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## IV. RELATED SUBJECTS

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### NUCLEAR MAGNETIC RESONANCE AND RELAXATION IN METALS CONTAINING MAGNETIC IMPURITIES

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#### I. INTRODUCTION

Over the past fifteen years or so, nuclear magnetic resonance (*NMR*) has proved to be a valuable tool for the study of both the static and dynamic disturbances caused by dilute impurities in metals. To facilitate our discussion let us arbitrarily divide dilute alloy systems into categories of "local-moment" and "nonmoment" impurities, where in the spirit of this conference we take the former classification to include only impurities sufficiently well-localized to allow study by *EPR* techniques.

In the loosely-defined "nonmoment" category we may find systems very near to the moment-formation condition in the Friedel-Anderson sense [1, 2]. Also, many nearly-magnetic systems are said to represent local moments which have "condensed" into a weakly-magnetic "Kondo" ground state [3]. Such "nonmoment" impurities have been found to have magnetic properties of great interest. Dilute alloy systems of this sort have been quite intensively studied by *NMR* techniques [4].

In the present instance, however, we focus attention on the "magnetic", i.e. local-moment dilute alloys, and more specifically on certain aspects of *NMR* studies of such alloys to be outlined presently. One may subdivide this topic into studies of (1) host and (2) impurity nuclei and the studies themselves into (a) static (i.e. shift and linewidth) and (b) dynamic (i.e. spin-lattice relaxation) component parts. Let us consider these various aspects of the subject in turn.

(1a) Static host *NMR* effects. The earliest resonance work on local-moment alloys [5, 6] revealed that the host *NMR* line is essentially unshifted by magnetic impurities, but is considerably broadened by the oscillatory (*RKKY*) spin-density disturbance [7] such impurities produce. An up-to-date review of host linewidth studies is also found in Reference 4, except for the fact that there is now a closed-

form theory for such impurity lineshapes [8]. In metals where the host nuclei possess quadrupole moments, there is also the static effect known as quadrupolar "wipeout" due to the Friedel charge oscillations, wherein certain nuclei close to an impurity site simply do not appear in the *NMR* line. This effect is, of course, not specific to local-moment impurities as it is primarily a function of the charge screened by the conduction electrons.

(1b) Dynamic host *NMR* effects. In the past decade or so there have been a number of studies of host nuclear relaxation effects due to magnetic impurities [9]. It is only with the recent work of Alloul and Bernier [10, 11], however, that a correct understanding of systems such as  $\underline{Cu Mn}$  has begun to emerge. This has come about as a result of their having correctly taken account of spin-diffusion barrier phenomena in these systems for the first time. Although a final resolution of the  $\underline{Cu Mn}$  case has not yet been reached, we describe briefly the host relaxation processes and summarize the progress to date in understanding this system in part II of the paper. We also discuss the beautiful results of the McHenry and Silbernagel [12] on host relaxation when spin-diffusion is absent.

(2a) and (2b) *NMR* of local moment nuclei. Apart from the anomalous cases of  $\underline{W Mo}$  and  $\underline{W Co}$  [13], where the *d*-spin hyperfine fields of the impurities are extraordinarily small, there had until recently been virtually no results available on the *NMR* of local moment impurity nuclei themselves. Clearly, the properties of such resonances would give the most direct contact with the dynamics of the localized spins. The recent work of Walstedt and Warren [14] on  $Al_{1-x}Cu_x:Mn$  has shown such studies to be feasible and profitable. In part III we describe this work and offer further explanation (beyond Ref. 14) for the results observed. The properties discussed include  $^{55}Mn$  *NMR* shift, relaxation time, *d*-spin hyperfine field,  $\chi$  susceptibility, and *s-d* exchange coupling.

## II. HOST NUCLEAR RELAXATION BY LOCAL-MOMENT IMPURITIES

We first describe briefly the various processes by which local moment fluctuations can cause nuclear relaxation. Basically, the same processes apply to both the host and impurity nuclei as was recently demonstrated by Walstedt and Narath [15]. At low temperatures one of the most important processes, known for the host nuclei as the Benoit-de Gennes-Silhouette (*BGS*) process [16], may be regarded as a second-order perturbation process [15], where, e.g., a mutual spin-flip between the nucleus and local moment spin is followed by another flip between the local moment spin and a conduction electron spin. Such a process is coherent with the direct Korringa process, and the cross term between these two is known for host nuclei) as the Giovannini-Heeger [17] process. This process is important only when the impurity effects are small, so we do not consider it further.

A third mechanism which may be important is the dipolar process, which is generated by the fluctuations of the local-moment spin operator  $S_z$ . These are transmitted via the coupling terms  $BS_zI_{\pm}$ .

The effects of the *BGS* and dipolar terms may be represented in terms of their frequency spectra as is shown in Figure 1. Since the *BGS* term embodies the fluctuations of the  $S_+$  operator, its spectrum is centred at  $\omega_{eo} = \gamma_e H_o$ , i.e. well above the nuclear Larmor frequency  $\omega_{no} = \gamma_n H_o$ . For the conditions shown in the figure,

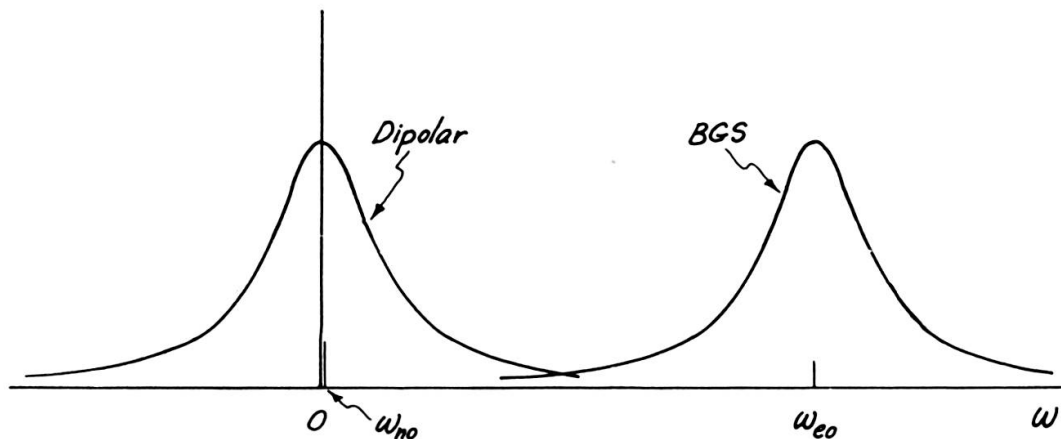


FIG. 1. — Frequency spectra associated with dipolar and *BGS* relaxation mechanisms as described in the text, for conditions such that  $\omega_{eo}T_{1,2e} << 1$ .

$\omega_{eo}T_{2e} \gg 1$ , the dipolar process predominates. Here  $T_{2e}^{-1}$  is the local moment *EPR* linewidth. In the opposite extreme,  $\omega_{eo}T_{2e} < 1$ , the spectral densities of the two processes at  $\omega_{on}$  would be comparable, and their relative strengths would depend on the coupling matrix elements.

#### A. Case of No Spin Diffusion

If the nuclei do not communicate with one another via spin diffusion, then nuclear relaxation dynamics become particularly simple. Such a case, namely,  $^{27}\text{Al}$  in  $\text{LaAl}_2:\text{Gd}$ , has been studied by McHenry and Silbernagel [12]. Here, spin diffusion among the  $^{27}\text{Al}$ , already reduced by the large internal quadrupole splitting, appears to be almost totally inhibited by the disordering effect of the *Gd* impurities.

The analysis of spin-lattice relaxation in this case rests on the assumption that the relevant coupling varies, on the average, as  $1/r^3$ , where  $r$  is the distance from the impurity to the nucleus in question. This would apply, for example, for dipolar or *RKKY* coupling. Any single impurity then relaxes exponentially with

$$1/T_1(r) = C/r^6. \quad (1)$$

In Eq. (1)  $C$  contains the coupling coefficients and spectral density function to be specified later. It was first shown by Tse and Hartmann [18] that after a brief initial period the system magnetization then relaxes as

$$1 - M(t)/M_0 \propto \exp[-(t/\tau_1)^{1/2}] \quad (2)$$

with

$$1/\tau_1 = (4N_0c/3)^2 \pi^3 C, \quad (3)$$

where  $N_0c$  is the volume density of magnetic sites. The striking feature of Eq. (2) and (3) is that the parameters—except  $C$ , which is to be determined—are readily available to the experimenter. This relaxation process is therefore subject to simple and direct interpretation.

Relaxation data [12] for  $^{27}\text{Al}$  in  $\text{La}_{1-c}\text{Gd}_c\text{Al}_2$  is shown in Figure 2, where we see that the behavior of Eq. (2) is dramatically realized. Values of  $\tau_1$  were extracted as a function of field  $H$ , temperature  $T$ , and concentration  $c$  from a series of such

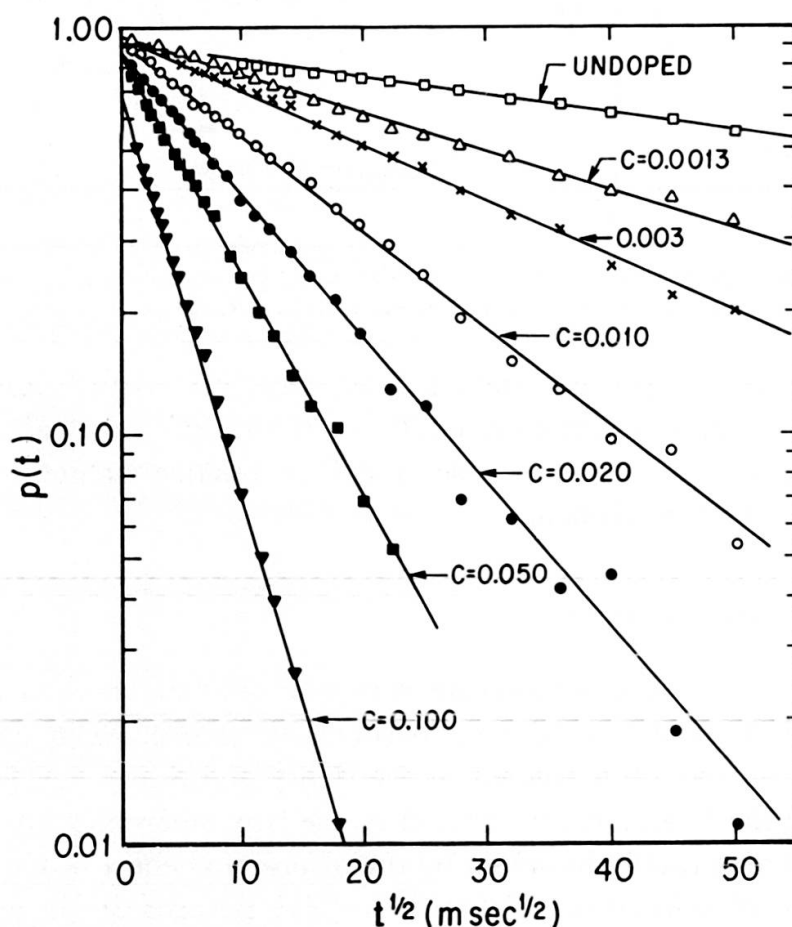


FIG. 2. — Relaxation curves  $\ln p(t)$  vs.  $t^{1/2}$  ( $p(t) = 1 - M(t)/M_0$ ) for  $^{27}\text{Al}$  in  $\text{La}_{1-c}\text{Gd}_c\text{Al}_2$ , illustrating behavior predicted by Eq. (2). Taken from Ref. 12.

experiments. The results are displayed, in part, in Figure 3, where several features are to be noted. First, the rate  $\tau_1^{-1}$  appears to vary much more slowly with  $c$  than  $\propto c^2$  [Eq. (3)]. Further, from the observed variation of  $\tau_1^{-1} \propto \delta B_s(x) / \delta x$ , where  $B_s(x)$  is the Brillouin function and  $x = g\mu_B H / kT$ , we conclude that the dipolar mechanism is predominant. The BGS mechanism varies, in contrast, as  $B_s(x) / x$

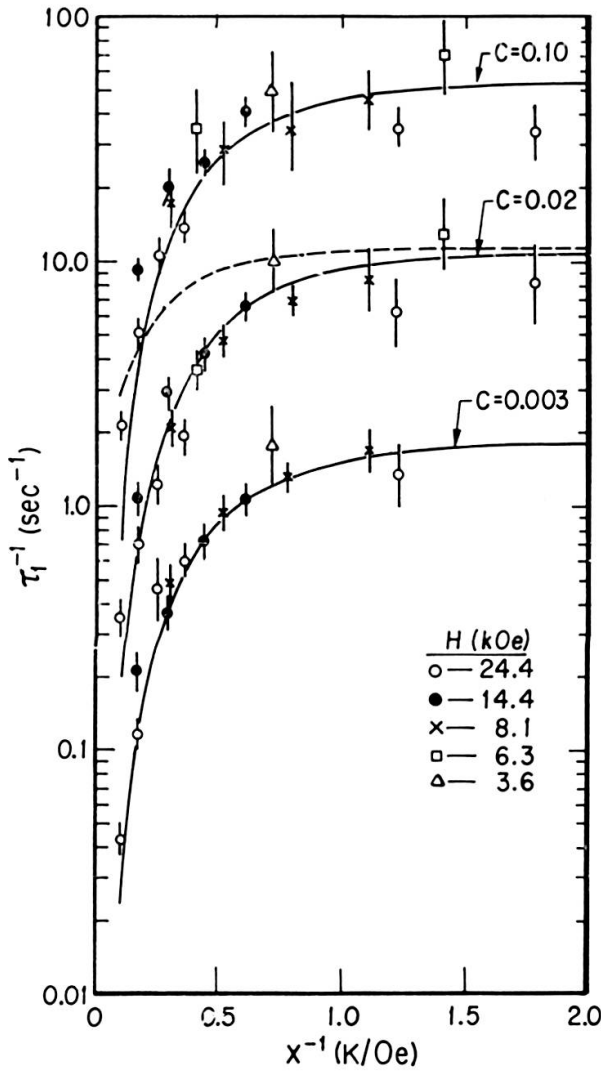


FIG. 3. — Measured rates  $\tau_1^{-1}$  (Eq. (3)) for  $^{27}\text{Al}$  in  $\text{La}_{1-c}\text{Gd}_c\text{Al}_2$ , plotted semilogarithmically against  $x^{-1}$ , where  $x = g\mu_B H/kT$ . Solid and dashed curves show saturation behavior of dipolar and BGS mechanisms, respectively, for correlation time independent of  $H$  and  $T$ . Taken from Ref. 12.

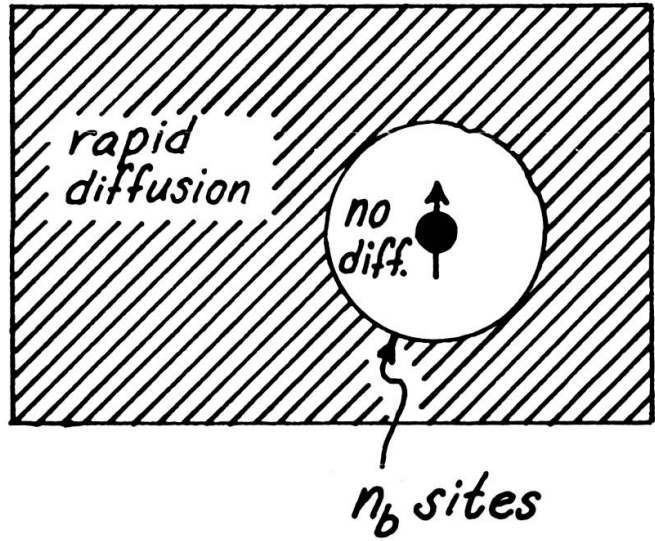


FIG. 4. — Illustrated division of  $\text{Cu}:\text{Mn}$  alloy into a diffusionless region containing  $n_b$  sites surrounding each impurity spin and a bulk region having rapid diffusion.

(dashed line, Fig. 3), which is in decidedly poorer agreement. For dipolar fluctuations  $C \propto \tau_m (1 + \omega_{on}^2 \tau_m^2)^{-1}$ , where  $\tau_m$  is the correlation time for  $Gd$  moment fluctuations. Since  $\omega_{on} \tau_m \ll 1$  (see Ref. [12]) one concludes that  $\tau_m^{-1} \propto c$  and is independent of  $H$  and  $T$  over this range. The motion of the  $Gd$  impurity moments is therefore dominated by spin-spin couplings. Analysis in detail [12] suggests that these originate from the *RKKY* interaction.

In conclusion, then, when nuclear spin diffusion is absent, the analysis of impurity-induced relaxation becomes straightforward and yields a considerable amount of useful information. For example, the  $Gd$  *EPR* line is probably exchange narrowed here, so that the numbers yielded for  $\tau_m$  are obtainable in no other way.

### B. Diffusion Barrier Phenomena

When some diffusion among host nuclei is possible on the time scale of  $\tau_1$  [Eq. (3)], the picture of part II-A above breaks down and the situation becomes



more difficult to analyze. In general the full interpretive apparatus developed for paramagnetic impurities in dielectric crystals [19] must be invoked.

We focus our attention on the particular case of  $\underline{Cu Mn}$ , which is being analyzed in a series of experiments by Alloul and Bernier [10, 11]. These authors have found for the purposes of analysis that the alloy may be divided into two regions spatially as shown in Figure 4. In an approximately spherical region surrounding each impurity the conduction-electron spin-density (and therefore local *NMR* shift) is varying so rapidly that neighboring nuclei cannot communicate via spin-diffusion. These nuclei therefore relax according to the analysis of part II-A above. The remaining "bulk" nuclei are in good enough contact to maintain a common spin temperature and relax exponentially. The radius of the spherical region is the diffusion barrier radius  $b$ . With the electron spin density varying as  $\sim r^{-3}$  it is easy to show that  $n_b \propto \langle S_z \rangle$ , where  $n_b = 4\pi N_0 b^3 / 3$  is the number of spins "isolated" within the diffusion barrier. The relaxation time of the bulk spins is simply obtained by volume integration of Eq. (1) from  $b$  to  $\infty$ . This yields

$$1/T_1(\text{bulk}) = \frac{4\pi N_0 c C}{3b^3} = \frac{16\pi^2 N_0^2 c C}{9n_b} \quad (4)$$

Equation (4) leads to the important observation, overlooked in previous work, that motion of the diffusion barrier as embodied in the factor  $n_b$  plays a major role in the  $H$  and  $T$  dependence of  $T_1(\text{bulk})$ .

The experimental results [10] bear out the picture presented here. We summarize the most important findings briefly. The observed relaxation curves [ $\ln(1 - M(t)/M_0)$  vs.  $t$ ] are found to consist of a superposition of an  $\exp(-at^{1/2})$  term and an exponential (bulk) term which predominates at large  $t$ . By extrapolation these terms can be separated, yielding data for both relaxation processes as well as for  $n_b$  from the fraction which relaxes as  $\exp\{-at^{1/2}\}$ . In this way  $n_b$  was indeed found to vary as  $\langle S_z \rangle$ . Taking account of this in Eq. (4), it was then found that  $C \propto T^{-1}$  and independent of  $H$ . The latter result was found to hold in the region where  $H/T$  is small enough so that  $\langle S_z \rangle \propto H/T$ . Further, the impurity relaxation was found to be linear in  $c$  and analysis of the  $\exp\{-at^{1/2}\}$  portion of the relaxation gave values of  $C$  consistent with the bulk behavior.

The principal finding, i.e. that  $C \propto T^{-1}$  and independent of  $H$ , suggests two possibilities for the underlying relaxation mechanism. Referring to Figure 1, the peak spectral densities for the dipolar and *BGS* mechanisms ( $\propto T_{1e}$  and  $T_{2e}$ , respectively) both vary as  $T^{-1}$  as found. Thus one has either  $\omega_{oe}T_{2e} \gg 1$  and therefore a dominant dipolar term, or  $\omega_{oe}T_{2e} \ll 1$  with both terms contributing but *BGS* (by estimate) predominant. The former possibility is rendered unlikely by the fact that no evidence for a *BGS* term appears at even the lowest fields used ( $\sim 1$  kG), making the *BGS* term unreasonably small. The latter option yields, however, a value for  $J_{sd}$  of several eV, in clear disagreement with the value obtained in *NMR*

studies of  $^{55}\text{Mn}$  in liquid  $\text{Cu Mn}$  (see part III) as well as negative magneto-resistance data [20].

While questions remain, then, the  $\text{Cu Mn}$  host *NMR* work has made important advances in understanding the nature of magnetic impurity relaxation in metals, with the clear demonstration of diffusion barrier phenomena being especially significant. For example, all previous work on this effect [21] must now be reexamined in the light of these developments. It remains an interesting challenge to unify the results of various experiments on the  $\text{Cu Mn}$  system, with particular regard to the conjecture [11] that Kondo condensation [3] may play a role here.

### III. *NMR OF $^{55}\text{Mn}$ IN LIQUID $\text{Al}_{1-x}\text{Cu}_x\text{:Mn}$*

We turn now to the subject of direct *NMR* of the local moment nucleus itself in dilute magnetic impurity systems. It is apparent that such experiments pose formidable technical difficulties, with broad lines, weak signals and a distinct possibility of unmanageably short relaxation times. Recently, however, such a study has been carried out at high temperatures on dilute *Mn* in  $\text{Al}_{1-x}\text{Cu}_x$  alloys [14]. In this final section of the paper we discuss the background for this experiment, give a brief summary of the results and some further interpretive remarks.

The possibility of this kind of experiment was recently discussed in a paper [15] examining the relaxation processes expected for nuclei on local moment sites, with particular reference to the case of  $^{55}\text{Mn}$  in  $\text{Cu Mn}$ . The nuclear relaxation appears to be dominated by a process which involves the localized spin as an intermediary, and which may be calculated in second-order perturbation theory. This process has been identified [15] with the *BGS* process for host nuclei. When the single-impurity *EPR* linewidth becomes comparable with the applied field  $H$ , the perturbation picture breaks down, giving at higher  $T/H$  a process which may be simply regarded as due to a fluctuating local-moment hyperfine field with a correlation time  $\sim T_{1e}$ :

$$1/T_{1n} = 2A_d^2 S(S+1) T_{1e}/3\hbar^2, \quad (5)$$

where  $T_{1e}$  is assumed to be given by a Korringa-type expression in terms of the exchange parameter  $J_{sd}$  [22]. Calculated rates  $T_{1n}^{-1}$  as a function of  $T$  for several values of  $H$  are shown in Figure 5 for  $\text{Cu Mn}$ , assuming  $J_{sd} = 1 \text{ eV}$ . Taking  $T_{1n}^{-1} \sim 10^5 \text{ sec}^{-1}$  as a rough upper limit of feasibility, we see that one must either work at *He* temperatures in a large field or in the neighborhood of the melting point of *Cu* ( $\sim 1350 \text{ K}$ ). The latter possibility formed the basis for the work considered here.

The  $\text{Al}_{1-x}\text{Cu}_x$  host alloy system was chosen as a host for *Mn* impurities for the reasons that (a) extensive studies of the impurity susceptibility and host *NMR* ( $^{27}\text{Al}$  and  $^{63}\text{Cu}$ ) were available and (b) study of the  $^{55}\text{Mn}$  *NMR* across this alloy series from pure *Al* to pure *Cu* permits an examination of the *Mn* moment-formation



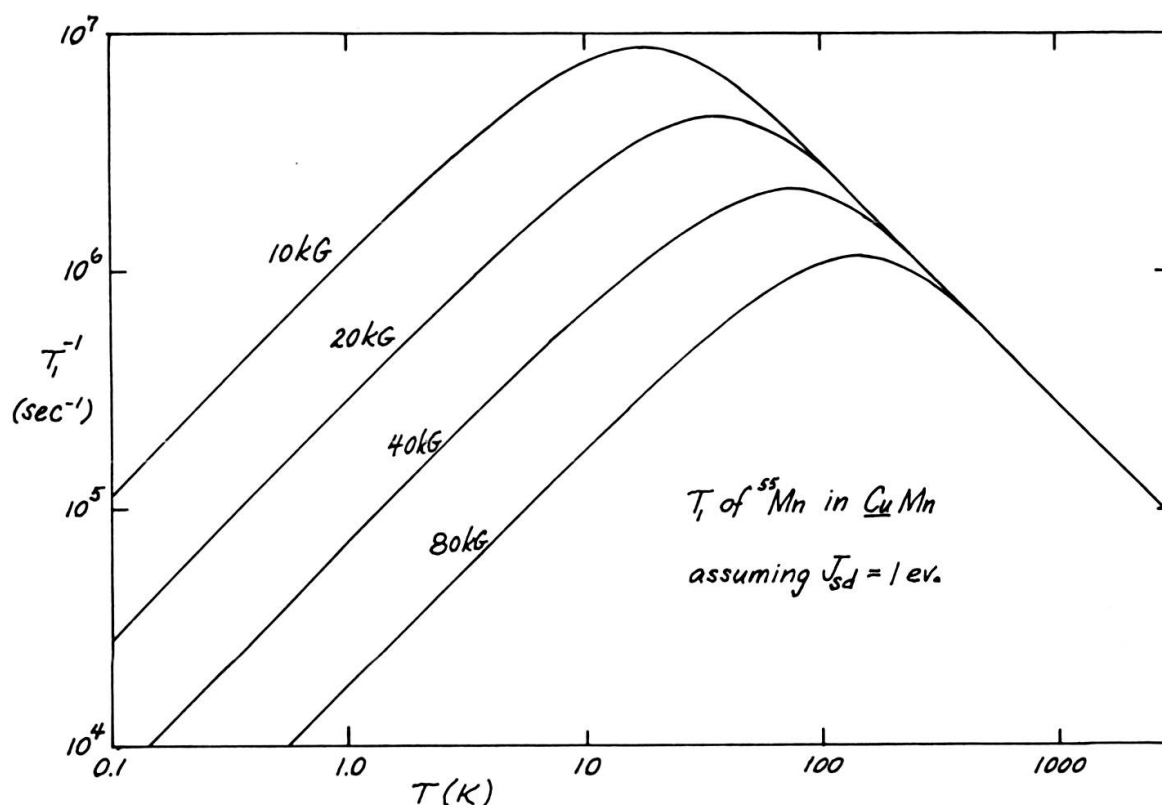


FIG. 5. — Calculated contribution to spin-lattice relaxation rate of local-moment nucleus from fluctuating hyperfine coupling with moment as a function of temperature for four values of applied field. Parameters assumed here:  $S = 5/2$ ,  $g = 2$ ,  $J_{sd} = 1$  eV,  $A_d = 44.10^{-4}$  cm $^{-1}$ , (host density of states)  $\rho_s = 0.16$  eV $^{-1}$  atom $^{-1}$  for each spin orientation. From Ref. 15.

process. The high-temperature  $Mn$  impurity susceptibilities across this alloy series, as taken from the literature [23-25], are shown in Figure 6. As we traverse the series  $Al \rightarrow Cu$ ,  $\chi_{Mn}$  increases by a factor  $\sim 3$  and goes from a slowly increasing function of  $T$  to the Curie law of pure  $CuMn$ . There is no sharp “transition” from nonmagnetic to magnetic behavior. One might say from  $\chi_{Mn}$  alone that local-moment behavior appears for  $x \geq 0.60$ . The  $NMR$  results serve to sharpen this rather broad conclusion and raise the “threshold” value of  $x$  to 0.80 or more.

A description of the experiments and discussion of the results has already been given [14]. Here we summarize the main results and discuss further the moment formation process as  $x \rightarrow 1$  in the host alloy series. The results are as follows:

(1) By plotting the observed  $^{55}Mn$  shift  $K_{Mn}$  against  $\chi_{Mn}$  with temperature the implicit parameter, one may partition the underlying structure of these quantities into orbital and localized  $d$ -spin components, yielding the variation of the orbital shift  $K_{orb}$  and the  $d$ -spin hyperfine coefficient  $\alpha_d$  with composition as shown in Figures 7 and 8, respectively.  $\alpha_d$  is proportional to the core-polarization hyperfine field per Bohr magneton  $H_{hf}^d$ . We return to a detailed discussion of these data after the summary.

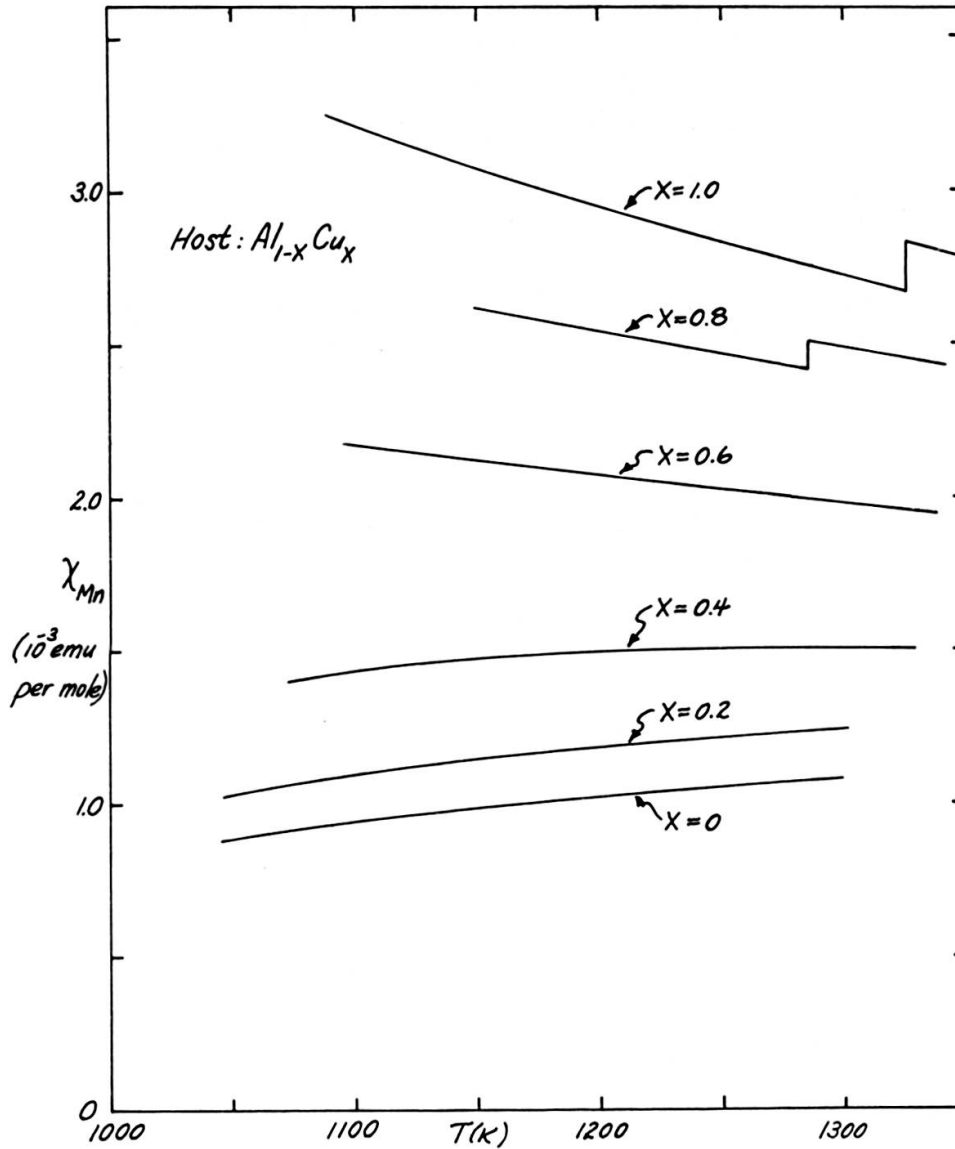


FIG. 6. — Manganese impurity susceptibility  $\chi_{Mn}$  in a series of liquid  $Al_{1-x}Cu_x$  alloys (Refs. 23-25). The discontinuity seen in the  $Cu$  and  $Al_{.20}Cu_{.80}$  data takes place at the melting point.

(2) The spin-lattice relaxation rate (corrected for variations of  $T$  and  $\alpha_d$ ), assumed to be dominated by the enhanced  $d$ -spin Korringa mechanism [26] at the  $Al$ -rich end, makes a rather sudden transition to a value larger by a factor  $\sim 5$  as pure  $Cu$  is approached. This is interpreted as the onset of the mechanism of Eq. (5). A detailed analysis leads to deduced values of  $J_{sd} = 0.82 \pm 0.10$  eV and  $1.22 \pm 0.15$  eV for the liquid and solid phases of  $Cu Mn$ , respectively. This may be compared with the low-temperature magnetoresistance value of 0.8 eV [20].

(3) The origin of the observed "jump" in  $J_{sd}$  across the melting point is not understood. It does, however, offer an explanation for the corresponding jump of  $\sim 6\%$  in  $\chi_{Mn}$  at the melting point [23] in terms of the  $(1 + \rho_s J_{sd})$  correction factor for the free-spin Curie susceptibility found on both the Anderson [27] and  $J_{sd}$  [3, 7]

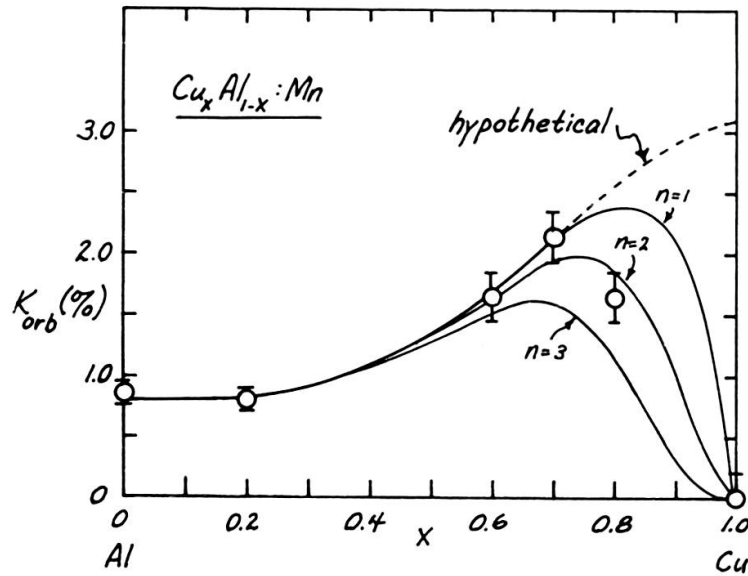


FIG. 7. — Experimental variation of  $K_{orb}$  for  $Al_{1-x}Cu_x:^{55}Mn$  with composition ( $x$ ), showing model theory curves calculated as described in the text.  $K_{orb}$  vanishes for pure Cu as expected for an S-like moment.

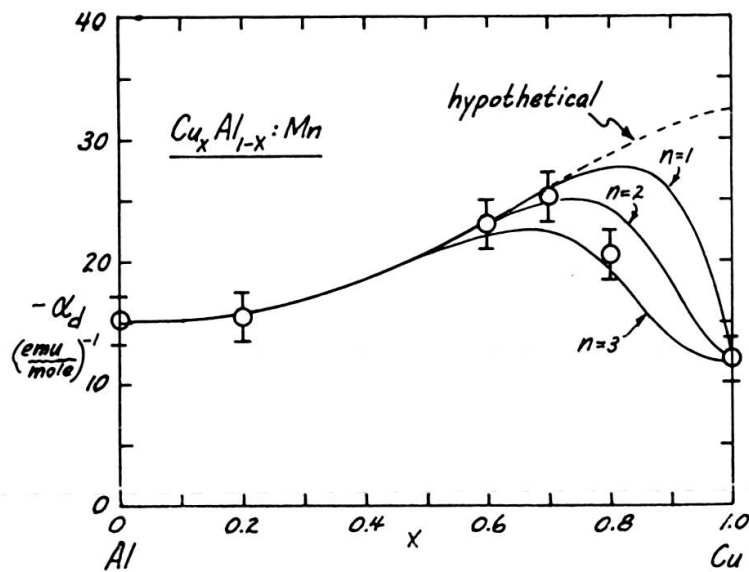


FIG. 8. — Experimental variation of  $\alpha_d$  for  $Al_{1-x}Cu_x:^{55}Mn$  with composition ( $x$ ), showing model theory curves calculated as described in the text.

models of the impurity state. Here  $\rho_s$  is the host density of states. The correction comes out to be of the right magnitude and sign.

For the remainder of the discussion we direct our attention to the behavior of the impurity state over the composition range where the moment “formation” process takes place as revealed by the above-mentioned data. In other words, we presume (contrary to the suggestions [24, 28] that  $\underline{Al}Mn$  represents an impurity system in the Kondo-condensation state) that  $\underline{Al}Mn$  does not meet the Anderson [2] criteria for moment formation because of the large virtual bound state width

$$\Delta = \pi \langle V_{kd}^2 \rangle \rho_s, \quad (6)$$

that  $\text{Cu Mn}$  (obviously) does, and that a transition from one to the other takes place as  $\rho_s$  and  $\Delta$  diminish across the  $\text{Al} \rightarrow \text{Cu}$  series.

As we see from Figures 7 and 8, this transition results in some rather curious behavior in  $K_{orb}$  and  $\alpha_d$ . Both parameters are seen to increase gradually at first, then drop sharply at the  $\text{Cu}$ -rich end. Nothing in the variation of  $\chi_{Mn}$  (Fig. 6), for example, would presage this behavior. The close correspondence between the  $K_{orb}$  and  $\alpha_d$  curves suggests a common mechanism, and we would like to propose that something at least closely related to the Jaccarino-Walker [29] (J-W) moment-formation phenomenon is operating here. It is recalled that these authors explained the occurrence of  $\text{Fe}$  impurity moments in  $\text{Nb-Mo}$  alloys in terms of near-neighbor configurations computed on the basis of statistical probabilities. The conclusion was simply that two or more  $\text{Nb}$  near-neighbors sufficed to quench the moment at a given  $\text{Fe}$  site.

Let us see how such a model might apply to the present situation, starting with the behavior of  $K_{orb}(x)$  (Fig. 7). We presume the observed variation of  $K_{orb}(x)$  as  $x \rightarrow 1$  to be the result of a statistical "transition" from the orbital shift of the non-moment state to the (zero-valued)  $K_{orb}$  of the fully developed moment. The initial increase of (nonmoment)  $K_{orb}$  with  $x$  is attributed to narrowing of the virtual bound state as  $\rho_s$  decreases [see Eq. (6)]. This follows because  $K_{orb} = \beta \chi_{orb}$ ,  $\beta = (2/A) \langle r^{-3} \rangle_{av}$  ( $A = \text{Avogadro's number}$ ), and  $\chi_{orb}$  varies as  $\Delta^{-1}$  or faster, if there is enhancement.

We make a quantitative estimate of  $K_{orb}(x)$  as follows. At any given instant the system consists of a mixture of magnetized and unmagnetized impurities. Because of the rapid liquid motion compared with nuclear Larmor periods, a given  $^{55}\text{Mn}$  nucleus will average the properties of all possible impurity states. Adopting the  $J$ - $W$  criterion for moment formation, the experimental result is then expected to be

$$K_{orb}(x) = P_n(x) K_{orb-nm}(x), \quad (7)$$

where  $P_n(x)$  is the probability of  $n$  or more  $\text{Al}$  atoms in the nearest-neighbor "shell" of a given  $\text{Mn}$ , and  $K_{orb-nm}(x)$  is the orbital shift of the  $\text{Mn}$  nonmoment state at  $\text{Cu}$  concentration  $x$ . We can only guess the behavior of the latter quantity; a hypothetical  $K_{orb-nm}(x)$  is plotted in Figure 7 as a dashed line. Corresponding  $K_{orb}(x)$  curves for  $n = 1, 2$ , and  $3$  are also plotted, giving reasonable accord with the data for  $n = 2$ . Although these results are at best semiquantitative, the data are shown to be at least consistent with such a model in which two or more  $\text{Al}$  neighbors quench the  $\text{Mn}$  moment.

Application of these ideas to  $\alpha_d$  is shown in Figure 8. Here the variation of the "nonmoment"  $\alpha_d$  is purely hypothetical as the behavior of hyperfine fields in metals is only poorly understood [30]. We simply extrapolate the trend in  $\alpha_d$  established

for  $x \leq 0.60$ . For the "moment"  $\alpha_d$  we adopt the value found for *Cu Mn* and assume it to be constant with  $x$ . The resulting statistical averages are again shown for  $n = 1, 2$ , or  $3$  *Al* neighbors required to quench the moment. The data appear to fall in the range of  $n = 2 \rightarrow 3$  and again show consistency with a model of this sort.

One may also attempt to apply these ideas to the powerful local-moment relaxation mechanism, which is seen [14] to change even more abruptly than  $K_{orb}$  or  $\alpha_d$  as  $x \rightarrow 1$ . It is not clear, however, that the relaxation mechanism itself is not influenced by the rapid fluctuations of environment in an  $Al_{1-x}Cu_x$  alloy. Thus, one may not be able to assume it is independent of composition for the "moment" impurities, and no firm conclusion can be drawn.

The *J-W* picture gives a qualitatively reasonable, if not rigorous, explanation for the variation of  $K_{orb}$  and  $\alpha_d$  with composition. The specific assumptions of this model may not be necessary here, but it offers at least a conceptual framework with which to take account of the inhomogeneous nature of these alloys, which clearly may play an important role.

The obvious question remaining is whether the *J-W* model can account for the occurrence of moments in these alloys in terms of the susceptibilities, as in the original work. The data of Gruber and Gardner [24] (Fig. 6) do not follow any well-defined temperature law; thus one is stopped by lack of knowledge about the unmagnetized susceptibility behavior. One can, however, compare with the Curie-Weiss behavior found for these alloys by Myers and Westin [31] in the neighborhood of room temperature. Surprisingly, these authors find little or no change of effective moment over the range  $0.82 \leq x \leq 1$  where the most dramatic changes in our parameters take place. Thus we are forced to conclude either (1) that the behavior we observe is limited to the liquid state, (2) that the *Mn* moment becomes less stable at high temperatures, or (3) that the solid-phase alloys are not random.

There appears to be little theoretical basis for possibilities (1) or (2) above. For example, the measured  $J_{sd}$  values [14] suggest via the Schrieffer-Wolff transformation [32] ( $J_{sd} \propto \langle V_{kd}^2 \rangle$ ) that the virtual-bound state is narrower in the liquid [Eq. (6)], rendering the moment *more* stable according to the Anderson [2] criterion.

Finally, we note the apparent contradiction between the impurity susceptibility results of References [24] and [31]. In particular, the  $Al_{.20}Cu_{.80}:Mn$  liquid-state results [24] appear to exhibit rough Curie-Weiss behavior with  $\theta \sim 350$  K, as opposed to  $\theta \sim 0$  K at lower temperatures [31]. Experiments are underway to resolve these inconsistencies.

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## DISCUSSION

RIVIER: How do you count the nearest neighbours in a liquid?

WALSTEDT: Well, in a liquid it turns out that people have done neutron scattering experiments that indicate that there really is a nearest neighbour shell which has essentially the same configuration as in the solid. I admit this is rather a murky point.



ALLOUL: I would just like to make some statements about what can be done by the techniques we used for the measurement of the nuclear relaxation of the host nuclei at low temperatures. You have explained how we obtained the information we are interested in, that is the fluctuations of the impurity moment. The fact is that we can measure a relaxation time of the impurity which is extremely different from the relaxation time measured by *EPR* in these systems which are bottlenecked. In fact we measure something that is unbottlenecked, which means that we measure directly the so-called  $T_{ds}$  which is very hard to get from *EPR*. In the case of *CuMn* and *CuCr* we find a very nice Korringa type of behaviour and the  $J$  value which can be drawn is much bigger than the *EPR* figure, at least a factor of two bigger. This is rather interesting because it could be related to the calculation that Götze did this morning.

DUPREE: I would like to say that it would be very nice if the statistical model you put forward is true, but there is some data around which you might have difficulty in explaining with this model, and these are the susceptibility measurements. These have been done on a much finer scale varying the electron densities in *AlSn* and *AlGa* for example. These show a bump analogous to the bump in the  $K$  orbital that you have there. I think a bump in the susceptibility, if true, is really difficult to explain on a statistical model.

WALSTEDT: I have been scrupulously careful to avoid saying anything about any other system !