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NMR study of Co impurities in liquid Cu-Al hosts*

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The Knight shift of dilute Co impurities in liquid Cu_xAl_{1-x} host alloys is reported. The Knight shift is positive and is a linear function of Co susceptibility over much of the range with host composition and temperature only implicit parameters. For the "nonmagnetic" composition range up to $x = 0.6$, this linearity is shown to imply that the ratio of Co spin-to-orbital susceptibility is constant. A deviation from linearity is found as $x \rightarrow 1$ and is attributed to a host dependence of the Co hyperfine coupling constants. The results are discussed in terms of the degenerate Anderson model, and it is shown that the Hund's exchange energy J can be no greater than 0.3 eV.

INTRODUCTION

The magnetic properties of transition-metal impurities dissolved in normal metals are found to depend very strongly on the host conduction-electron density.[1,2] The magnetic susceptibility of the $3d$ elements Cr, Fe, and Mn, for example, is large and varies inversely with temperature when they are present as dilute impurities in noble metals. In polyvalent metal hosts, however, these impurities have a much smaller and less-temperature-dependent susceptibility. These two situations are usually described theoretically in qualitatively different terms. In the first case the impurity is pictured as an ion interacting weakly with the conduction band and having strong internal exchange which favors magnetic alignment of the d spins. In the second case the system is described by a locally distorted conduction band which has an increased density of states near the impurity $3d$ energy level. The impurity susceptibility in this latter model is simply related to the increased density of states at E_F. In the so-called spin-fluctuation region between the two extremes one generally is forced to describe the system by a perturbative extension of one or the other limiting case. Unfortunately the thermodynamic properties of these two models turn out to be surprisingly similar, and it is seldom clear which, if either, is appropriate to a given experimental system.

In an attempt to clarify this situation somewhat we undertook an experimental study of Co impurities in liquid Cu_xAl_{1-x} host alloys. In this system the impurity state apparently undergoes a transition from a nonmagnetic to a strong spin-fluctuation regime as x is increased from 0 to 1. Since the nonmagnetic model is expected to be valid near $x=0$, it was felt that this system could yield some insight into the transition region where magnetic fluctuations become important. In this paper we give the results of our Knight-shift measurements. The Co Knight shift was found to be positive and to vary linearly with Co susceptibility over most of the composition range with no indication of any explicit temperature or host dependence. An exception was found only for Co in pure liquid copper hosts for which the Knight shift is considerably larger than the linear extrapolation would indicate. We tentatively attribute this anomaly to a positive change in a Co hyperfine coupling constant as the host Al concentration approaches zero.

We interpret the linearity of the Knight shift versus susceptibility as an indication that the ratio of orbital to spin susceptibility is constant. If this impurity state is described by the Anderson model, the Hund's exchange energy $\bar{J}$ must be considerably smaller than it is for other $3d$ impurities. The results are discussed in terms of the Narath-Dworin solution of the degenerate Anderson model, and we show that $\bar{J}$ can be no larger than 0.3 eV. If $\bar{J}$ is neglected entirely, these and prior results give the product of the impurity density of states ρ_d with the enhancement factor $(1-\frac{1}{10}\bar{U}\rho_d)^{-1}$. If the Coulomb energy $\bar{U}$ is no greater than 5 eV, then the enhancement factor is smaller than 2 in the composition range from $x=0$ to 0.6. Consequently, the model solution should be semiquantitatively valid in this range, and we can define a probable range of values for ρ_d, for the orbital and spin hyperfine fields, and for the orbital and spin susceptibilities of Co.

EXPERIMENTAL PROCEDURE

The NMR measurements were made with a conventional single-coil cw spectrometer which was locked to the resonance absorption mode. A molybdenum-wound furnace provided sample temperatures up to 1200 °C. With a 10-sec lock-in time constant, the Co signal-to-noise ratio was never greater than 10:1 and was typically 1:1 or smaller. Signal averaging times up to 15 min were often used to detect the weaker signals. Co Knight shifts could be detected in alloys containing as little as 1.5-at.% Co, and the results were found to depend little on Co concentration up to 5 at.%.

The samples were made by melting the (five 9's purity) metals in an alumina crucible under partial pressure of argon and stirring for two or more hours to ensure homogeneity. The alloy was then quenched and either filed or crushed to obtain 200-mesh powder for NMR samples. Spectroscopic analysis showed the alloy to be macroscopically homogeneous, and within the accuracy of the analysis the concentrations were equal to their nominal values.

EXPERIMENTAL RESULTS

The susceptibility of dilute Co impurities in liquid Cu_xAl_{1-x} hosts has been published previously.[3] For $x=0$ to 0.6, the Co susceptibility varies from approximately 6×10^{-5} to 20×10^{-5} cm^3/mole Co. Throughout this range χ_{Co} has a significant positive slope with temperature. This strange temperature dependence is characteristic of many transition impurities in liquid polyvalent host metals even though the low-temperature impurity susceptibility is relatively constant.[4-7] No completely satisfactory explanation for this anomaly has been given previously, but the present Knight-shift results suggest strongly that ρ_d is temperature dependent in the liquid hosts and that the susceptibility is simply tracking the changing density of states. Above $x=0.6$, the Co susceptibility rises rapidly with x, and the temperature dependence changes smoothly to a Curie-Weiss form in pure liquid copper hosts. Just above the liquidus, the Co susceptibility in pure copper is 1.2×10^{-3} cm^3/mole with a Weiss temperature of 900 K.

In Fig. 1 the Co Knight shift in several liquid *Al*Co alloys is shown versus temperature. K_{Co} is positive and like the susceptibility, increases with temperature. For a given *Al*Co sample, K_{Co} was reproducible within a random experimental uncertainty of 0.01%, but discrepancies typically of order 0.05% occurred between data taken with different samples of the same composition. The reason for this discrepancy is not completely understood, but it may be due to slight sample contamination during preparation. The slope $\Delta K_{Co}/\Delta T$ was reproducible from sample to sample within a random uncertainty of approximately 10%.

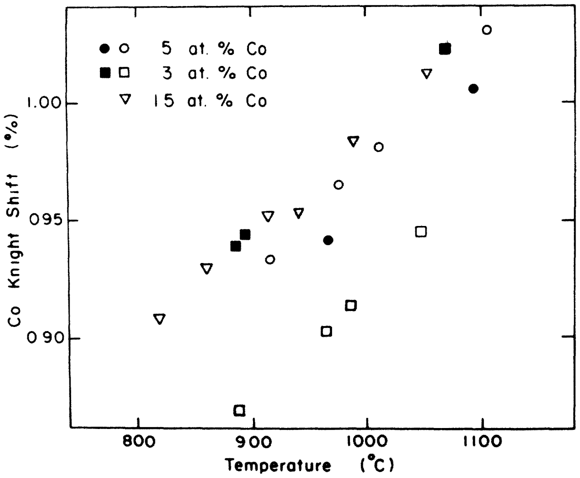

FIG. 1. Co Knight shift in *Al*Co. Solid and open symbols of the same shape refer to different samples of the same nominal composition.

In Fig. 2 we show $(T_1T)^{-1}$ which we obtain from the Co linewidth in *Al*Co. In liquid metals $T_1 = T_2$ because of rapid diffusional narrowing, and provided spurious broadening mechanisms are eliminated T_1^{-1} is proportional to the linewidth. For these data the only significant extra broadening arises from concentration differences among different liquid droplets in the sample. The data shown in Fig. 2 were taken with splat-quenched samples for which we believe the spurious broadening is smaller than the random error bars. We find $(T_1T)^{-1} = 6.2 \pm 1.0$ (sec K)$^{-1}$.

In hosts containing copper, the Co resonance linewidth was several times broader and consequently weaker than in the pure Al hosts. The extra broadening is caused largely by concentration differences among sample droplets. The broaden-

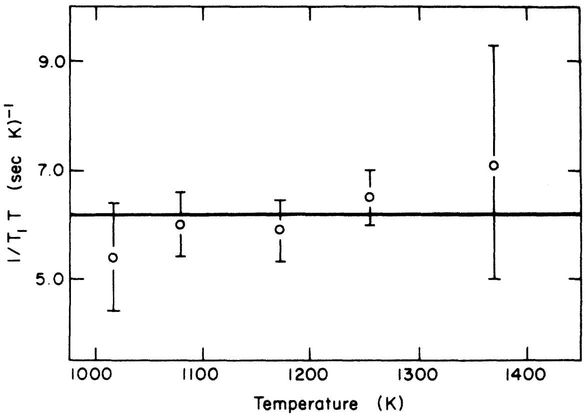

FIG. 2. Co nuclear relaxation rate in dilute *Al*Co vs T. The line represents $(T_1T)^{-1} = 6.2$ (sec K)$^{-1}$.

ing could be reduced considerably by rapid sample quenching during preparation, but we were unable to eliminate it entirely. The additional experimental uncertainty introduced by this broadening was of little importance in the host composition range below $x=0.6$. Here the Knight shift and its slope with temperature could be measured with only slightly less precision than in pure aluminum hosts. For these aluminum-rich host alloys, K_{Co} was found to depend only on the Co-impurity susceptibility with no detectable explicit host or temperature dependence. In Fig. 3 we show K_{Co} vs χ_{Co} for alloys having host compositions ranging from $x=0$ to $x=0.55$ and Co concentration between 1.5 and 3.0 at.%. Within experimental uncertainty, the data is well described by

$$K_{\mathrm{Co}}=(0.0054\pm0.003)+(40\pm4)\chi_{\mathrm{Co}}\,, \qquad (1)$$

where χ_{Co} is expressed in cm^3/mole. The line in Fig. 3 represents this relation. The uncertainty in the intercept is dominated by the quoted uncertainty of ±2 Hz/G in the Co gyromagnetic ratio.[8] A more detailed illustration of the lack of explicit temperature dependence is given by Fig. 4 in which $\Delta K_{\mathrm{Co}}/\Delta\chi_{\mathrm{Co}}$ is shown for all samples for which the slope was measured. The slope with temperature of both the Knight shift and susceptibility increases by a factor of 3 in this range, but their ratio remains very nearly constant. The line in Fig. 4 is the slope given in Eq. (1). The susceptibilities for these two figures are taken from Ref. 3 and were all measured in alloys containing 1-at.% Co.

The liquidus temperature of copper-rich alloys is quite high, and the experimentally available temperature range was too restricted to find the temperature dependence of K_{Co}. The Co Knight shift at 1100°C in copper-rich hosts is shown in Fig. 5 versus χ_{Co}. The solid line is the extrapolation of Eq. (1), and it is clear that this line adequately describes all data except for the liquid *Cu*Co data point.

The host Knight shifts were measured in a few aluminum-rich samples and are shown in Fig. 6. These shifts are only weakly dependent on temperature. We find $\Delta K_i/c_{\mathrm{Co}}K_i\approx-1$, which is comparable to values found for nontransition metal impurities in liquid metal hosts.[9] Here ΔK_i is the observed change in the Knight shift of the ith host component when concentration c_{Co} is added. Since s-, p-, and d-wave scattering from the impurity all contribute to ΔK_i and cannot easily be separated, the host Knight shifts give limited information about the d-wave phase shifts which are of primary interest. It is known that the d-wave phase shift does dominate ΔK_{Cu} in *Cu*Co,[10] but the host shift even in this case is subject to some interpretive ambiguities, and we did not investigate the host shifts in the copper-rich hosts.

DISCUSSION

Even when a $3d$ impurity is nonmagnetic, the primary contribution to the susceptibility arises from the spin and orbital susceptibility associated with the $3d$ resonant states. The diamagnetic and other paramagnetic contributions are normally much smaller and probably largely cancel. The spin-orbit coupling energy is small, and we may therefore write the impurity susceptibility as a sum of d spin and orbital terms,

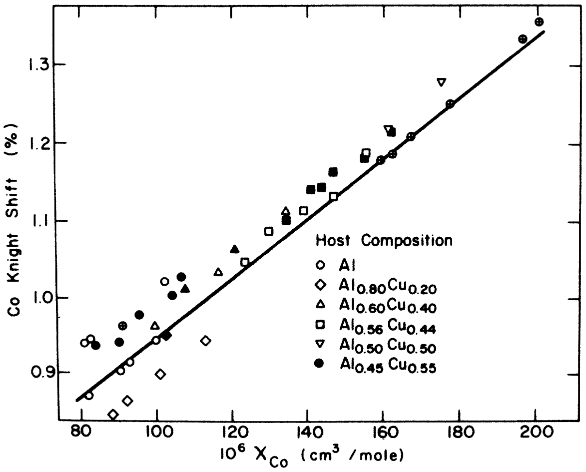

FIG. 3. Co Knight shift vs Co susceptibility. Co concentration is 3 at. % (open symbols) or 5 at. % (solid symbols). Temperature and host composition are implicit parameters. The line is Eq. (1) in the text.

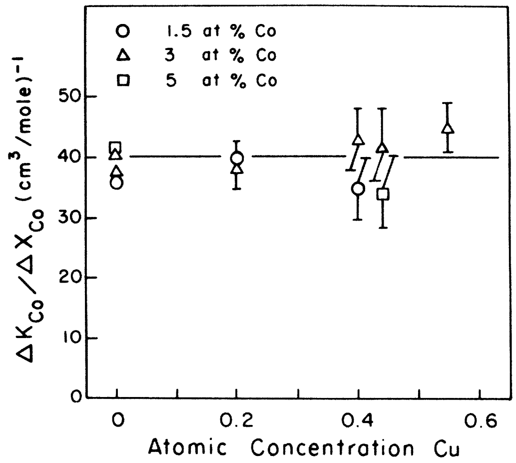

FIG. 4. Ratio of dK_{Co}/dT to $d\chi_{\mathrm{Co}}/dT$ for Co dissolved in liquid $\mathrm{Cu}_x\mathrm{Al}_{1-x}$ host alloys. The Knight shift and susceptibility are both linear in temperature for all alloys shown.

$$\chi_{\mathrm{Co}} = \chi_{\mathrm{spin}} + \chi_{\mathrm{orb}} \,. \tag{2}$$

The Co Knight shift is coupled to the two susceptibilities by

$$K_{\mathrm{Co}} = K_{\mathrm{Pauli}} + \frac{H_{\mathrm{spin}}}{\mu_B N_0}\, \chi_{\mathrm{spin}} + \frac{H_{\mathrm{orb}}}{\mu_B N_0}\, \chi_{\mathrm{orb}} \,, \tag{3}$$

where $K_{\mathrm{Pauli}} \approx 0.3\%$ for metals with atomic weight near Co, and H_{spin} and H_{orb} are, respectively, the spin and orbital hyperfine fields per Bohr magneton. Typically H_{spin} is negative and of order 0 to -50 kG, whereas H_{orb} in a metal is estimated to be about 600 kG.[11]

Since over the entire range investigated K_{Co} is at least several times larger than 0.3%, the orbital contribution must dominate the spin part. The linear dependence of K_{Co} on susceptibility up to approximately 10^{-3} cm^3/mole implies either that χ_{spin} is constant or negligibly small or that it is proportional to χ_{orb}. If χ_{spin} is constant or negligible we find H_{orb} from the slope of Fig. 2 to be 220 kG. This is considerably smaller than the theoretical estimate mentioned above. In addition we are unable to suggest any simple physical mechanism which could cause the spin moment to be everywhere an order of magnitude smaller than the orbital or to remain constant while the orbital susceptibility changes significantly. The possibility that χ_{spin} and χ_{orb} are proportional is much more reasonable, particularly for the nonmagnetic region. In fact, simple band pictures for very weakly magnetic impurities predict that the orbital moment should be roughly twice as large as the spin moment, with each being proportional to ρ_d. This proportionality is not expected *a priori* to extend to the more strongly magnetic region, however, because the spin moment normally becomes relatively much larger here.

Other possible reasons for the observed linearity of K_{Co} vs χ_{Co} seem very unlikely. It is extremely unlikely, for example, that the spin-orbit energy could be large enough to have a significant effect, or that H_{spin} and H_{orb} are equal. It is possible, of course, that the coupling constants are host dependent and that their changes mask a nonlinear Knight shift. This appears to be ruled out, at least for $\chi < 0.6$ by the lack of explicit host dependence in Figs. 3 and 4.

We do see some evidence for host-dependent hyperfine coupling constants near $x = 1$. As we show later, the anomalously large Knight shift in *Cu*Co is quite possibly due to a coupling-constant change. In the region below $x = 0.6$, however, the only reasonable explanation of the linearity of Fig. 3 is that the hyperfine coupling constants and the ratio of Co spin to orbital moment remain approximately constant everywhere. The remainder of the discussion will be within the framework of the Anderson model, but it should be emphasized that the above conclusion is not itself model dependent.

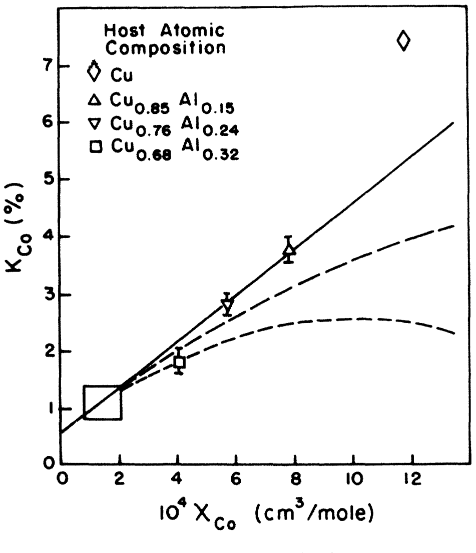

FIG. 5. K_{Co} vs χ_{Co} at 1100 °C. The box represents the area shown in Fig. 2, and the solid line is Eq. (1). The upper (lower) dashed line is Eq. (12) with $\bar{J}\,(H_{\mathrm{orb}} - H_{\mathrm{spin}}) = 50(100)$ eV/kG.

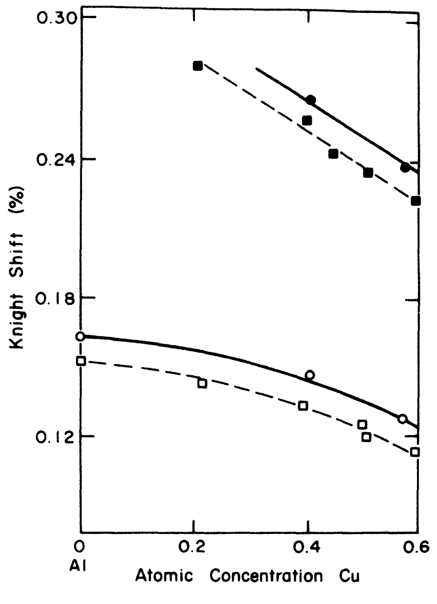

FIG. 6. Cu (solid circles) and Al (open circles) Knight shifts in liquid Cu-Al alloys at 1000 °C. The squares show the resonance positions when 5-at.% Co is added. The temperature dependence of these shifts is slight and within experimental uncertainty is the same for samples with and without Co.

Nonmagnetic range ($x = 0$–0.6)

The Anderson model[12] describes an impurity having Coulomb and Hund's exchange energies $\bar{U}$ and $\bar{J}$, respectively, interacting with the metal conduction band. In the nonmagnetic limit the molar spin and orbital susceptibilities are given by[2,13]

$$\chi_{\text{spin}} = \mu_B^2 N_0 \rho_d \eta_{\text{spin}} , \qquad \chi_{\text{orb}} = 2\mu_B^2 N_0 \rho_d \eta_{\text{orb}} , \tag{4}$$

where

$$\eta_{\text{spin}} = [1 - (\bar{U} + 4\bar{J})\rho_d/10]^{-1} \tag{5}$$

and

$$\eta_{\text{orb}} = [1 - (\bar{U} - \bar{J})\rho_d/10]^{-1}$$

are the spin and orbital enhancement factors. Here Δ is the impurity band half-width and ρ_d is the impurity density of states, given by

$$\rho_d = \frac{10}{\pi} \frac{\Delta}{\Delta^2 + (\epsilon_F - \epsilon_d)^2} , \tag{6}$$

where ϵ_d is the "unperturbed" impurity d-state energy. These expressions for χ_i break down when $\bar{U}$ or $\bar{J}$ become too large or Δ too small, but will remain valid as long as both enhancement factors do not become much greater than unity. These equations must be modified if finite crystal-field effects are taken into account, but it has been shown[13] that these corrections are negligible provided the relevant crystal-field splitting energies are much smaller than Δ. For these alloys, the instantaneous crystal-field energies should be approximately the same magnitude as for the solid—about 0.1 eV, but we will show later Δ is an order of magnitude larger, and we are justified in neglecting crystal-field corrections.

The temperature- and host-dependent changes of χ_{Co} must be attributed to variation of ρ_d and possibly $\bar{U}$. Clearly $\bar{J}$ must be negligibly small or the ratio of spin to orbital moment will have to increase as χ_{Co} becomes larger. In the limit of $\bar{J} = 0$, the orbital susceptibility is exactly twice the spin part, and the Knight shift will be given by

$$K_{\text{Co}} = K_{\text{Pauli}} + \frac{H_{\text{spin}} + 2H_{\text{orb}}}{3\mu_B N_0} \chi_{\text{Co}} . \tag{7}$$

Applying this relation to the data shown in Fig. 3, we find that K_{Pauli} is $0.54 \pm 0.3\%$, in acceptable agreement with our *a priori* estimate of 0.3%. The slope of K_{Co} vs χ_{Co} yields the result that

$$\tfrac{1}{2}H_{\text{spin}} + H_{\text{orb}} = 340 \pm 40 \text{ kG}. \tag{8}$$

We cannot find either hyperfine field separately, but we can define a probable range of values for each. The theoretical estimate of 600 kG should be taken as an upper limit for H_{orb}. This value is based on atomic Hartree-Fock theory, and delocalization of the d electrons will probably reduce H_{orb} somewhat. If H_{spin} is negative, then H_{orb} must lie between 340 and 600 kG, and H_{spin} must lie between 0 and −520 kG. Spin hyperfine fields for Co are found experimentally to be considerably smaller in magnitude than 520 kG, but H_{spin} is sensitive to the shape of the conduction-electron wave function and for other $3d$ metals is sometimes as great as −200 kG.[11]

Within the hyperfine-field limits given above, the Co Knight shift in *Al*Co can be separated into a Pauli part of about 0.5%, an orbital part of 0.4–0.7%, and a spin part equal to $0.4\% - K_{\text{orb}}$. In the $\text{Cu}_{0.55}\text{Al}_{0.45}$ host, the latter two are approximately double their value in *Al*Co. We have available a rough check on the consistency of this separation in *Al*Co. It has been shown that the three parts of the Knight shift all obey separate Korringa-like relations.[13] Within the above limits, the major contribution to the Co nuclear relaxation comes from the Pauli term which follows the usual Korringa relation,

$$(K_{\text{Pauli}})^2 (T_1 T)_{\text{Pauli}} = \mu_B^2 / \pi k_B \hbar \gamma_n^2 . \tag{9}$$

If we ignore other contributions to $(T_1)^{-1}$, we find from this equation and the relaxation rate given previously another estimate of $K_{\text{Pauli}} \approx 0.54\%$, in excellent agreement with the previous result. This number is a bit larger than our estimate of 0.3% (based on the Knight shift of Cu in these hosts), but within the rather large experimental uncertainty, the difference is not significant.

If $\bar{J}$ is zero, the total Co susceptibility reduces to

$$\chi_{\text{Co}} = 3N_0 \mu_B^2 \rho_d \eta , \tag{10}$$

where

$$\eta = (1 - \bar{U}\rho_d/10)^{-1}$$

and for the range of susceptibilities shown in Fig. 3, $\rho_d \eta$ lies between 0.8 and 2.0 states/eV. Unfortunately these data provide no means to separate the density of states from the enhancement factor, but again we can find probable ranges for each. $\bar{U}$ is not known but is generally believed to be no larger than about 5 eV. Optical experiments on magnetic $3d$ impurity systems have been interpreted to give $\bar{U} + 4\bar{J} \approx 5$ eV,[14] so $\bar{U} \leq 5$ eV. These results have been questioned recently[15] and other techniques indicate somewhat lower values.[16] For nonmagnetic Co systems $\bar{U}$ should be no larger than in magnetic systems, so it is reasonable to assume that $\bar{U}$ is no greater than 5 eV. If $\bar{U}$ is zero, η is unity and $\rho_d = \rho_d \eta$. If $\bar{U} = 5$ eV, η ranges from 1.4 to 2.0 and ρ_d from 0.60 to 1.0 states/eV in these systems. An enhancement factor of 2 may be too large for this model to remain rigorously valid, but even so these results should not be seriously in error.

The density of states half-width Δ is related to ρ_d by Eq. (6). For Co there should be approximately seven electrons in the d resonant states, so $(\epsilon_F - \epsilon_d) \approx \Delta$, and

$$\Delta = 10/2\pi\rho_d . \tag{11}$$

If ρ_d lies between 0.60 and 2.0 states/eV, then Δ must be between 0.8 and 2.7 eV in this nonmagnetic range.

Magnetic range ($x = 0.6-1$)

For the more-magnetic impurity states in hosts with $x > 0.6$, the nonmagnetic solution of the Anderson model becomes questionable. If $\bar{J}$ is strictly zero and if crystal fields and spin-orbit coupling remain negligible, it is not difficult to show that the Anderson-model orbital moment remains twice as large as the spin moment even when $\bar{U}/\Delta$ becomes very large. Under these assumptions we expect the K_{Co} vs χ_{Co} curve to remain linear over the entire range. In Fig. 5 we observe that the curve remains linear up to the $\text{Al}_{0.15}\text{Cu}_{0.85}$ host, but that the point corresponding to the pure liquid copper host is well above the linear extrapolation. A positive deviation, however, cannot be attributed to a breakdown in any of the above assumptions. This could cause only an increase in the ratio of spin to orbital moment and a negative deviation from the line. The most likely reason for the positive deviation at pure copper in Fig. 5 is that one of the Co hyperfine fields becomes more positive as the host Al composition is reduced to zero. The Mn-spin hyperfine field is known to undergo a significant positive change in this host range,[17] so it is not unlikely that a similar effect happens for Co impurities.

In view of this probable coupling-constant change near $x = 1$, and lacking any direct evidence about the host dependence of the coupling constants above $x = 0.6$, we clearly must include the possibility of nonconstant H_{spin} and H_{orb} in discussing Fig. 5. Even allowing for a wide variation of these fields, it is possible to establish a probable limit for the magnitude of $\bar{J}$ using the nonmagnetic model discussed previously. While there is some question about the applicability of the model to these more strongly magnetic impurities, it has been used for such cases in the past with reasonable results.

Equation (7) can be extended by expanding in $\bar{J}$, and to first order it becomes

$$K_{\text{Co}} = K_{\text{Pauli}} + A\chi_{\text{Co}} + \frac{\bar{J}(H_{\text{spin}} - H_{\text{orb}})}{27\mu_B^3 N_0^2}\chi_{\text{Co}}^{\;2} . \tag{12}$$

The coefficient of the linear term is the same as in Eq. (7).

In Fig. 5 we have drawn two dashed lines corresponding to $\bar{J}(H_{\text{orb}} - H_{\text{spin}}) = 50$ eV/kG (upper curve) and 100 eV/kG (lower curve). This construction assumes H_{orb} and H_{spin} remain constant at their values in the aluminum-rich hosts. It is most unlikely that any reasonable host dependence of these quantities could be folded together with the lower curve to reproduce the experimental results. We therefore take 100 eV/kG as the maximum probable value. From the previous section $H_{\text{orb}} - H_{\text{spin}}$ has a minimum of 340 kG, and $\bar{J}$ consequently has a maximum of 0.3 eV. Unfortunately, little information can be obtained about other parameters.

CONCLUSIONS

The linearity of the Co Knight shift versus Co susceptibility indicates that the ratio of spin to orbital susceptibility varies little over more than an order-of-magnitude change in χ_{Co}. Our analysis of this result based on the degenerate Anderson model indicates that $\bar{J}$ can be no larger than 0.3 eV. It is interesting to contrast Co with the Mn impurity behavior in this liquid $\text{Cu}_x\text{Al}_{1-x}$ host system.[17] The Mn Knight shift is everywhere negative, and the slope with χ_{Mn} is also negative. Evidently $\bar{J}$ for Mn is so large that the spin susceptibility and spin contribution to K_{Mn} are dominant. Using an analysis based on this same model, Warren *et al.* find $\bar{J} \sim 1$ eV for Mn.[18]

It is not clear why Co should have such a small $\bar{J}$, since the atomic values are about the same for all $3d$'s. Co impurities in other hosts (*Au*Co, for example, has a Co Knight shift of +29% at low temperature[19]) also behave in a qualitatively different fashion than other $3d$'s. A number of possible reasons for this peculiarity have been advanced, and an anomalously low $\bar{J}$ is one possibility. It is also possible that the Anderson model fails for Co. It is known that the model does not give proper term values in the ionic (strongly magnetic) limit, and this could be a serious deficiency in particular instances. The term values for Co are particularly poorly represented by the Anderson model,[20] and a better parametrization of the intra-atomic exchange may be required to account for these experimental data. Hirst[21] has shown how such complexities can be included, but it is not presently clear how greatly they affect the impurity behavior when the ionic configurations are strongly perturbed by conduction-electron mixing as in these systems.

If the Anderson model does prove to be too simple for Co, our analysis of the data in the magnetic region must be modified. Since the Co susceptibility enhancement is small in the nonmagnetic host range below $x = 0.6$, the analysis of these data should remain valid, however.

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