Magnetic properties of dilute Mn impurities in liquid Cu-Ga alloys

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The Mn-impurity susceptibility and the perturbation of the ^{63}Cu and ^{69}Ga nuclear resonances by Mn impurities in liquid Cu_xGa_{1-x} host alloys are given. The Mn susceptibility is larger and the conduction-electron polarization by Mn smaller in these hosts than in the Cu_xAl_{1-x} liquid-host-alloy system. The Mn susceptibility in the Cu-Ga hosts can be fit to a Curie-Weiss temperature dependence and does not display the unusual nonlinear increasing temperature dependence found for Mn in the Al-rich Cu-Al hosts.

I. INTRODUCTION

Elements having partially filled d or f electronic shells are often found to be strongly paramagnetic when present as dilute impurities in normal metals. The $3d$ and $4f$ series have been investigated extensively, and it is found that the magnetic properties of $4f$ impurities are well described by a free-ion model weakly perturbed by crystalline fields and small conduction-electron interactions. For the $3d$ series, crystalline fields and conduction-electron interactions are much stronger and can be considered as perturbations only in a few special cases such as Fe, Mn, and Cr impurities in noble-metal hosts. In contrast to these magnetic-impurity systems, the magnetic susceptibility of $3d$ impurities in polyvalent metal hosts is typically much smaller and temperature independent below 300 K.

This magnetic-to-nonmagnetic transition as a function of host composition has been studied previously for Mn impurities in liquid-Cu_xAl_{1-x} host alloys.[1-5] We have undertaken a further experimental investigation of Mn impurities in liquid alloy hosts and give here our results for the magnetic susceptibility and host nuclear-resonance perturbation in Cu_xGa_{1-x} hosts. We find several experimental indications that the interaction between the Mn d electrons and the host conduction band is weaker in Cu-Ga than the Cu-Al alloys. One indication of this difference is that the ^{63}Cu-host Knight shift is more strongly perturbed by Mn impurities in Cu-Al than Cu-Ga, indicating a larger conduction-electron spin polarization in Cu-Al. A second indication is that Mn is more strongly paramagnetic in Cu-Ga. Alloying either Al or Ga with copper causes a reduction in the Mn-impurity susceptibility, but the reduction is much more pronounced for large Al additions. The temperature derivative of χ_{Mn} also changes sign in liquid-Cu-Al alloys having more than 50% Al but remains negative in Cu-Ga. Similarities and differences between the Mn-impurity state in Cu-Ga and Cu-Al are discussed below, and we suggest that a Kondo model with significant interconfigurational fluctuations in Al-rich hosts might provide a proper description for these interacting impurity-host systems.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The Mn susceptibility was measured by a standard Faraday method. The experimental procedure was to measure the susceptibility of the host alloy versus temperature in an alumina sample holder, add Mn, and then measure the susceptibility of the impurity-host alloy in the same sample holder. During susceptibility runs and intermediate alloying steps, the sample was kept in vacuum or a low pressure of purified argon. Previous experience with similar liquid alloys has shown that the Mn susceptibility

$$\chi_{Mn} = (\chi_{total} - \chi_{host})/c \qquad (1)$$

is independent of Mn concentration c provided c is smaller than 5 at. %. The Mn susceptibility shown in Fig. 1 was measured for samples in which c was between 1 and 2 at. %. The error bars in Fig. 1 give the over-all uncertainty in magnitude of χ_{Mn} due to errors in Mn concentration, calibration errors, etc. The relative temperature dependence of χ_{Mn} is affected by trace ferromagnetic impurities in the alumina sample holders which cause significant irreproducibility below 800 °C. The relative error in χ_{Mn} between 800 and 600 °C is no greater than 10^{-4} cm^3/mole, but becomes very large at lower temperature, and no attempt was made to measure susceptibilities below 600 °C. For comparison χ_{Mn} in several Cu_xAl_{1-x} liquid host alloys is also shown.

If χ_{Mn} is fit to a $(T+\Theta)^{-1}$ form, Θ is approximately zero for liquid CuMn and 700 ± 150 K for liquid GaMn. The Curie constant is 3.5 ± 0.2

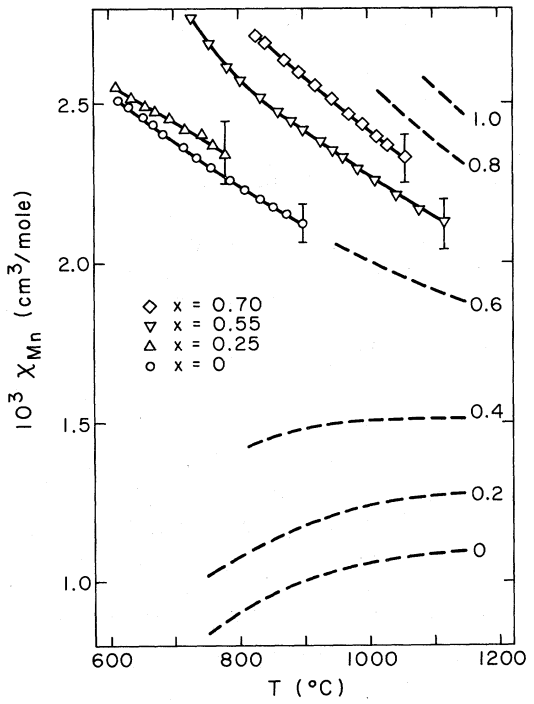

FIG. 1. Magnetic susceptibility of Mn impurities in Cu_xGe_{1-x} liquid host alloys. Dashed lines show the Mn susceptibility in Cu_xAl_{1-x} liquid hosts where x is shown. Data are taken from Refs. 1, 4, and 5 and are subject to experimental uncertainty of approximately the same size as that shown for Cu-Ga hosts.

cm^3 K/mole in Cu and 3.9 ± 0.3 cm^3 K/mole in Ga liquid hosts. These correspond to effective moments of 5.3 and 5.6 bohr magnetons, respectively. The Mn susceptibility in Ga is in good agreement with a previous measurement by Peters and Flynn.[6] Host suceptibilities were not measured precisely but were roughly the same as found by Uemura and Takeuchi.[7]

Knight-shift measurements were made using a standard field-swept cw NMR spectrometer operating at 13.5 MHz. Alloys were made in a specially designed induction-heated chamber which allowed the alloy to be quickly quenched from the melt in order to minimize inhomogeneities. The alloys were filed to a powder with diameter less than 70 μm, mixed with alumina powder to separate the droplets when liquified, and sealed into an evacuated quartz capsule with a small amount of Ti getter. Cooling with liquid nitrogen was necessary for filing the softer alloys.

In liquid metals, NMR lines are motionally narrowed, and one observes line shifts but little line broadening in alloys. It is convenient to define a normalized measure of the impurity-induced shift by

$$\Gamma_{\text{Mn-}\alpha} = [\kappa(T) - \kappa_0(T)]/c\kappa_0(1100\,^\circ\text{C}), \qquad (2)$$

where κ, κ_0 are, respectively, the host Knight shift with and without concentration c of Mn added; α refers to either the Cu or Ga host resonances. κ, κ_0, and Γ are functions of temperature and host composition and depend on the nuclear species α being observed. In these alloys the Mn concentration is between 1 and 3 at.%. Within experimental uncertainty Γ is independent of c and is linear in temperature. The experimentally available temperature range is restricted by a maximum of 1150°C in the present furnace. Figure 2 shows both $\Gamma_{\text{Mn-Cu}}$ and $\Gamma_{\text{Mn-Ga}}$ at 1100°C. Experimental errors are due to composition uncertainties and differences among different sample droplets. Figure 3 shows the slope with temperature of $\Gamma_{\text{Mn-Cu}}$. Experimental uncertainty is due to time-dependent irreproducibilities in resonance position which are probably caused by slow compositional changes by

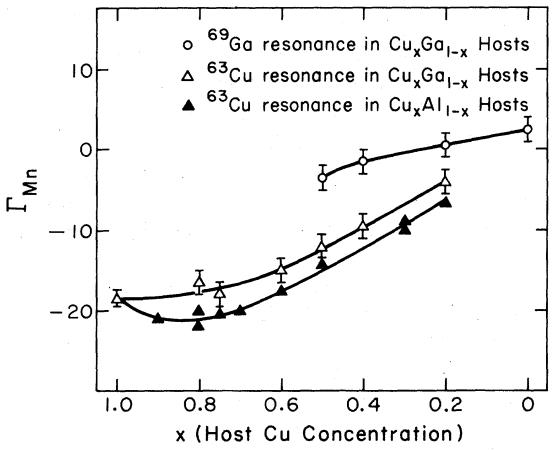

FIG. 2. Relative host Knight-shift perturbation by Mn impurities at 1100°C normalized to unit Mn concentration. Cu-Al data from Ref. 2.

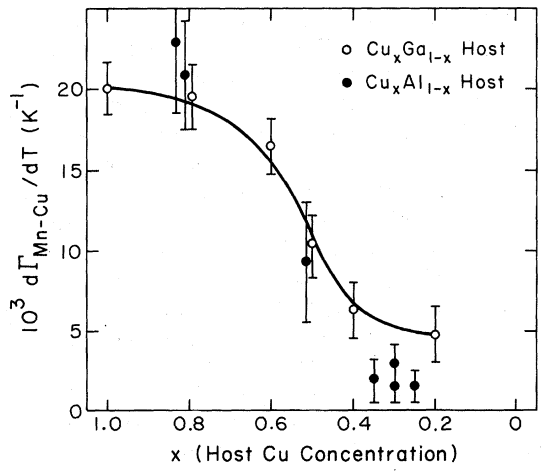

FIG. 3. Slope of ^{63}Cu Knight-shift perturbation with temperature at 1100°C. Cu-Al data from Ref. 2.

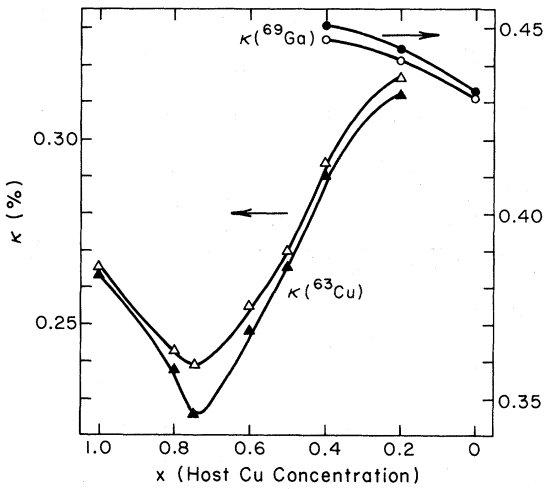

FIG. 4. Knight shifts of ^{63}Cu and ^{69}Ga in liquid Cu_xGe_{1-x} alloys. Open (closed) points are data taken at 1000 °C (900 °C) extrapolated where necessary.

vapor transport among the separated sample droplets. The Knight shifts of ^{63}Cu and ^{69}Ga in the Cu_xGa_{1-x} liquid alloys are shown in Fig. 4 at (extrapolated where necessary) temperatures of 900 °C and 1000 °C. These were the two isotopes observed in all NMR data reported in this paper.

III. DISCUSSION

Γ is an average measure of the z component of conduction-electron-spin polarization $s(r)$ by a Mn impurity located at $r=0$. If one ignores noncontact contributions to the Knight shift and assumes that the penetration factor is not significantly affected by the impurity, it can be shown[8] that

$$\Gamma_{\text{Mn-}\alpha} = N_\alpha \langle s(r) \rangle / s_P , \tag{3}$$

where s_P is the unperturbed Pauli spin density, and the brackets denote a spatial average over all N_α nuclei of type α. Sotier *et al.*[2] pointed out that since $s(r)$ is an oscillatory and rapidly decreasing function of r, the average will normally be strongly dominated by the large perturbation at the first-neighbor shell surrounding the Mn. Equation (3) may be approximated by

$$\Gamma_{\text{Mn-}\alpha} = n s(r_\alpha)/s_P , \tag{4}$$

where n is the total number of neighbors in the first shell and r_α is the average distance to the type-α nuclei in the first shell.

In liquid CuMn, $n \approx 10$, and $s(r_{Cu}) \approx -2s_P$ at 1100 °C. The relative dependence of $s(r_{Cu})$ on x should be qualitatively similar to that of $\Gamma_{\text{Cu-Mn}}$, although s_P may vary by a factor of two over the host composition range. The nearly identical values found for κ_{Cu} in Cu_xAl_{1-x} and Cu_xGa_{1-x} alloys imply that s_P is the same for Cu-Ga and Cu-Al and that the magnitude of $s(r_{Cu})$ is ~20% greater in Cu-Al hosts between $x=0.8$ and 0.2 than in Cu-Ga. An interesting consequence of Eq. 4 is that $\Gamma_{\text{Mn-Cu}} - \Gamma_{\text{Mn-Ga}}$ is proportional to $s(r_{Cu}) - s(r_{Ga})$ and provides a rough measure of the radial dependence of $s(r)$ near the first-neighbor shell. In the Cu_xAl_x host alloys $\Gamma_{\text{Mn-Al}}$ is considerably smaller in magnitude than $\Gamma_{\text{Mn-Cu}}$ for $x>0.5$, but the two are about equal for $x<0.5$.[2] Since $r_{Al} > r_{Cu}$, this observation is taken as an indication that $s(r)$ has a node just beyond the first-neighbor shell when Mn is "magnetic" but that the node is further away when Mn is "nonmagnetic." Although the Ga resonance data is less complete, it appears from Fig. 2 that $s(r)$ has a node near r_{Ga} in the Cu-Ga alloys.

The Mn magnetic susceptibility shown in Fig. 1 indicates that the impurity state in the liquid Cu-Ga system is similar to the impurity state in the portion of the Cu_xAl_{1-x} host system above $x=0.5$. These impurity states can be described qualitatively by a Kondo[9] model in which $J\rho$ increases as x decreases and is larger for Cu-Al than for Cu-Ga hosts of the same x. This would account both for the larger $s(r)$ and more rapid decrease of χ_{Mn} in Cu-Al. The temperature dependence of χ_{Mn} reflects the expected rapid increase of T_K with x under these circumstances. The sign and magnitude of $d\Gamma_{\text{Mn-Cu}}/dT$ shown in Fig. 3 are consistent with the expected approximate proportionality of $ds(r)/dT$ to $d\chi_{Mn}/dT$. In terms of this model, the striking change in the character of χ_{Mn} for $x<0.5$ in the Cu-Al system probably indicates that ionic fluctuations to different term or configuration levels are important. These are neglected in the simple Kondo model and were first discussed in detail by Hirst.[10] Such fluctuations could account for the peculiar temperature dependence of χ_{Mn} as well as the finite orbital magnetism[3] of Mn in the Al-rich host alloys. This type of model does account semiquantitatively for many features of Co impurity systems where orbital magnetism is quite pronounced.[11] For Mn impurities a quantitative analysis cannot be undertaken at present because very little is understood about the impurity ionic level structure or about the dynamics of fluctuations appropriate to such a state. Since ionic fluctuations in rare-earth magnetism are now being studied extensively, some more quantitative application of this model to transitional impurities may soon become feasible.

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