18.3 eV^{-1} (1.2×10^{-14} sec), respectively. If we assume that this Drude behavior stems primarily from a disordered structure, then we must associate the change in plasma energy with a decrease in the quantity n/m^* by some 30%, n being the volume density of electrons and m^* the effective mass. However, the present data do not allow us to assess individual changes in n and m^*.

We cannot associate the additional absorption denoted by $\Delta\epsilon_2$ with anything other than interband absorption, and it is noticeable that this absorption sets in at an energy very close to that of the (111) edge in crystalline aluminum, although the detailed shape of the deduced extra absorption does not have the same geometrical form as the crystalline edge. We shall call the observed extra absorption a pseudo (111) edge. On the other hand, we find it difficult to understand how the occurrence of a pseudo (111) edge, implying a well-defined (111) translational symmetry, can be reconciled with the complete absence of the stronger similar (200) edge. We might argue that the aluminum atoms condensing on a very cold, crystalline aluminum film tended to form close-packed planar clusters of very limited average diameter which did not join up laterally in an ordered manner, but which might have piled up in the thickness direction thereby maintaining a large degree of the *ABCABCABC...* pattern characterizing the (111) translational symmetry. Studies of the crystal structure of aluminum films condensed on cold substrates by Buckel[5] do not substantiate the above contention since both the (111) and (200) diffraction peaks were clearly seen above a rather intense diffuse background [although the (200) peak appeared to be much weaker for films formed on cold substrates]. The observed optical absorption of aluminum could have been associated with another crystal modification but this is very unlikely, partly in view of the above mentioned diffraction experiments, partly because the (200) peak disappeared in a progressive manner and not discontinuously as the temperature of the substrate was lowered.

Clearly our optical data demonstrate a condition intermediate between the customary crystalline state and an amorphous state, but one that is not readily specified in detail.

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^{55}Mn NMR Study of Local-Moment Formation in *Cu*Mn

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NMR shifts and relaxation times are reported here for ^{55}Mn impurity nuclei in a series of liquid $Al_{1-x}Cu_x$:Mn alloys over the composition range $0 \leq x \leq 1$ and at temperatures from 1050 to 1425 K. Analysis of shifts and susceptibilities reveals abrupt changes in d-spin hyperfine field and orbital susceptibility at the Cu-rich end. A sharply increased value of the relaxation rate for $x \rightarrow 1$ is analyzed to give $J_{sd} = 0.82$ and 1.22 eV for the liquid and solid phases, respectively.

Nuclear magnetic resonance (NMR) in alloys containing dilute magnetic impurities has been employed extensively to investigate electronic structure and dynamics in the vicinity of the nonmagnetic-host nuclear sites.[1] In this Letter we report NMR observations on the local-moment site itself in such a system: ^{55}Mn in solid and liquid *Cu*Mn. The nature of the impurity state and the process of moment formation were studied by measuring the ^{55}Mn frequency shifts and relaxation rates in *liquid* $Al_{1-x}Cu_x$ host alloys for a series of Cu concentrations x varying from 0 to 1.[2] The Mn-impurity susceptibility (χ_{Mn}) in this liquid-alloy system has been found[3-5] to change continuously from an increasing function of temperature for $x = 0$ (Al)[4,5] to the T^{-1} behavior characteristic of a nearly free spin at $x = 1$ (Cu),[3] while increasing in magnitude by a factor of ~3. Our results show that the d-spin part of χ_{Mn} increases smoothly with x while the d-spin hyperfine field and the orbital part of χ_{Mn} change abruptly near $x=1$. The ^{55}Mn spin-lattice relaxation rate also increases sharply as $x \to 1$, revealing a strong mechanism due to local-moment hyperfine fluctuations. These we attribute to exchange scattering of conduction electrons, giving a direct measure of s-d exchange ($J_{sd} \sim 1$ eV). We also find a disparity of J_{sd} values across the melting point of *Cu*Mn of the correct sign and magnitude to explain the observed discontinuity in χ_{Mn}[3] in terms of a model calculation by Scalapino.[6]

The direct observation of dilute local-moment nuclei by resonance methods (in nonferromagnetic hosts) has not hitherto been generally regarded as feasible. A recent calculation[7] has suggested that linewidths might become narrow enough to observe NMR either at very low or very high temperatures, the latter case requiring a sufficiently strong moment-lattice coupling (i.e., J_{sd}). The present work was carried out in the range 1050–1425 K with a conventional pulsed NMR apparatus at 16.3 MHz. The minimum T_2 (inverse linewidth) encountered was ~2.5 μsec for *Cu*Mn, resulting in a loss of signal amplitude by a factor of ~100 simply from the effects of finite pulse width and receiver blocking time. For Mn concentrations of a few percent, signal-to-noise ratios of ~10 were obtained in a maximum of several hours integration time using standard signal-averaging methods.

The shifts and susceptibilities were analyzed using the well-known[8] K-χ plot technique. A composite plot of K_{Mn} versus χ_{Mn} for three representative alloys is given in Fig. 1. To interpret these plots we adopt the relations[8] $K_{\mathrm{Mn}} = K_s + K_d + K_{\mathrm{orb}}$ and $\chi_{\mathrm{Mn}} = \chi_s + \chi_{\mathrm{dia}} + \chi_d + \chi_{\mathrm{orb}}$, with $K_d = \alpha_d \chi_d$ and $K_{\mathrm{orb}} = \beta \chi_{\mathrm{orb}}$, and take the following steps: (1) The s-band shift K_s is estimated from Cu metal to be ~0.2% and $\chi_s + \chi_{\mathrm{dia}}$ assumed to be negligibly small on the scale of Fig. 1. (2) β is estimated to be 65 (emu/mole)$^{-1}$.[9] (3) The orbital shift and susceptibility (K_{orb}, χ_{orb}) are assumed to be essentially temperature independent, the temperature dependence residing therefore in the d-spin parts (K_d, χ_d).[10] The partition of χ_{Mn} into $\chi_d + \chi_{\mathrm{orb}}$ is then obtained by finding the intersection of a line drawn from the point ($K_{\mathrm{Mn}} = 0.2\%$, $\chi_{\mathrm{Mn}} = 0$), with slope $\beta = 65$, with a straight line through the data, as illustrated in Fig. 1. The plot for $x = 0.0$ confirms that the (rather curiously) increasing $\chi_{\mathrm{Mn}}(T)$ with T[4,5] for liquid *Al*Mn is in fact associated with d-spin paramagnetism. Values deduced from such plots for K_{orb} and α_d are displayed in Fig. 2.

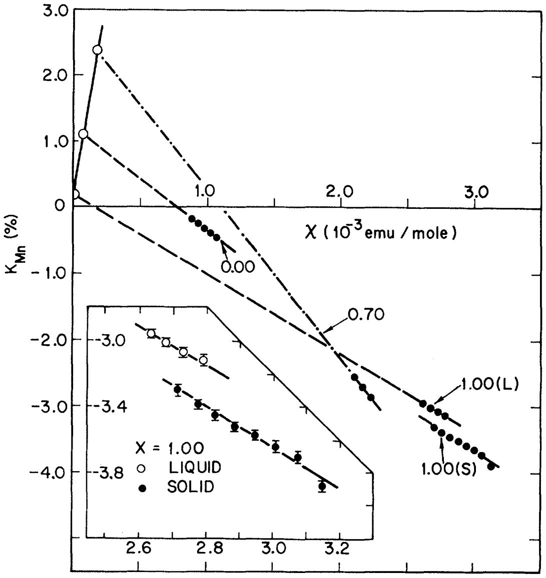

FIG. 1. Plots of K_{Mn} versus χ_{Mn} for three host alloys $\mathrm{Al}_{1-x}\mathrm{Cu}_x$ (x's given in figure), showing analysis into orbital and d-spin components.

Regarding the data of Fig. 2 we first note that for *Al*Mn, we find $K_{\mathrm{orb}} \simeq 0.8\%$, in qualitative agreement with a relaxation-rate analysis[11] of He temperature results. Secondly, we find that K_{orb} first increases with x, then drops suddenly to zero for $x = 1$, as would be expected for the very nearly S-like *Cu*Mn ground state. Thirdly, the slope α_d of the data in Fig. 1 is related to the d-spin hyperfine field H_{hf}^{d} (in gauss/Bohr magneton) through the relation $\alpha_d = 1.79 \times 10^{-4} H_{\mathrm{hf}}^{d}$ (emu/mole)$^{-1}$. $|H_{\mathrm{hf}}^{d}|$ is therefore seen to increase with x at first, then, between $x = 0.7$ and 1.0, drop by nearly a factor of 2 to a value in essential agreement with that obtained from nuclear orientation studies[12] at $T < 1$ K. Further, a detailed comparison of liquid- and solid-phase data for *Cu*Mn (see inset, Fig. 1) shows that $|\alpha_d|$ decreases by ~7% on melting, where we note that $\chi_{\mathrm{orb}} = 0$ within experimental error in both cases.

Measurements of the spin-lattice relaxation time T_1 have been carried out for a range of temperatures above the melting point for alloy compositions up to $x = 0.6$, after which only T_2 could be measured because of the shortness of T_1. For $x > 0.6$, the reasonable assumption was made that $T_1 = T_2$ in the liquid phase. To compare results from different compositions at different tempera-

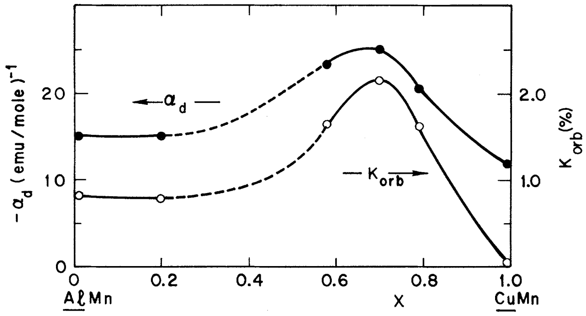

FIG. 2. Values of d-spin shift coefficient α_d and orbital shift K_{orb} obtained from K_{Mn}-χ_{Mn} plots, plotted here against host-alloy composition.

tures, we assume the relaxation to be dominated at small x by the locally enhanced d-spin term for which one has the modified Korringa relation[13]

$$(T_1T)_d^{-1} = K_d^2/(2l+1)\mathcal{S}, \tag{1}$$

where $\mathcal{S} \equiv (\gamma_e/\gamma_n)^2(\hbar/4\pi k_B)$, and $2l+1$ is the degeneracy of the localized orbital, here taken to be 5. To eliminate effects resulting from the variation of H_{hf}^d, we make a plot of $[\alpha_d^2T_1T]^{-1}$ versus χ_d^2 (as deduced from Fig. 1) in Fig. 3 for all the alloys studied. In these terms Eq. (1) becomes $[\alpha_d^2T_1T]^{-1} = \chi_d^2/(2l+1)\mathcal{S}$, which is plotted as a dashed line in Fig. 3.

Although the temperature dependence for some alloys deviates from that of Eq. (1), the general trend through the series up to $x \simeq 0.6$ is one of reasonable accord with the enhanced Korringa process. As $x \to 1$, however, there is a sharp increase in relaxation rate which is clearly a result of some other process. We identify this with the local-moment hyperfine fluctuation mechanism discussed recently by Walstedt and Narath.[7] At high temperatures this is given by

$$T_1^{-1} = T_2^{-1} = 2A_d^2S(S+1)T_{1e}/3\hbar^2, \tag{2}$$

where A_d is the hyperfine coupling constant and T_{1e} the spin-lattice relaxation time of the Mn local moment. To our knowledge this mechanism has not been previously identified in a metallic system.

If we assume Eq. (2), the ^{55}Mn T_2 becomes a direct measure of the local-moment relaxation rate and of J_{sd}^2 when we employ the expression[14]

$$T_{1e}^{-1} = (\pi/\hbar)J_{sd}^2n_s(\epsilon_F)^2k_BT. \tag{3}$$

In Eq. (3) $n_s(\epsilon_F)$ is the conduction-electron density of states for one spin direction, and J_{sd} is the *dynamic* s-d exchange parameter where the coupling energy is written $J_{sd}\vec{s}\cdot\vec{S}$. The temperature dependence implied by Eqs. (2) and (3), $T_2 \propto T$, is obscured by the scatter in the *Cu*Mn data (Fig. 3), which were taken for $1350 \leq T \leq 1425$ K. From the straight line drawn, however, we obtain $|J_{sd}(\text{liquid})| = 0.82 \pm 0.10$ eV for the liquid phase using $\alpha_d = -12$ (emu/mole)$^{-1}$ (Fig. 2), $S(S+1) \simeq 7.18$ from measurements of χ_{Mn},[3] and $n_s(\epsilon_F) = 0.153$ eV^{-1} atom^{-1}.[15] An "effective" value of $S(S+1)$ is used on the assumption that $1/T_1$ is reduced below the free-spin value by the same amount as χ_{Mn}.

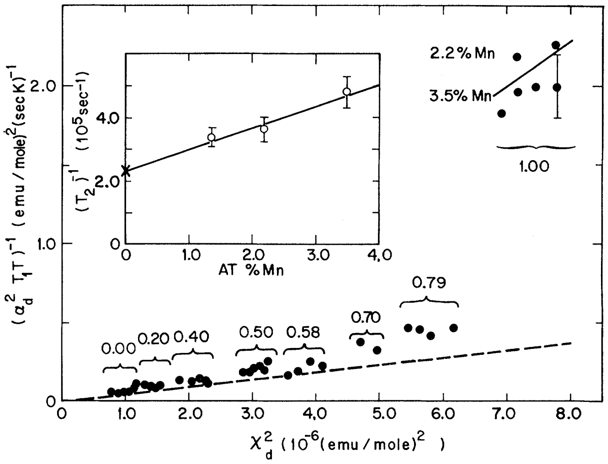

FIG. 3. Plot of normalized spin-lattice relaxation rate versus d-spin susceptibility squared for ^{55}Mn in *liquid* $\text{Al}_{1-x}\text{Cu}_x$ host alloys (x's given in figure). Inset: *solid* phase relaxation rate versus Mn concentration at 1200 K.

T_2 measurements were also carried out in the solid phase of *Cu*Mn near the melting point. Here, however, the situation is complicated by the presence of another, concentration-dependent relaxation process. A study of the T_1 and T_2 of the host ^{63}Cu and ^{65}Cu nuclei showed the process to be of quadrupolar origin and linear in Mn concentration. A detailed analysis of these data will be left to a future publication. Here we simply note that the ^{55}Mn single-impurity relaxation rate [Eq. (2)] is extracted by plotting experimental rates $(1/T_2)_{\text{expt}}$ against Mn concentration c and extrapolating to $c = 0$.

Such a plot is shown in the inset to Fig. 3 for solid *Cu*Mn at $T = 1200$ K. The quadrupolar contribution to $(1/T_2)_{\text{expt}}$ is of the same order as for the Cu nuclei, as expected, but somewhat surprisingly the intercept is ~40% smaller than the relaxation found for the liquid phase. Although the accuracy is not great, this discrepancy is thought to be real. With the same parameters as used previously [except $S(S+1)=6.75$ from $\chi_{\rm Mn}$ for the solid phase],[3] Eqs. (2) and (3) lead to $|J_{sd}(\text{solid})|=1.22\pm0.15$ eV. The discrepancy between solid and liquid J_{sd} values suggests that a J_{sd}-dependent Curie-law correction such as calculated by Scalapino[6] on the Anderson model may be responsible for the corresponding ~6% discontinuity in $\chi_{\rm Mn}$.[3] On the basis of the experimental Curie-law behavior, we neglect the logarithmic terms in Ref. 6, leaving

$$\chi_{\rm Mn}=\chi_{\rm Curie}[1+n_s(\epsilon_{\rm F})J_{sd}]. \tag{4}$$

This result has also been obtained by Kondo[16] with the J_{sd} model. Assuming J_{sd} is dominated by the negative admixture contribution,[17] Eq. (4) then gives a reasonable estimate of the Curie-law correction factor. This factor is found with the present results to change by ~7% between solid and liquid phases, in perhaps fortuitously good agreement with the observed change.

We conclude with a number of remarks about the results presented here.

The J_{sd} values obtained here are only slightly larger than that given by Monod[18] from *Cu*Mn magnetoresistance studies ($|J_{sd}|=0.8\pm0.2$ eV). The latter value was revised downward, however, in a later interpretation of Monod's results[19] including higher-order effects. Our values are, in addition, larger by a factor of ~2 than an EPR linewidth value deduced for *Ag*Mn.[20] It is also interesting to note that Shanabarger[21] has found a positive g shift in *Cu*Mn doped with gold to reduce the bottleneck effect. This may be in conflict with our interpretation of the Curie-law correction.

The liquid-solid disparity in J_{sd} poses an interesting theoretical question, and one immediately suspects that the s-d mixing term[17] is responsible for this. This conjecture is at least consistent with the approximate continuity of $H_{\rm hf}{}^d$ across the melting point (Fig. 1, inset), since the s-d admixture effect is expected to make very little contribution to the impurity hyperfine field.[22]

Finally, it is important to note that the properties of the *Cu*Mn moment appear to be changing much more rapidly with added Al than was revealed by susceptibilities[4] alone. The most major changes in $\chi_{\rm orb}$, $H_{\rm hf}{}^d$, and T_2 occur between $x=0.8$ and 1.0, a region where $\chi_{\rm Mn}$ changes by only ~10%. Thus it requires only a few percent of Al admixture to render the Mn moment lifetime shorter than the spin-lattice relaxation time $T_{1e}\sim10^{-13}$ sec of the fully developed moment at $T=1350$ K.

We wish to thank J. H. Wernick, who provided the samples for this work.

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