

## Conduction-electron-spin polarization near Mn impurities in Cu<sup>†</sup>

N. Karnezos\* and J. A. Gardner<sup>†</sup>

*Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174*

(Received 23 July 1973)

The perturbation of <sup>63</sup>Cu hyperfine fields by nearby Mn impurities was measured by detecting copper satellite-nuclear-resonance lines. Three satellites were found and were attributed to the resonance of copper nuclei in second-, third-, and fourth-neighboring shells to an impurity. The hyperfine-field perturbation of first-neighbor nuclei and the envelope of the oscillating disturbance at distant neighbors can be estimated from other information. We have expressed the experimental results in a form which can be readily compared with free-electron calculations of conduction-electron-spin polarization by magnetic impurities. The Rudermann-Kittel-Kasuya-Yosida (RKKY) mechanism is apparently too weak to account for the observed polarization, and we have calculated the conduction-electron-spin disturbance which arises from hybridization of conduction states with the impurity *d* states. Near the impurity this computed spin polarization is not particularly sensitive to details of the model. It depends primarily only on the impurity density-of-states bandwidth, and agreement with experiment is very good for a halfwidth of about 0.2 eV.

### INTRODUCTION

When magnetic impurities are dissolved into normal metals, the conduction-electron spin near the impurity is polarized.<sup>1</sup> The exact radial and temperature dependence of this polarization is of considerable interest, and in this paper we report NMR measurements of the spin polarization around Mn impurities in copper. We have detected three <sup>63</sup>Cu satellite resonances in dilute CuMn alloys which we attribute to the resonance of copper nuclei in second-, third-, and fourth-neighboring shells to isolated Mn impurities. The second-neighbor satellite is positively identified but the other two are presently only tentatively identified. The positions of the satellites with respect to the main copper resonance line were measured over a temperature range of 77–300 K and in external fields of 12 and 21 kG and were found to be proportional to  $H/T$ . The approximate position of the first-neighbor satellite can be inferred from other data, but no clear resonance was detected there. This particular satellite is subject to extreme broadening because of the proximity of the strong impurity magnetic dipole, and it would be difficult to detect with our present NMR spectrometer. We made only a cursory attempt to find it. A preliminary report of the satellite detection was given in a previous paper<sup>2</sup> along with the main <sup>63</sup>Cu resonance linewidths and intensities in these CuMn alloys.

It has been observed<sup>3,4</sup> that the conduction-electron-spin polarization around magnetic impurities is a good bit larger than one would expect from an *sd* interaction. In order to produce a polarization of the magnitude observed experimentally in CuMn, an exchange energy of more than an electron volt

would be required. This is several times larger than the coupling energy one finds from other experiments.<sup>1</sup> It is known that hybridization of conduction states and impurity *d* states can also cause a sizeable conduction-electron-spin polarization. We have computed this contribution to the spin polarization in CuMn using a free-electron model for the copper conduction band and an adjustable impurity density-of-states band. In the region of the first few neighbors to the impurity, the computed polarization is roughly proportional to the width of the impurity band and is otherwise surprisingly insensitive to details of the model. For an impurity band having a half-width of  $\sim 0.2$  eV, the computed polarization agrees with experiment in both sign and magnitude.

In the remainder of the paper we give a brief review of the NMR properties of metals with magnetic impurities and describe in detail the experimental results and computation of the spin polarization. We also discuss briefly the results of the model calculation with respect to other impurity systems whose relevant NMR properties are known.

### HOST NMR IN THE PRESENCE OF MAGNETIC IMPURITIES

When a small amount of Mn is alloyed into copper, most of the copper nuclei do not have a Mn ion close by. Their magnetic hyperfine field is changed only slightly by dipolar fields and conduction-electron-spin polarization from many distant Mn ions. This random superposition of fields broadens but does not greatly shift the position of the copper-nuclear-resonance line. Sugawara<sup>5</sup> has shown experimentally that broadening of the host resonance line by magnetic impurities can be represented by a Lorentzian broadening function convoluted with the

(approximately Gaussian) pure-copper NMR line. He found that the Lorentzian half-width (at half-maximum) was given by

$$\Delta = \alpha cH/T, \quad (1)$$

where  $c$  is the atomic concentration of impurity. Sugawara found a value of approximately 30 for  $\alpha$  in  $CuMn$  when  $T$  is expressed in K. Others<sup>6-8</sup> have also reported line broadening of this magnitude, and we found  $\alpha = 23 \pm 3$  K.<sup>2</sup>

In addition to the magnetic hyperfine perturbation, a  $^{63}Cu$  nucleus is subject to quadrupolar interaction with electric field gradients. The central  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  nuclear transition is very weakly affected by small electric field gradients, but the noncentral NMR transitions can be greatly broadened.<sup>9</sup> Even in pure-copper metal, noncentral nuclear transitions are so greatly shifted by electric field gradients from dislocations, etc. that they are not visible in normal NMR experiments unless sample filings are carefully annealed.<sup>10</sup> In this work we observe only the central  $^{63}Cu$  nuclear transition and need only be concerned with the possibility of second-order quadrupolar broadening. This varies inversely with the external magnetic broadening described above by its different dependence of  $H$ . Electric field gradients far from impurities are apparently too small to affect the main copper resonance in external fields as large as 10 kG, because no  $H^{-1}$ -dependent width is observed experimentally.

Host nuclei which are very close to an impurity are subject to a substantial hyperfine-field perturbation which depends on the relative positions of the nucleus and impurity. Conduction-electron-spin polarization by an impurity produces an isotropic hyperfine-field disturbance which shifts equally the resonant frequency of nuclei in a given neighboring shell. If the frequency shift is large enough the shell will split out of the main resonance into a separate satellite. From the concentration dependence of the main-resonance intensity we have shown that as many as five separate  $^{63}Cu$  satellites may exist in the  $CuMn$  systems we have studied.<sup>2</sup> Satellite resonances are quite weak and have previously been detected only in a few nonmagnetic dilute alloys.

In addition to this isotropic perturbation, nearby host nuclei may be subject to an anisotropic second-order quadrupolar interaction with electric field gradients around the impurity and to the anisotropic magnetic field of the impurity dipole. In powder samples these two interactions can broaden satellite resonance lines which otherwise would have the same shape as the main resonance.

#### EXPERIMENTAL PROCEDURE AND RESULTS

Sample alloys were prepared from 99.999%-purity Cu and 99.99%-purity Mn by melting the con-

stituents in sealed quartz capsules, shaking vigorously for an hour or more, and quenching in water. In order to minimize sample oxidation, the metals and sample capsule were degassed by heating in the presence of a getter before sealing. The Mn concentration varied from 0.07 to 1.0 at.%. All alloys were chemically analyzed and were discarded if any departure from nominal composition or any evidence of inhomogeneity was discovered. The NMR samples were made from 400-mesh metal filings which were potted in epoxy.

The NMR experimental work was done with a field-swept spectrometer operating at a frequency of 13.6 or 24 MHz (corresponding to external magnetic fields of approximately 12 or 21 kG, respectively). The spectrometer was locked to the resonance absorption mode and the absorption derivative recorded as  $H$  was swept through resonance. A 30- or 100-sec lock-in time constant was used, and to minimize baseline drift problems the field-sweep rate was set just slow enough to avoid distorting the satellites.

Figure 1 is a recorder trace showing the main  $^{63}Cu$  resonance line and the satellites. Our field-sweep range was insufficient to sweep over all three satellites in one run, and in Fig. 1 the up-field satellite trace is from another experimental run on the same sample but at a slightly higher temperature. We found the main-line properties at 24 MHz to be consistent with Eq. (1) using the coupling constant given previously.<sup>2</sup> The up-field satellite was clearly visible in all samples and at all temperatures and frequencies investigated. The two down-field satellites could be clearly resolved only in the two most dilute samples (0.07- and 0.15-at. % Mn) and at temperatures below 150 K. At higher concentration and temperature the two satellites merged together and into the main line. The existence of the far left-hand satellite was not confirmed prior to the high-frequency work, and it was not reported previously.

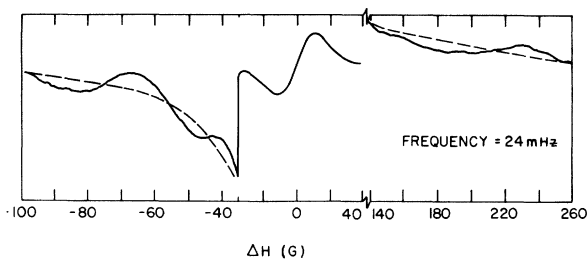


FIG. 1. Recorder trace showing satellites and main line in a 0.15-at. %-Mn sample. The temperature was 115 K for the left-hand part and 145 K right of the break. The sensitivity was reduced by 100 in the main-line portion.

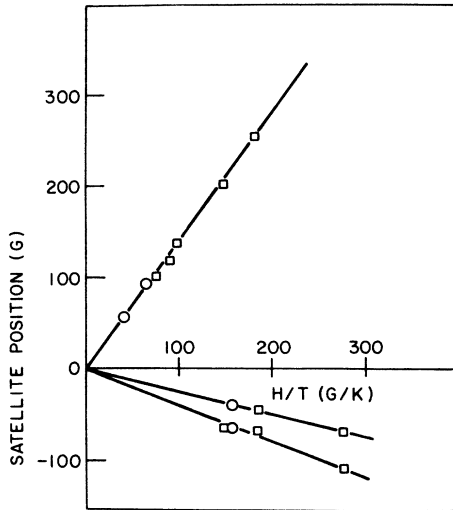


FIG. 2. Satellite positions relative to the main  $^{63}\text{Cu}$  resonance. Circles are data at 13.6 MHz and squares are at 24 MHz.

The center-to-center separations of the three satellites from the main line are shown in Fig. 2. Within an experimental uncertainty of  $\pm 5$  G the separations are independent of Mn concentration and proportional to  $H/T$  with proportionality constants 1.35,  $-0.25$ , and  $-0.42$  K. The peak width of the up-field satellite is shown in Fig. 3. Experimental

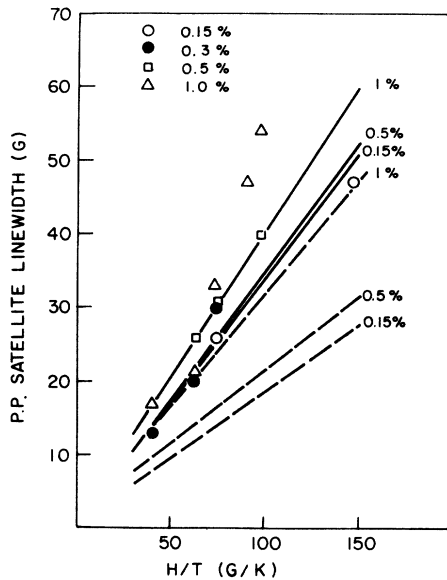


FIG. 3. Peak-to-peak linewidth of the up-field satellite. Solid (dashed) lines are second- (third-) neighbor satellite widths where broadening in excess of the main line is attributed to the impurity dipolar field.

uncertainty is less than 25% except for the 1.0-at. %-Mn sample for which the main-line overlap made it difficult to obtain an accurate baseline. Within the experimental uncertainty, the satellite width is proportional to  $H/T$  and unlike the main line is not strongly dependent on Mn concentration. The peak-to-peak amplitude of this satellite relative to the main line is shown in Fig. 4. It is divided by  $c_{\text{Mn}}$  for normalization purposes.

Because of sensitivity to drift and possible systematic errors in baseline determination, the amplitudes shown in Fig. 4 are accurate to only about a factor of 2. The two down-field satellites were narrower and several times stronger than the up-field one. Unfortunately, the proximity of the main line made it impossible to determine an accurate baseline for these two satellites, and we were unable to measure any meaningful widths or amplitudes.

#### HYPERFINE-FIELD DISTURBANCE

The radial dependence of the host hyperfine-field perturbation close to an impurity may be found by identifying the shells responsible for the satellites. We can positively identify the up-field satellite on the basis of the width and amplitude data, but at present we can only tentatively identify the other two. Combined with additional information, however, the single identified satellite allows us to assemble a qualitatively complete picture of the host hyperfine-field perturbation.

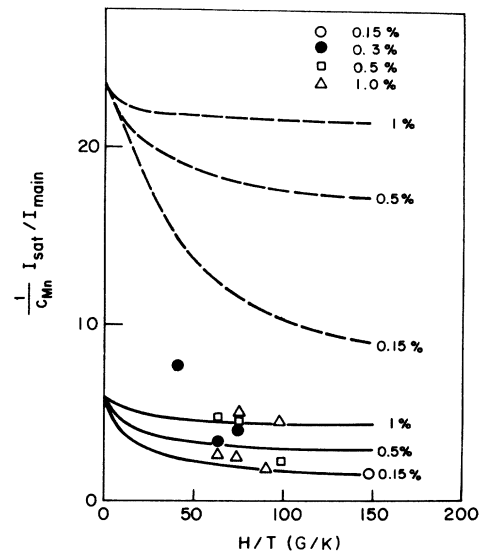


FIG. 4. The up-field satellite resonance derivative amplitude relative to main line. Solid (dashed) lines are the relative second- (third-) neighbor satellite amplitudes which are reduced at finite  $H/T$  by impurity dipolar broadening.

Identification of the up-field satellite proceeds directly from the observation that its width varies as  $H/T$ . This indicates that the dominant satellite-broadening mechanism is magnetic dipolar broadening by the neighboring Mn ion. The dipolar-broadening function depends only on distance from the impurity and the thermal average impurity moment. The latter is known from susceptibility data, and it is approximately proportional to  $H/T$  in this temperature range. The satellite absorption line is a convolution of the dipolar-broadening function with the main-resonance absorption line, and its integrated intensity is  $n_i c$  times that of the main line. Here  $n_i$  ( $= 12, 6, 24, 12, 24$  for the first through fifth shells, respectively) is the number of nuclei in the shell. We computed the convolutions appropriate to the first few neighboring shells and found that only a resonance of second-neighbor nuclei could reproduce the data of Figs. 3 and 4. The computed widths and amplitudes of the second neighbor and the next best fit, the third neighbor, are shown in Figs. 3 and 4. The computed satellite resonances are asymmetric, but the distortion is too small to be experimentally significant.

Both down-field satellites are much too narrow to arise from a first-neighbor-shell resonance, so they must be from third, fourth, or possibly fifth shells. Satellites from more distant shells are ruled out on the basis of main-line intensity data.<sup>2</sup> A reasonable tentative identification is to assign the wider split satellite to the third shell and the closer one to the fourth shell.

The first-neighbor satellite position can be estimated from NMR data in liquid-metal alloys. When Mn is dissolved into liquid copper, the Cu resonance line is shifted by the average hyperfine-field disturbance. This average is strongly dominated by the first-neighbor perturbation, and one can therefore determine the approximate first-neighbor satellite splitting from the liquid NMR shift.<sup>11</sup> We find that a first-neighbor satellite should appear at a separation of  $(5.5 \text{ K})H/T$  from the main resonance line. Below 300 K this satellite must be quite wide and weak, and we were unable to locate any clear resonance at this position. Some "bumps" were

seen in the expected region, but our signal-averaging capability was too limited to obtain any information which could be considered significant.

In Table I we list the relative hyperfine-field shifts  $\Delta H_{\text{hf}}(r)/H_k$  which are derived from the satellite splittings.  $\Delta H_{\text{hf}}(r)$  is simply the negative of the appropriate satellite splitting, and  $H_k$  ( $= 0.0024H$ ) is the <sup>63</sup>Cu Knight shift.

At more distant neighbors, the conduction-electron-spin perturbation and  $\Delta H_{\text{hf}}(r)$  are known to oscillate in sign and become small far from the impurity. If we assume that in this region

$$\Delta H_{\text{hf}}(r) = H_0 \frac{\cos(2k_{\text{F}}r + \delta)}{(2k_{\text{F}}r)^3}, \quad (2)$$

we can find  $H_0$  from a moment analysis of the main line.<sup>12,13</sup> Equation (2) is strictly valid only asymptotically, but it should serve adequately as an estimate of the perturbation beyond the fifth neighbor. By using the above form we implicitly ignore all anisotropic perturbations, but these are known to contribute negligibly to the main-line-broadening function.<sup>12</sup> The main line is broadened by fields from impurities lying at random locations more distant from the nucleus than  $r_c$ . In this case  $r_c$  is approximately the fifth-neighbor distance, but its precise value is unimportant. To first order in concentration the  $l$ th moment ( $l \geq 2$ ) of such fields is

$$\langle \Delta H^l \rangle \simeq \frac{cH_0^l}{6\pi} \frac{\langle \cos^l(x) \rangle}{(3l-3)(2k_{\text{F}}r_c)^{3l-3}}. \quad (3)$$

Here we have assumed a free-electron conduction band. To find  $H_0$  we compare the second and fourth moments with experiment. The experimental broadening function is approximately Lorentzian near the center, but it must go to zero more rapidly in the wings. For simplicity one normally assumes a simple cutoff  $H_c \gg \Delta$ .  $H_c$  is related to  $r_c$ , but  $H_0$  depends only on  $\Delta$  as

$$H_0 = 36\sqrt{3} \Delta/c.$$

For CuMn,  $\Delta = (23 \text{ K})cH/T$ ,<sup>2</sup> and we find  $H_0 = (1.4 \times 10^8 \text{ K})H/T$ . This estimate for  $\Delta H_{\text{hf}}$  at distant neighbors is also listed in Table I.

#### CONDUCTION-ELECTRON-SPIN POLARIZATION BY MAGNETIC IMPURITIES

The conduction-electron-spin disturbance  $\Delta s_{\pm}(r)$  by an impurity is related to the host hyperfine-field disturbance by

$$\Delta s_{\pm}(r)/s_p = \Delta H_{\text{hf}}(r)/H_k, \quad (4)$$

where  $s_p$  is the Pauli spin polarization. The experimental quantity on the right is tabulated in Table I to allow direct comparison with theory. It is irrelevant whether actual or pseudospin densities are considered since the spin enhancement at the nucleus cancels in Eq. (4).

TABLE I. Conduction-electron-spin polarization near Mn impurities in Cu.

Neighbor	$k_{\text{F}}r$	$\Delta H_{\text{hf}}/H_k$
1	3.5	$-(2300 \text{ K})/T$
2	4.9	$-(570 \text{ K})/T$
3	6.0	$(170 \text{ K})/T$
4	6.9	$(100 \text{ K})/T$
> 5	> 8	$(5.7 \times 10^5 \text{ K}) \cos(2k_{\text{F}}r + \delta) / T(2k_{\text{F}}r)^3$

One mechanism by which a magnetic impurity polarizes the conduction-electron spin is a spin-spin interaction.

$$\Delta = J(r)\vec{s}(r) \cdot \vec{S} \quad ,$$

between the conduction-electron-spin density  $s(r)$  and the impurity spin  $S$ . Since the spatial form of  $J(r)$  is not known it is usually approximated by a  $\delta$  function  $J\delta(r)$ . This approximation is inadequate except for the asymptotic region of large  $r$  where the polarization is given by the well-known Ruderman-Kittel-Kasuya-Yosida (RKKY) form,<sup>14</sup>

$$\Delta S_{\mathbf{z}}^{\text{RKKY}}(r) = \frac{9\pi}{4\Omega} \frac{J}{E_F} \langle S_{\mathbf{z}} \rangle \frac{\cos(2k_F r)}{(2k_F r)^3} \quad . \quad (5)$$

$\Omega$  is the atomic volume of the host metal. If small  $g$  shifts and nonlocal contributions to the impurity susceptibility are ignored,

$$\langle S_{\mathbf{z}} \rangle = -\chi_{\text{imp}} H / 2\mu_B = -2\mu_B \langle S(S+1) \rangle_{\text{eff}} H / 3kT \quad (6)$$

In the temperature range of interest,  $\langle S(S+1) \rangle_{\text{eff}} \approx 25/4$ .<sup>15</sup> Using

$$s_p = 3\mu_B H / (4E_F \Omega)$$

and Eq. (4), we find the asymptotic hyperfine-field polarization

$$\left( \frac{\Delta H_{\text{hf}}(r)}{H_k} \right)_{\text{RKKY}} = \frac{2\pi J \langle S(S+1) \rangle_{\text{eff}}}{kT} \frac{\cos(2k_F r)}{(2k_F r)^3} \quad . \quad (7)$$

If the spin polarization beyond the fifth neighbor in  $\text{CuMn}$  is attributed to this mechanism,  $|J| = 1.3$  eV. This value for  $J$  in  $\text{CuMn}$  was also obtained by Behringer.<sup>12</sup> That is several times larger than the coupling energy found in other types of experiments,<sup>1</sup> and it seems probable that some other mechanism is contributing significantly to the hyperfine-field perturbation.

Another mechanism by which a magnetic impurity can polarize the conduction spin is hybridization of the polarized impurity  $d$  orbitals with the conduction electrons. In a magnetic field the two conduction-electron-spin subbands are perturbed differently, and the difference results in a substantial spin perturbation. In order to calculate the density perturbation in the two conduction-electron-spin directions we assume a free-electron conduction band and the usual model for the Mn impurity density of  $d$  states having five nearly filled and five nearly empty bands of opposite spin.<sup>16</sup> If the impurity spin is polarized in the  $\sigma$  direction the density of conduction electrons with spin  $\pm\sigma$  is perturbed by  $5\Delta\rho_{\pm\sigma}(r)$ , where

$$\begin{aligned} \Delta\rho_{\pm\sigma}(r) = & \frac{1}{2\pi^2} \int_0^{k_F} k^2 dk \{ [n_2^{\pm\sigma}(kr) - j_2^{\pm\sigma}(kr)] \\ & \times \sin^2 \eta_2^{\pm\sigma}(k) - n_2(kr) j_2(kr) \sin 2\eta_2^{\pm\sigma}(k) \} \quad . \quad (8) \end{aligned}$$

The phase shifts are related to the impurity density

of  $d$  states by the Friedel sum rule<sup>17</sup> which in this case may be written

$$\eta_2^{\pm\sigma}(k) = \pi \int_0^k \rho_d^{\pm\sigma}(k') dk' \quad .$$

$\rho_d^{\pm\sigma}(k)$  is the impurity density of  $d$  states for one of the filled ( $+\sigma$ ) or unfilled ( $-\sigma$ ) bands.

The conduction-electron-spin polarization in the  $\sigma$  direction is

$$\begin{aligned} \Delta s_{\sigma}(r) = & \frac{5}{2} [\Delta\rho_{\sigma}(r) - \Delta\rho_{-\sigma}(r)] \\ = & S_{\sigma} [\Delta\rho_{\sigma}(r) - \Delta\rho_{-\sigma}(r)] \quad , \quad (9) \end{aligned}$$

and the thermal average in the  $z$  direction is given by

$$\Delta s_{\mathbf{z}}(r) = \langle S_{\mathbf{z}} \rangle [\Delta\rho_{\sigma}(r) - \Delta\rho_{-\sigma}(r)] \quad . \quad (10)$$

Using Eqs. (4) and (6), the hyperfine-field perturbation can be written

$$\frac{\Delta H_{\text{hf}}(r)}{H_k} = \frac{4E_F \langle S(S+1) \rangle_{\text{eff}}}{9} \frac{P(k_F r)}{kT} \quad , \quad (11)$$

where

$$P(k_F r) = 2\Omega [\Delta\rho_{\sigma}(r) - \Delta\rho_{-\sigma}(r)] \quad .$$

$(2\Omega)^{-1} = \frac{1}{2} \rho_{fe}(r)$  is the unperturbed conduction-electron density per spin, and the two parts of  $P(k_F r)$  have simple physical meanings.  $2\Omega\Delta\rho_{\pm\sigma}(r)$  is the fractional charge polarization of the conduction-electron  $\pm\sigma$  spin subband by each (partially) occupied impurity  $d$  band of that spin.

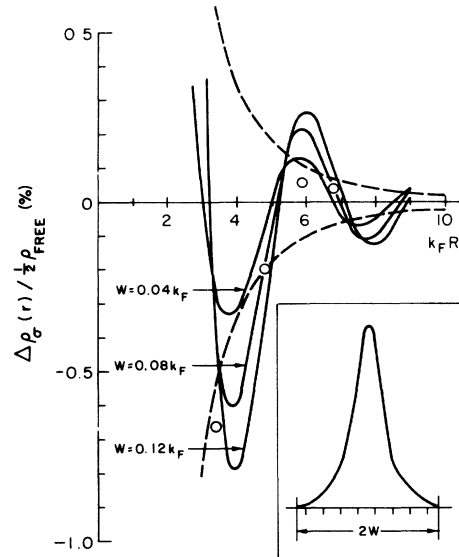


FIG. 5. Conduction-electron charge-density disturbance per 95% occupied impurity  $d$  band. The  $d$ -band shape shown in the inset is the central portion of a Lorentzian with a constant subtracted so that  $\rho_d^{\pm\sigma}(k)$  goes to zero at four times the Lorentzian half-width. Data are calculated from Table I using Eq. (11). The dashed line represents the envelope of distant oscillations given in Table I.

Daniel and Friedel<sup>17</sup> have shown that when  $r$  is much greater than the inverse of the impurity bandwidth, the density oscillations  $\Delta\rho_{\pm\sigma}(r)$  are proportional to  $\sin\eta_{\pm\sigma}^2(k_F)$  and are independent of other details of the impurity band. The region of physical interest is much closer to the impurity however, and there the asymptotic formula is known to be incorrect.<sup>18</sup> We have computed the fractional density disturbance  $\Delta\rho_{\pm\sigma}(r)/\frac{1}{2}\rho_{F\sigma}$  for a number of different impurity bands, and two representative sets of results are shown in Figs. 5 and 6. We have assumed that the impurity fits into the lattice without distortion, and have taken the impurity-band shape as a function of  $k/k_F$  so that the results depend only on  $k_F r$ .

The impurity band was taken to be the central portion of a Lorentzian from which a constant is subtracted to make the density of states go to zero for  $k > 0$ . Cutting off the band is necessary to avoid an unphysical divergence at low  $k$ . We chose the subtracted constant so that the density of states goes to zero at 1, 2, and 4 times the Lorentzian half-width. The conduction-electron-density disturbance in the near-neighbor region was found to be qualitatively different from the asymptotic formula. The  $+\sigma$  density disturbance is very weakly dependent on the precise location of the impurity band provided 80% or more of the band area lies below  $k_F$ . If 20% or less of the  $-\sigma$  impurity band area lies below  $k_F$ , the  $-\sigma$  conduction-electron-density disturbance contributes little to  $P(k_F r)$ . Conse-

quently, the computed spin-density polarization depends primarily only on the shape and width chosen for the  $+\sigma$  impurity density-of-states band.

In Figs. 5 and 6 we show the fractional density polarization computed for  $+\sigma$  impurity bands cut off at 1 and 4 times the Lorentzian half-width and located so that 95% of the area lies below  $k_F$ . The experimental points are taken from Table I, using Eq. (11) and neglecting  $\Delta\rho_{-\sigma}(r)$ . For impurity bands of total width  $2w < 0.2k_F$ , the spin disturbance scales roughly as  $w$  for all band shapes. Best overall agreement with the experimental points occurs when  $w$  is about  $0.04k_F$ . This corresponds to a half-width at half-maximum of about  $0.01k_F$  or an energy of order 0.2 eV. The impurity bandwidth in  $\text{CuMn}$  is not known, but most experimental evidence indicates a width of about this magnitude.<sup>1</sup>

#### DISCUSSION

In view of the rather simple model, the agreement with experiment indicated in Figs. 5 and 6 must be considered excellent. For a reasonable impurity-band half-width of about 0.2 eV, both the sign and approximate magnitude of the hyperfine-field perturbation are obtained. It is interesting to compare the predictions of this model with other experimental information about spin-density oscillations. One can show easily that if  $\Delta\rho_{-\sigma}(r)$  always contributes negligibly, Eq. (11) remains valid for magnetic impurities of any spin. The implication is that the ratio of the conduction-electron-spin-density oscillations to the impurity-spin susceptibility is a function only of the impurity bandwidth.

Unfortunately, far too little is known experimentally about the bandwidth and spin polarization in magnetic impurity systems to provide any definitive test of this conclusion. The only  $3d$  impurities which are strongly magnetic in a simple metal host are Cr, Mn, and Fe. The relative impurity bandwidths are not known, and previous experimental information on spin polarization is limited to NMR line-broadening and liquid-state Cu-NMR-shift measurements. These data give somewhat ambiguous results. The liquid-state shifts<sup>11</sup> are proportional to the impurity susceptibility, indicating that  $P(k_F r)$  is independent of the particular impurity. The Cu linewidths in solid  $\text{CuCr}$ <sup>15</sup> and  $\text{CuFe}$ <sup>4,5</sup> are relatively larger than in  $\text{CuMn}$  however which would indicate that  $P(k_F r)$  is larger in the first two systems. Lang *et al.*<sup>18</sup> have recently suggested that impurity interactions in nonsolid solutions like  $\text{CuCr}$  and  $\text{CuFe}$  may significantly increase the NMR linewidth, and this could be the source of the apparent discrepancy between the solid and liquid data.

The only other magnetic impurity systems in which satellite resonances have been reported are  $\text{CuCo}$  and  $\text{AlMn}$ . Neither of these is really a

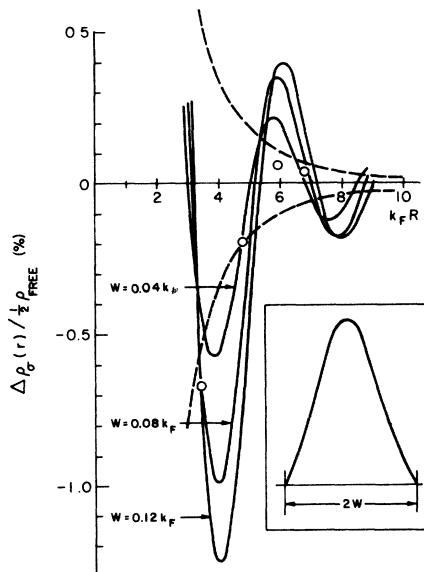


FIG. 6. Conduction-electron charge-density polarization per 95% occupied impurity  $d$  band. The  $d$ -band shape shown in the inset is the central portion of a Lorentzian with a constant subtracted so that  $\rho_d^0(k)$  goes to zero at the Lorentzian half-width.

strongly magnetic impurity, but each has a very large spin susceptibility, and it may still be reasonable to use Eq. (11) to describe the polarization. It would be more appropriate to use a model impurity density of states which fluctuates rapidly between different spin configurations. Since  $\Delta\rho_\sigma(r)$  is not very sensitive to minor changes, these fluctuations may not qualitatively change our results. The relative hyperfine-field shift  $\Delta H_{\text{hf}}/H_k$  of the first-neighbor satellite in *CuCo* at low temperature is  $-1.65$ . Satellites shifted by  $0.82$  and  $-0.31$  were tentatively identified as second and third or fourth, respectively.<sup>20</sup> The low-temperature Co susceptibility in this system is difficult to measure accurately because of the influence of magnetic pairing and ferromagnetic impurity clustering.  $\chi$  is about  $2 \times 10^{-3}$ /mole<sup>21,22</sup> but the uncertainty is at least 20%. In addition, perhaps as much as a third of the susceptibility is associated with the orbital motion of the *d* electrons.<sup>23</sup> Under these circumstances we can find only a rough estimate of  $P(k_F r)$  in *CuCo*. Taking the spin susceptibility to be  $2 \times 10^{-3}$  cm<sup>3</sup>/mole, the above hyperfine-field shifts are equivalent to charge polarization  $P(k_F r) = -1.00\%$ ,  $0.51\%$ , and  $-0.21\%$ , respectively. If the tentative satellite identifications are correct, the latter two shifts are in clear disagreement with the computed polarization. If the second two satellite identifications are reversed, the charge polarization is consistent with  $\Delta\rho_\sigma(r)$  for a Co band which

is a bit wider than the Mn impurity band in Cu.

Two satellites found in *AlMn* have relative hyperfine-field shifts of  $-1.09$  and  $-0.32$  at low temperature.<sup>24</sup> Neither was positively identified, but the first is probably a first-neighbor satellite. This identification is consistent with Al NMR shifts observed in liquid *AlMn* alloys.<sup>25</sup> The low-temperature susceptibility is  $1.5 \times 10^{-3}$  cm<sup>3</sup>/mole.<sup>26</sup> Assuming the orbital susceptibility is negligible, we find charge polarizations  $P(k_F r)$  equal to  $-0.65\%$  and  $-0.20\%$  for the above two satellites. The first three near-neighbors in Al are located at  $k_F r = 5.0, 7.1,$  and  $8.7$  which are unfortunately close to the nodes of the computed polarization. The experimental polarization is not inconsistent with  $\Delta\rho_\sigma(r)$  if the Mn bandwidth is somewhat wider than in Cu, but otherwise we can say very little. The unidentified second satellite could be either a second or third neighbor or a superposition of both.

Obviously, more experimental and theoretical work is required on this problem. The good agreement between the experimental and theoretical polarization for *CuMn* is encouraging, but the ambiguities and possible disagreement with other results need to be resolved.

*Note added in proof.* J. B. Boyce and C. P. Slichter [Phys. Rev. Lett. **32**, 61 (1974)] recently reported satellites in *CuFe*. The first-neighbor satellite is in good agreement with our model. Other satellites were not positively identified.

<sup>†</sup>Work supported in part by the National Science Foundation, the Advanced Research Projects Agency and the Research Corporation.

\*Present address: Department of Physics, Northwestern University, Evanston, Ill. 60201.

<sup>†</sup>Present address: Department of Physics, Oregon State University, Corvallis, Ore. 97331.

<sup>1</sup>Recent reviews of the impurity problem have been given by A. Narath, Crit. Rev. Solid State Sci. **3**, 1 (1972); A. J. Heeger, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23; M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. **40**, 380 (1968).

<sup>2</sup>N. Karnezos and J. A. Gardner, AIP Conf. Proc. **10**, 801 (1972).

<sup>3</sup>A. Narath and A. C. Gossard, Phys. Rev. **183**, 391 (1969).

<sup>4</sup>J. E. Potts and L. B. Welsh, Phys. Rev. B **5**, 3421 (1972).

<sup>5</sup>T. Sugawara, J. Phys. Soc. Jap. **14**, 643 (1959).

<sup>6</sup>J. Owen, M. Browne, W. D. Knight, and C. Kittel, Phys. Rev. **102**, 1501 (1956).

<sup>7</sup>A. C. Chapman and E. F. W. Seymour, Proc. Phys. Soc. Lond. **72**, 797 (1958).

<sup>8</sup>A. J. Heeger, A. P. Klein, and P. Tu, Phys. Rev. Lett. **17**, 803 (1966).

<sup>9</sup>A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, 1961).

<sup>10</sup>N. Bloembergen and T. J. Rowland, Acta Met. **1**, 731 (1953).

<sup>11</sup>J. A. Gardner and C. P. Flynn, Phys. Rev. Lett. **17**, 579 (1966).

<sup>12</sup>R. E. Behringer, J. Phys. Chem. Solids **2**, 209 (1957).

<sup>13</sup>C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

<sup>14</sup>K. Yosida, Phys. Rev. **106**, 893 (1959).

<sup>15</sup>J. Bensele and J. A. Gardner, J. Appl. Phys. **15**, 1157 (1970).

<sup>16</sup>P. W. Anderson, Phys. Rev. **124**, 41 (1961).

<sup>17</sup>E. Daniel and J. Friedel, in *Proceedings of the Ninth International Conference on Low Temperature Physics* (Plenum, New York, 1964), p. 933.

<sup>18</sup>P. Jena and D. J. W. Geldart, Phys. Rev. B **7**, 439 (1973).

<sup>19</sup>David V. Lang, David C. Lo, James B. Boyce, and C. P. Slichter (unpublished).

<sup>20</sup>D. V. Lang, J. A. Boyce, D. C. Lo, and C. P. Slichter, Phys. Rev. Lett. **29**, 776 (1972).

<sup>21</sup>J. Bensele, thesis (University of Pennsylvania, 1973) (unpublished).

<sup>22</sup>R. Tournier and A. Blandin, Phys. Rev. Lett. **24**, 397 (1970).

<sup>23</sup>A. L. Ritter, J. Bensele, and J. A. Gardner, AIP Conf. Proc. **10**, 1639 (1972).

<sup>24</sup>H. Launois and H. Alloul, Sol. State Commun. **7**, 525 (1969).

<sup>25</sup>C. P. Flynn, D. A. Rigney, and J. A. Gardner, Philos. Mag. **15**, 1255 (1967).

<sup>26</sup>F. T. Hedgecock and P. L. Li, Phys. Rev. B **2**, 1342 (1970).