this case

$$\Delta K_j / K_j = (s_j - s_p)/s_p , \qquad (2)$$

where s_j is the average pseudo-wave-function spin density at nucleus of type j and s_p is the constant Pauli spin density. It follows that Γ_{ij} may be written in terms of an average of the spin-density polarization $\Delta s_i(r)$ around impurity i:

$$\Gamma_{ij} = \int \Delta s_i(r) P_{ij}(r)\, d^3r / s_p P_j . \qquad (3)$$

Here $P_{ij}(r)$ is the probability of finding a nucleus

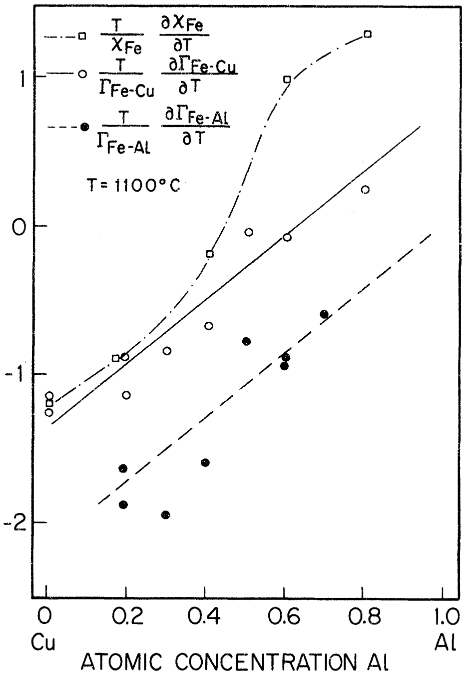

FIG. 5. Temperature derivative at 1100 °C of the Fe impurity susceptibility and host-Knight-shift perturbation in liquid Cu-Al alloys. Susceptibility data are taken from Ref. 1. The derivative in each case is normalized to be equal to − 1 if the temperature dependence is a Curie law. The lines are intended only to show the trend of the data.

of type j at distance r from the impurity and P_j is the average probability of j in the particular alloy.

The virtue of discussing the pseudo-wave-function spin density is that the entire dependence of Γ_{ij} on j is reduced to a dependence on the radial distribution function $P_{ij}(r)/P_j$, which has a sharp peak at the "near-neighbor" distance R_{ij}. Since $\Delta s_i(r)$ is known to decrease rapidly in magnitude and oscillate in sign far from the impurity, we shall neglect all contributions to the above integral beyond the first peak and approximate P_{ij} by a δ function at R_{ij}. For a randomly packed liquid, in which the radii of the j atoms are about the same size, the weight under the peak of P_{ij}/P_j (roughly the number of nearest neighbors to the impurity) depends little on j, and we shall take the weight of the δ function to be 12, corresponding to the number of nearest neighbors in the fcc solid. With these approximations, Eq. (3) becomes

$$\Gamma_{ij} = 12\Delta s_i(R_{ij})/s_p\,, \tag{4}$$

from which the spin polarization at R_{ij} can be obtained from the measured Γ_{ij}. In Fig. 6 we show Δs_{Fe} and Δs_{Mn} at the two points $R_{i\text{-}Cu}$ and $R_{i\text{-}Al}$ in each host alloy. The polarization is shown at 1100 °C and at a temperature 20% lower. Values at the arbitrarily chosen lower temperature were obtained by extrapolation of $\Gamma_{ij}(T)$ in alloys with high liquidus temperatures. We also estimated Δs_i at $R_{i\text{-}Al}$ in pure Cu by extrapolation of $\Gamma_{i\text{-}Al}$ to zero Al concentration, and these results are also given in Fig. 6. Since the atomic volume of Cu is smaller than that of Al, the distance from the impurity to the nearest Cu atom is slightly smaller than the distance to an Al. In Fig. 7 we approximate the distance R_{ij} by the sum of the near-neighbor radii of i and j in their respective pure solids and show Δs_{Mn} in both pure copper and pure aluminum. The magnitude and temperature dependence of the spin polarization at first and second neighbors to Mn impurities in solid aluminum are known,[4] and these values extrapolated to 1100 °C are shown in Fig. 7 as well.

Since $\Delta s_i(r)$ in the liquid hosts is not measured directly but is derived from Γ_{ij}, it is important

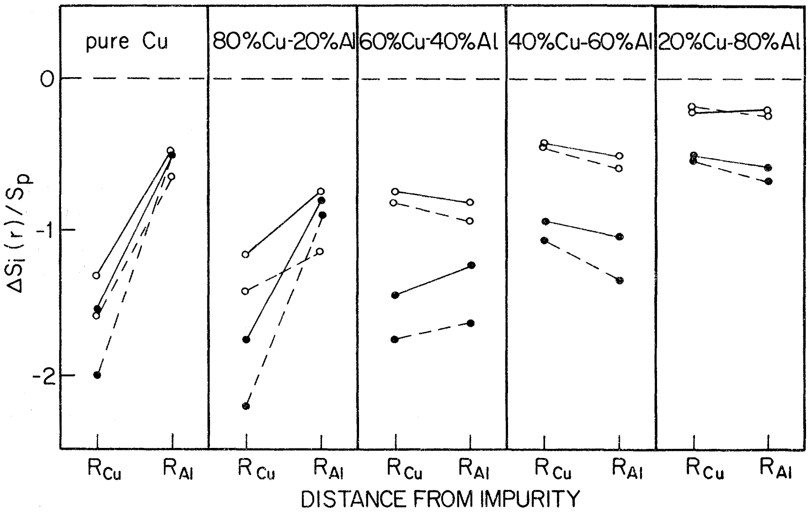

FIG. 6. Conduction-electron spin polarization at the nucleus of the first copper and first aluminum neighbor to the impurity in the host alloy shown. The filled circles are for Mn impurities and the open circles are for Fe. The solid lines join the two values of Δs_i at 1100 °C and the dashed lines join the values of Δs_i at a temperature 20% lower. Concentrations are in atomic percent.

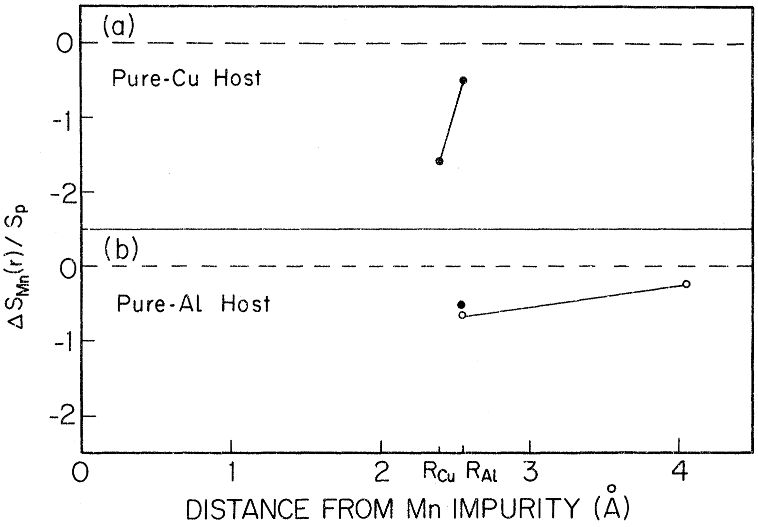

FIG. 7. Conduction-electron spin polarization vs distance from a Mn impurity in (a) pure-liquid-copper host, and (b) pure-liquid-aluminum host at 1100 °C. The open circles in (b) are the polarization at first- and second-neighbor Al sites extrapolated from solid-state results given in Ref. 4.

that we establish what the limits of confidence in the results are. We discuss below the probable uncertainty in the several approximations used in deriving Δs_i. By comparison, experimental error is negligible, except possibly for the temperature dependence of the spin polarization, for which the error is indicated by the scatter in the data of Figs. 4 and 5.

Although our assumption of a δ-function form for P_{ij} is too crude to be quantitatively reliable, the magnitude of Δs_i which results from this approximation is probably not seriously in error. The major error is caused by our neglect of the integral of Eq. (3) beyond the first-neighbor site. From resonance-line-broadening experiments in the solid state one can determine that contributions to Γ_{ij} beyond roughly the third-neighbor position are negligible at liquid-state temperature.[5] Unless the spin polarization at the first-neighbor site is fortuitously close to a node, the second and third neighbors (peaks of P_{ij}) should each contribute less than 25% to the integral, and since they are probably of opposite sign, should largely cancel each other. The relatively good agreement between the two measurements of Δs_{Mn} at the first neighbor in *Al*Mn shown in Fig. 7 supports the validity of this approximation. The relative error in Δs_i at $R_{i\text{-Cu}}$ and $R_{i\text{-Al}}$ should be smaller than the absolute error at either point since both integrals are affected in approximately the same way by the additional terms. The temperature dependence of Δs_i is less reliably estimated by the δ-function approximation. Since the width of the first peak of P_{ij} increases with temperature, the temperature dependence of Γ_{ij} is due both to the intrinsic temperature dependence of $\Delta s_i(r)$ and to the change in the average nuclear position as P_{ij} broadens. The latter effect is neglected by our approximation, and it may be important, particularly for the copper-rich alloys in which Δs_i is a strong function of distance.

The validity of our assumption that the relative perturbation of the Knight shift is exactly equal to the relative pseudo-wave-function spin-density perturbation [Eq. (2)] is difficult to assess. There is little question that the assumption is valid for the aluminum resonance, but we cannot completely rule out the possibility of an unexpectedly large noncontact part of the copper Knight shift. In this case $\Gamma_{i\text{-Cu}}$ would be incorrectly normalized by using the experimental value of K_{Cu} in Eq. (2), and the spin polarization at $R_{i\text{-Cu}}$ would be incorrect in the same proportion. Fortunately, we have a strong experimental indication that noncontact terms are not large. It is clear from Fig. 1 that the ratio of K_{Al} to K_{Cu} does not depend strongly on alloy composition. Barring some extremely fortuitous cancellation, it would appear that the "penetration factors" of the two host metals do not change greatly and that the Knight shifts respond only to a change in the Pauli susceptibility as the alloy composition is altered. The constant ratio of the two Knight shifts indicates that the contact interaction dominates in both metals. It is unlikely that this "normalization" uncertainty could result in a relative error of more than 25% in the spin polarization at the two sites.

At worst, it would seem that the magnitude of Δs_i should be in error by no more than 50%, and the relative error at the two radial distances is probably half as large. Qualitatively, such errors would be most significant when the radial derivative is small, in which case the value and even the sign of the derivative are in doubt. The temperature dependence of Δs_i is also uncertain. Despite the rather large experimental uncertainty in determination of the slope of Γ_{ij} with temperature, it is clear from Figs. 4 and 5 that $\Gamma_{i\text{-Cu}}$, $\Gamma_{i\text{-Al}}$, and χ_i do not in general have exactly the same temperature dependence. No significance can be attached to these differences however, because they may be due entirely to the temperature dependence of P_{ij} and do not necessarily indicate a lack of proportionality between s_i and χ_i.

IV. SPIN POLARIZATION IN KONDO REGIME

In I it was shown that the impurity susceptibilities in the copper-rich composition range were well described by a Kondo model. The unperturbed magnetic moment for Mn (Fe) corresponds rather well to a free ion of spin $\frac{5}{2}$ (2), and its interaction with the conduction band results in a Kondo temperature T_K which increases rapidly with increasing Al concentration. The parameters were established by fitting the susceptibility to an expression which is valid for $T \gg T_K$. Unfortunately, T_K becomes comparable to the temperature of measurement near the center of the host composition range, and this expression cannot be used in the aluminum-rich host alloys. Neither a Kondo model nor any simple spin-fluctuation model adequately describes the experimental results for the impurity state in these latter hosts, and we shall discuss only the copper-rich region in which the impurity state can be described by the Kondo approximation.

The Kondo-interaction Hamiltonian between the impurity spin $\vec{S}$ and the conduction-electron spin density $\vec{s}$ is given by[6]

$$H_K = -J(r)\vec{S}\cdot\vec{s}\,, \tag{5}$$

where $J(r)$ is a predominantly negative energy density. The Fourier transform $J(q)$ is usually approximated by a negative constant J for scattering within a bandwidth q_c (energy bandwidth D) of the Fermi surface and zero otherwise. It is characteristic of this interaction that perturbation expansion in J fails to converge unless the temperature is much greater than the Kondo temperature T_K where

$$T_K = (D/k_B)\, e^{1/\rho J}\;. \tag{6}$$

Here ρ is the conduction-electron density of states. The natural perturbation-expansion parameter is ρJ, and for liquid-metal temperature the requirement that $T \gg T_K$ is automatically fulfilled if the expansion parameter is small.

The expression which was used to fit the susceptibility is a sum to all orders in ρJ of most divergent terms. Only T_K appears explicitly in the result, but ρJ may be estimated by assuming that D is equal to the Fermi energy. We find that ρJ is about -0.05 to -0.2 for Mn and Fe in pure Cu. In pure copper the lowest-order terms in ρJ are adequate to describe the experimental susceptibility, but in the alloy hosts the fully summed expression must be used.

Unfortunately, there is at present no corresponding calculation of the spin polarization around a Kondo impurity. To first order in the coupling constant, the polarization is given by the familiar Ruderman-Kittel-Kasuya-Yosida (RKKY) oscillation.[7,8] Higher-order terms have been considered by several authors,[9,10] and apart from the observation that the spin polarization should be driven by the self-consistent interacting impurity spin,[10] rather than the zero-order value, all have found negligible corrections to the first-order polarization in the region near the impurity. We will assume the first-order term alone to be adequate for the near spin polarization. Heeger[6] has shown that the spin polarization to first order can be written simply as the Fourier transform of the q-dependent conduction-electron susceptibility

$$\chi(q) = \mu_B^2\rho\left(1 + \frac{1-(q/2k_F)^2}{q/k_F}\,\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right) \tag{7}$$

and the effective field

$$h(q) = [J(q)/g\mu_B]\,\langle S_z\rangle$$

experienced by the conduction electrons in interaction with the impurity spin $\langle S_z\rangle$. We have

$$\Delta s_i(r) = \frac{1}{g\mu_B}\int h(q)\chi(q)e^{i\vec{q}\cdot\vec{r}}\,d^3q\;. \tag{8}$$

Yosida[8] has evaluated the integral for $q_c \to \infty$, and he finds

$$\Delta s_i(r) = \frac{k_F^3}{2\pi}\,(J\rho)\,\frac{j_1(2k_F r)}{(2k_F r)^2}\,\langle S_z\rangle. \tag{9}$$

We need consider only one qualitative feature of the above expression to see that it does not agree with the spin polarization shown in Fig. 6. The polarization given by Eq. (9) is negative (with respect to $\langle S_z\rangle$) for very small r and goes to zero first when $2k_F r = 4.5$, corresponding to $r = 1.7$ Å for a copper host. The experimental polarization shown in Fig. 7 is negative for distances out to about 2.7 Å, however. The disagreement is undoubtedly due to the approximation of $q_c \to \infty$ used in Eq. (9). It is well known that the Kondo interaction energy J can be related to the parameters of the Anderson model through the Schrieffer-Wolff transformation.[11] This transformation shows that $J(q)$ should be cut off at a momentum corresponding to the energy of the impurity state, which implies that $q_c < 2k_F$. Equation (9) is a Fourier transform of a function of width $2k_F$. If J is cut off at $q_c < 2k_F$, a simple uncertainty-principle argument shows that the first zero of the spin polarization will occur at a distance of very roughly $2k_F/q_c$ times the value we found above for constant J. From our experimental results we estimate that q_c should be about $1.2k_F$.

Since the radius of the negative-spin-polarization region does not change qualitatively as aluminum is added, we suppose that the shape of $J(q)$ is roughly independent of host composition, but that the magnitude must increase with aluminum concentration to account for the observed increase in T_K. It is somewhat surprising that ρ apparently decreases initially as Al is added to pure copper, so the increase in $-J$ must be large enough to cause $-\rho J$ to increase. The decrease in ρ is indicated by the negative slope of both K_{Cu} and K_{Al} in Fig. 1 near pure copper composition.

A quantitative analysis of the spin polarization requires a better understanding of the form of $J(q)$. Up to this time there has been little motivation for any theoretical determination of the q dependence of J, because very little is known experimentally about the radial dependence of Δs_i in Kondo systems. Resonance line broadening in low-temperature solids is sensitive to the oscillation amplitude of the polarization at large distances from the impurity, but the details of the radial dependence are undetermined. The present results, which yield both the phase and approximate magnitude of the spin polarization at the near-neighbor position to the impurity, are an important addition to our knowledge of the spin polarization, and we hope they will stimulate further thought about the form of the q dependence of the interaction.

V. EXPERIMENTAL PROCEDURE

The experimental apparatus is similar to that described previously.[3] The powdered sample is suspended in finely powdered alumina which does not allow the liquid droplets to coalesce. The sample is sealed into a quartz capsule along with a small Ta wire getter. Bridge detection is used, and all data were taken at an oscillator frequency of 13 mHz. Samples were made by placing the appropriate amount of Cu, Al, and impurity metal in an alumina crucible, sealing in quartz, and heating the metals at 1200 °C for approximately an hour with frequent shaking. The melt was quenched into water, filed, and passed through a 250-mesh sieve. The samples were chemically analyzed, and those which showed macroscopic inhomogeneity or any significant departure from the nominal concentration of any constituent were discarded. Previous experience has shown that microscopic inhomogeneity in the sample powders quickly disappears on melting, because the vapor pressures of the various metals reach equilibrium rapidly at high temperature.[12]

VI. CONCLUSIONS

The spin polarization around Mn and Fe impurities in liquid Cu-Al alloys is calculated from experimental measurements of the perturbation of Cu and Al Knight shifts. The approximations made in the analysis introduced some quantitative uncertainty into the radial derivative of the spin polarization and into the precise temperature dependence, but the uncertainty is qualitatively unimportant for the very copper-rich alloys in which the impurities are clearly "magnetic." Qualitative comparison of the spin polarization around these magnetic impurities with first-order Kondo perturbation theory indicates that the q-dependent spin-spin interaction energy $J(q)$ is cut off at a momentum of order $1.2k_F$. Our present ignorance of the form of $J(q)$ precludes quantitative analysis of the data, and it is suggested that these results may be very helpful in future theoretical work on this problem

Our original purpose in taking up this work was to study experimentally the transition from the magnetic to nonmagnetic state of these transitional impurities. This purpose has been incompletely realized. We have observed a transition from a magnetic state which we can describe semiquantitatively by the Kondo model, but the transition is incomplete because the "nonmagnetic" impurity state of Mn or Fe in pure aluminum does not seem to be properly described by any simple "nonmagnetic" theory. This problem was discussed in considerable detail in I. We are currently continuing this work with other hosts and other impurities in order to observe a transition into a state which can be unambiguously described by the well-understood nonmagnetic small spin-fluctuation limit of the Anderson model. If such a transition can be attained, it may then be possible to clarify the physics of this questionable region by extrapolation from the well-understood "magnetic" and "nonmagnetic" regimes.

ACKNOWLEDGMENTS

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Magnetic Susceptibility at Zero Temperature for the One-Dimensional Hubbard Model*

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The magnetic susceptibility at absolute-zero temperature for the one-dimensional Hubbard model is studied exactly as a function of the concentration of electrons by using Lieb and Wu's theory for this system. Our analysis essentially follows Griffiths's method for the magnetic susceptibility of the one-dimensional Heisenberg antiferromagnet, and is a generalization of Takahashi's calculation to the systems with an arbitrary concentration of electrons. The ground-state energy and the magnitude of local moments at each site are also studied. Combined with the results on the susceptibility, they should suggest how the effect of the Coulomb interaction on the properties of the system at low temperatures changes with the concentration of electrons.

I. INTRODUCTION

One-dimensional systems are fascinating for various reasons. They are usually easier to handle mathematically than higher-dimensional systems. One can often give exact statements without resorting to approximations.[1] Moreover, in some cases and for some properties, they are remarkably different from higher-dimensional systems. The one-dimensional Hubbard model, a model of interacting itinerant electrons, is not an exception.

The one-dimensional Hubbard Hamiltonian has the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 ;$$

$$\mathcal{H}_0 = -\sum_{ij\sigma} t_{ij}\, c^\dagger_{i\sigma} c_{j\sigma} , \qquad (1.1)$$

$$\mathcal{H}_1 = U \sum_{i} c^\dagger_{i\uparrow} c_{i\uparrow} c^\dagger_{i\downarrow} c_{i\downarrow} ,$$

where t_{ij} is assumed to be t for $|i-j|=1$ (nearest-neighbor hopping) and zero otherwise. For this model Lieb and Wu[2] first gave an exact analysis on the ground state by essentially the same approach as that for the one-dimensional Heisenberg spin system[3,4] and for the one-dimensional fermion gas with δ-function interactions.[5]

In our Hamiltonian (1.1) there are three fundamental parameters for the thermodynamic properties of the system, that is, the strength of the Coulomb interaction relative to the transfer integral U/t, the concentration of electrons N/N_a (N and N_a are the total number of electrons and lattice points, respectively), and the temperature of the system k_BT. Let us review previous work on this system and then make the purpose of the paper clear, using these parameters.

A. Case (i): Half-Filled Band ($N/N_a = 1$)

1. Absolute-Zero Temperature ($k_BT = 0$)

The ground-state energy was obtained in an analytic form by Lieb and Wu.[2] According to them, the ground state is antiferromagnetic and insulating. Following this work, the spin-wave spectrum and the magnetic susceptibility at zero temperature were calculated by Ovchinnikov[6] and Takahashi,[7] respectively. By these calculations the properties of the one-dimensional half-filled Hubbard model were clarified almost completely as far as the absolute-zero temperature is concerned.

2. Finite Temperature ($k_BT \neq 0$)

Unfortunately, no exact solution is available for finite-temperature properties of the infinite system. But the thermodynamic properties of finite chains were calculated exactly by Shiba and Pincus.[8] Based on this calculation, we can guess a gradual "transition" from the paramagnetic and metallic state at high temperatures to the antiferromagnetic and insulating state at low temperatures.

B. Case (ii): System with $N/N_a \neq 1$

According to the Lieb-Mattis theorem[9] the ground state of our system is a singlet irrespective of the concentration of electrons. Even if $N/N_a \neq 1$, Lieb and Wu's theory should be useful and, in fact, it predicts a metallic ground state. But the dependence of the ground-state energy and other quan-