PHYSICAL REVIEW B VOLUME 11, NUMBER 9 1 MAY 1975

Conduction-electron–local-moment exchange coupling in dilute *Cu*Mn and *Ag*Mn

R. E. Walstedt and L. R. Walker
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 7 November 1974)

The theory of spin-density oscillations (SDO) caused by local-moment–conduction-electron (s-d) exchange in simple metals is reviewed and restated in terms of spherical components of the exchange interaction on the Fermi surface. Both direct and s-d mixing exchange sources are included, and calculations are presented to account for the effects of potential scattering, in terms of phase shifts, and conduction-band exchange enhancement of the SDO. The SDO amplitude is related to inhomogeneous broadening of host nuclear-magnetic-resonance lines using the theory of such broadening given recently by the authors. The measurements of s-d exchange parameters by impurity-state susceptibility and EPR linewidth are also discussed, with particular emphasis on the effect of conduction-band exchange on these phenomena. We apply the above considerations to the alloy systems *Cu*Mn and *Ag*Mn. For *Cu*Mn, estimates of the predominant s-d mixing exchange from (i) ^{63}Cu NMR linewidths, (ii) Mn impurity-state susceptibility, and (iii) indirect high-temperature measurement of the single-impurity EPR linewidth are compared. Values so obtained range over a factor of ~ 1.5 with the SDO values smallest and the susceptibility values largest. This variation is in apparent conflict with the Hartree-Fock solution of the Anderson model. The exchange values found may also be combined with the Anderson-model theory to establish an upper limit of ~ 5.5 d electrons on the Mn site. For *Ag*Mn the impurity susceptibility corresponds to a rather smaller mixing exchange coupling in agreement with recent EPR work by Davidov *et al.* The ^{109}Ag NMR linewidth results of Mizuno are shown to be caused by more than one species of broadening agent, preventing a firm conclusion on the SDO measurement of exchange from being drawn.

I. INTRODUCTION

Over the past two decades numerous studies have been reported on the properties of $3d$ local moments in simple metals, and several model theories have been advanced to describe such systems.[1] Only in rare cases, however, have quantitative determinations of the fundamental physical parameters which govern these systems been reported.[2] We report here an attempt to make such a determination for the case of *Cu*Mn; the *Ag*Mn situation is discussed as well.

The particular quantities sought in the present work are the local-moment–conduction-electron (s-d) exchange parameters. These originate from direct exchange coupling as well as from the mixing of the localized d orbitals with band states nearby in energy.[3] The mixing effect is found (as expected) to dominate in the systems considered and will become our main focus of attention in Sec. V. The mixing exchange involves all the basic parameters of the Anderson model.[4] It is a major point of emphasis here that the comparison of various measures of this quantity which we undertake constitutes an interesting experimental test of the consistency of this model.

The s-d exchange interaction is reflected in a wide variety of experimental effects. For *Cu*Mn, one primary source of exchange data, namely EPR studies, is excluded because the relaxation bottleneck has never been successfully broken. We therefore turn to other measures of s-d exchange, three in particular being analyzed in detail in this paper. They are (a) long-range spin-density oscillations[5] (SDO) caused by the impurity, as reflected by host NMR line broadening, (b) high-temperature ^{55}Mn nuclear relaxation by moment fluctuations due to exchange scattering of conduction electrons, and (c) saturation moment or susceptibility of the impurity. We comment on these effects in turn.

(a) The long-range SDO generated by the direct exchange and also by s-d mixing are derived here in a coherent formulation. The mixing effect is discussed in terms of the degenerate Anderson model,[4,6] whereas the direct exchange effect is formulated in terms of the impurity Green's function[7] in order to take into account potential scattering effects. The resulting spin-density-oscillation (SDO) range function is expressed in terms of Fermi-surface exchange matrix elements such as determine the g shift and dynamic width of an isolated moment. A similar result, without the potential scattering effects, has been given by Davidov *et al.*[8] The SDO amplitude is subsequently related to host NMR linewidth data using recent calculations of impurity-induced NMR line shapes.[9]

(b) Recent high-temperature NMR studies of ^{55}Mn in *Cu*Mn[10] have revealed a dominant relaxation process originating in the fluctuating local-moment hyperfine field. These fluctuations are in turn governed by s-d exchange coupling. This experiment yields data equivalent to the EPR linewidth in the single-impurity limit.

(c) The total impurity-state moment is known to reflect changes from the free-spin value due to (direct) exchange polarization of the host band.[11] It is also known that the mixing effect is expressible in the same form,[4,12] except that the moment reduction does not correspond to an actual spin polarization in the band. Thus, the net moment should reflect the same exchange parameters as (a) and (b) above, given that the deviation from free-spin behavior is not great.

One might also have included here the negative magnetoresistance work by Monod[13] as a measure of s-d exchange. This was excluded from detailed consideration because of theoretical uncertainties,[14] but will be commented upon later in the paper.

Much of the theory necessary to interpret the foregoing effects was either contained in or implied by earlier work. The primary task here has been one of assembly, with two pieces of minor theoretical development relegated to appendixes. Our general approach has been to express the relevant measured quantities in terms of phase shifts and exchange parameters evaluated on an assumed spherical Fermi surface. Band-theoretical refinements of such a picture do not seem warranted at the present time.

Conduction-band exchange effects in Cu and Ag metals are thought to be appreciable,[15] though smaller than earlier evidence[16] indicated. Care has been taken to include them here, using the susceptibility-enhancement model developed by Singwi, Sjölander, and co-workers.[17] This model has been successfully applied to the interpretation of nuclear-relaxation enhancement in alkali metals by Shaw and Warren[18] and by Bhattacharyya *et al.*[19] In the present context we use this formulation to derive the exchange enhancement of the SDO and to calculate the enhanced local-moment–conduction-electron relaxation process using a slight modification of the random-phase-approximation (RPA) model theory of Moriya.[20] Enhancement effects are also incorporated in the saturation-moment expression for the Mn-impurity state. No attempt is made here to take account of Kondo condensation phenomena, the temperature being assumed well above T_K in the measurements considered. Furthermore, it was recently demonstrated experimentally[21] that SDO are unaffected by the Kondo transition.

The paper is organized as follows. The theory of SDO in these systems is spelled out in Sec. II. In Sec. III we discuss the conduction-electron enhancement effect. Formulas for local-moment relaxation rates and the saturation moment of the impurity state, including band enhancement effects, are given in Sec. IV. In Sec. V we discuss the interpretation of NMR line shapes in terms of SDO amplitudes, review the available host NMR line-width data on *Cu*Mn,[22–27] and *Ag*Mn,[28] and work out experimental s-d exchange parameters for the systems considered using the formulas of Secs. II, III and IV. Some discussion of the Anderson-model parameters is also presented in Sec. V. Conclusions are discussed in Sec. VI.

II. THEORY OF SPIN-DENSITY OSCILLATIONS

The potential disturbance created by a magnetic impurity in a metal generates both charge and spin-density oscillations. The SDO are caused by the spin-dependent nature of the potential, which in turn is a direct consequence of the s-d exchange coupling energy of the impurity. In this section we relate the long-range SDO amplitude to the Fermi-surface s-d exchange parameters and scattering phase shifts.

The present problem separates conveniently into two parts, namely, the effects of direct and mixing contributions to the s-d exchange, respectively. We shall consider these contributions in separate calculations. In both cases the results may be expressed in terms of the scattering phase shifts $\delta_l^{\pm}$ at the Fermi energy and the Fermi wave vector k_F in a spherical band[29,30]:

$$n^{\pm}(r) \cong n_0 - \frac{1}{4\pi^2}\sum_l (2l+1)\sin(\delta_l^{\pm})\cos(2k_F r+\delta_l^{\pm})/r^3 \tag{1}$$

(valid for large r), where ± denotes spin orientation and the index l labels the spherical components of the scattered wave.

The spin density $\Delta n(r) = n^{+}(r) - n^{-}(r)$ follows immediately from (1):

$$\Delta n(r) = -\frac{1}{4\pi^2}\sum_l (2l+1)\sin(\delta_l^{+}-\delta_l^{-}) \times \cos(2k_F r+\delta_l^{+}+\delta_l^{-})/r^3 \quad . \tag{2}$$

From (2) and the Friedel sum rule,

$$Z^{\pm} = \sum_l Z_l^{\pm} = \frac{1}{\pi}\sum_l (2l+1)\,\delta_l^{\pm} \quad , \tag{3}$$

we see that the amplitude of the SDO contribution of symmetry l depends only on the net polarization $Z_l^{+} - Z_l^{-}$ of the screening charge bound in the lth partial wave. The total screening charge of the impurity state is $Z^{+} + Z^{-}$ and is determined by the number of electrons outside closed shells in the neutral impurity atom.

The polarization of the partial waves which give rise to the SDO via Eq. (2) is presumed to come about as follows. The $l = 2$ term is driven by the s-d mixing effect and is controlled by the magnitude of the $3d$ moment itself, which is

$$Z_2^+ - Z_2^- = (5/\pi)(\delta_2^+ - \delta_2^-) \text{ (in } \mu_B) \ .$$

In our discussion below, an expression for this quantity will be given in terms of Anderson-model parameters.[4,6] On the reasonable assumption of a spherically symmetric mixing potential, polarization of the $l \neq 2$ waves comes about only through direct exchange between Bloch electrons and the $3d$ moment.[31] Let us first consider the formulation of the direct-exchange problem.

We treat the polarization effect due to direct exchange in a Green's function perturbation scheme in order to include the effects of potential scattering. The direct-exchange Hamiltonian is conventionally written[32]

$$\mathcal{H}_{\text{ex}} = \frac{1}{2N} \sum_{\vec{k}', \vec{k}} J_{\vec{k}', \vec{k}} [S_z (c^{*}_{\vec{k}'+} c_{\vec{k}+} - c^{*}_{\vec{k}'-} c_{\vec{k}-}) + S_+ c^{*}_{\vec{k}'-} c_{\vec{k}+} + S_- c^{*}_{\vec{k}'+} c_{\vec{k}-}] \ , \tag{4}$$

with

$$J_{\vec{k}', \vec{k}} = \tfrac{2}{5} N \sum_{\mu} \int d\vec{r}_1 \int d\vec{r}_2 \, \varphi^{*}_{\vec{k}'}(\vec{r}_2) \, \varphi^{*}_{d\mu}(\vec{r}_1) \times \varphi_{d\mu}(\vec{r}_2) \, \varphi_{\vec{k}}(\vec{r}_1) \, |\vec{r}_1 - \vec{r}_2|^{-1} \ , \tag{5}$$

where $\varphi_{\vec{k}}(\vec{r})$ is a Bloch function and the sum on μ is taken over five equally occupied d orbitals which form the spin-only moment. For $\vec{k}$ and $\vec{k}'$ in the vicinity of the Fermi surface it is convenient to expand the exchange as[33]

$$J_{\vec{k}', \vec{k}} = \sum_l (2l+1) J_l(|\vec{k}'|, |\vec{k}|) P_l(\cos\theta_{k'k}) \ . \tag{6}$$

The impurity-state properties of interest in this paper are expressible in terms of the $J_l(k_F, k_F) \equiv J_l$. It is noteworthy that the mixing exchange contribution also has the form of the appropriate l term in Eq. (6).[3]

The direct-exchange polarization effect is altered by the presence of the impurity potential $V(r)$ seen by the conduction electrons. First, $V(r)$ gives rise to SDO phase effects [$\delta_l^+ + \delta_l^- > 0$, Eqs. (2) and (3)] through charge screening. In addition, the Bloch functions $\varphi_{\vec{k}}(\vec{r})$ are no longer the eigenfunctions of the unperturbed Hamiltonian (i.e., omitting $\mathcal{H}_{\text{ex}}$) when $V(r)$ is important; thus, the exchange parameters in Eqs. (5) and (6) must be redefined. These matters can be dealt with by using the retarded Green's function G to calculate the SDO via

$$\Delta n(r) = -\frac{1}{\pi} \int_0^\infty dE f(E) \, \text{Im} \, \text{Tr}(\sigma_z \langle r | G | r \rangle), \tag{7}$$

where the trace is over spin coordinates and $f(E)$ is the Fermi function. For this purpose we have adopted a free-electron model with the impurity potential $V(r)$ assumed to be spherically symmetric. The direct exchange is treated as a first-order perturbation, with the Green's function expanded as

$$G = G_0 + G_0 J_{\text{op}} G_0 + \cdots , \tag{8}$$

where

$$G_0 = \frac{1}{T + V - E - i\delta} \ , \tag{9}$$

and J_{op} is the exchange operator corresponding to Eqs. (4) and (5). The main body of this calculation, in which we have drawn upon Anderson's discussion of G for the impurity problem in the r representation,[7] is presented in Appendix A.

The principal result from Appendix A is

$$\Delta n(r) = -\frac{\langle S_z \rangle \rho(E_F)}{4\pi r^3} \sum_l (-1)^l (2l+1) J_l \times \cos(\delta_l^+ - \delta_l^-) \cos(2k_F r + \delta_l^+ + \delta_l^-), \tag{10}$$

where $\rho(E_F)$ is the density of states at the Fermi surface for one spin direction exclusive of electron-electron and electron-phonon coupling effects, and J_l is the direct-exchange parameter generalized to the case of $V(r) \neq 0$ by Eq. (A7). The δ_l are the phase shifts due to $V(r)$ in the absence of exchange, where $\delta_l^+ = \delta_l^-$ for $l \neq 2$. Comparing Eq. (2) with Eq. (10) one finds that exchange produces equal and opposite changes in $\delta_l^\pm$ in first order, the difference being

$$\Delta(\delta_l^+ - \delta_l^-) = \pi (-1)^l \langle S_z \rangle \rho(E_F) J_l \ . \tag{11}$$

Equation (11) establishes the connection between scattering phase shifts and exchange parameters of the same symmetry. Comparison with Eq. (6) shows, as expected, that scattering for $\theta_{kk'} = \pi$ dominates the picture. In the absence of potential scattering $\delta_l^+ + \delta_l^- = 0$. Equation (10) then reduces for large r to Yosida's[11] Eq. (2.23), where only $l = 0$ exchange is considered.

We only need expressions for the phase shifts $\delta_2^\pm$ caused by s-d mixing to complete our formulation of long-range SDO. These are straightforwardly obtained from the Green's function for the degenerate Anderson model,[6,34] assuming the five spin-up d orbitals to be degenerate and nearly full with the spin-down ones degenerate and nearly empty. Under these circumstances the required phase shifts are given by

$$\begin{aligned} \sin\delta_2^\pm &= \Delta[(E_F - E_d^\pm)^2 + \Delta^2]^{-1/2} \ , \\ \cos\delta_2^\pm &= -(E_F - E_d^\pm)[(E_F - E_d^\pm)^2 + \Delta^2]^{-1/2} \ , \end{aligned} \tag{12}$$

where $E_d^\pm$ is the energy of the ± spin d state and $\Delta = \pi\rho(E_F) \langle V_{kd}^2 \rangle_{\text{av}}$ is the d-state width parameter evaluated at the Fermi surface. In Δ the squared matrix element V_{kd} is averaged over the Fermi surface. It is clear from Eq. (12) that for $\Delta \ll |E_F - E_d^\pm|$, the limit we consider here, δ_2^- and $\pi - \delta_2^+$ are small, positive angles. We therefore write

$$\sin(\delta_2^+ - \delta_2^-) = \frac{\Delta(E_d^- - E_d^+)}{[(E_F - E_d^+)^2 + \Delta^2]^{1/2}[(E_F - E_d^-)^2 + \Delta^2]^{1/2}} \tag{13}$$

and

$$\delta_2^+ + \delta_2^- = \pi + \tan^{-1}[\Delta/(E_d^- - E_F)] - \tan^{-1}[\Delta/(E_F - E_d^+)] \, . \tag{14}$$

The phase of the *d* wave is therefore nearly π, and it is convenient to define the SDO exchange parameter due to mixing as

$$J_{\text{SDO}}^m = -\frac{\langle V_{kd}^2 \rangle_{\text{av}}}{\langle S_z \rangle_{\max}} \times \frac{E_d^- - E_d^+}{[(E_F - E_d^+)^2 + \Delta^2]^{1/2}[(E_F - E_d^-)^2 + \Delta^2]^{1/2}} \, , \tag{15}$$

where $\langle S_z \rangle_{\max}$ is the saturated spin value of the magnetized impurity, and where we take $\cos(\delta_2^+ - \delta_2^-) \sim -1$ throughout. Equation (10) may then be taken to include both direct and mixing exchange sources, where for $l = 2$ we have $J_2(\text{total}) \cos(\delta_2^+ - \delta_2^-) \cong -(J_{\text{SDO}}^m + J_2)$. The mixing contributions to exchange which characterize other experimental quantities are discussed in Sec. IV.

III. ENHANCEMENT OF HOST-BAND SUSCEPTIBILITY BY CONDUCTION-BAND EXCHANGE : SDO ENHANCEMENT

The band susceptibility $\chi(q, \omega)$ of a nearly-free-electron gas is known to be enhanced by intraband exchange coupling.[35] It follows generally that the SDO generated by a magnetic impurity will also be enhanced. This was explicitly shown to be the case by Moriya[36] in a study of host-band polarization effects using the Anderson model with a q-independent conduction-band exchange potential. However, calculations of nuclear relaxation enhancement using a q-independent potential[20] have been found to give incorrect results for the alkali metals,[16] where the theory can be tested directly.

We have sought to avoid the assumption of a q-independent potential by making use of a recent theory of susceptibility enhancement,[17] in which the particle distribution-function equations of motion are decoupled in second order. Self-consistent numerical solution of these equations has been found to yield better pair-correlation functions than previous theories. The susceptibility is found[17] to be given by

$$\chi(q, \omega) = \frac{\chi_0(q, \omega)}{1 - I(q)\, \chi_0(q, \omega)} \, , \tag{16}$$

where $\chi_0(q, \omega)$ is the noninteracting band susceptibility and $I(q)$ is a functional of the pair correlation functions for parallel and antiparallel spins. As is well known, however, the solution of the RPA-model integral equation[35] is not of the form of Eq. (16). There has apparently been no attempt to solve the RPA model with a realistic potential.

Equation (16) has been used with some measure of success to calculate enhanced nuclear spin-lattice relaxation rates.[18,19] We adopt this equation for the calculation of enhancement effects in this and the following sections. The choice of the function $I(q)$ is taken up in Sec. IV.

In calculating the SDO enhancement, we shall utilize the spin-density response to a δ-function potential, namely, the Fourier transform of Eq. (16). The long-range (r^{-3}) part of this response will then yield the desired enhancement factor. For $I(q) = 0$, this procedure yields simply the Ruderman-Kittel-Kasuya-Yosida (RKKY) function.[11,37] Equation (16) is Fourier transformed using the methods in Lighthill's book,[38] and the r^{-3} term is calculated explicitly in Appendix B. The associated enhancement factor is found to be $[1 - I(2k_F)\, \chi_0(2k_F)]^{-2}$, i.e., the square of the enhancement of Re $\chi(q, 0)$ at $q = 2k_F$. A similar inverse-squared deenhancement factor for charge-density oscillations has been derived by Langer and Vosko[39] and by Blandin.[40] For the discussion of experimental data, then, Eq. (10) is modified to read

$$[\Delta n(r)]_{\text{interact}} = \gamma(2k_F)^2 \Delta n(r) \;\; [\text{Eq. (10)}] \, , \tag{17}$$

with

$$\gamma(2k_F) = [1 - \tfrac{1}{2}\alpha \bar{I}(2k_F)]^{-1} \, , \tag{18}$$

where $(1 - \alpha)^{-1}$ is the uniform susceptibility-enhancement factor and $\bar{I}(q) = I(q)/I(0)$.

IV. OTHER MEASUREMENTS OF EXCHANGE

In Sec. V we discuss *s-d* exchange values yielded by several types of measurement on the alloys considered in addition to the SDO amplitude. The effects discussed include impurity susceptibility and EPR linewidth as measured directly or through high-temperature nuclear spin-lattice relaxation.[10] Here we summarize the theoretical results needed to discuss these measurements. Effects of electron-electron coupling in the host band have been included according to the discussion of Sec. III.

A. Impurity-state susceptibility

This effect measures the diagonal component of $\mathcal{H}_{\text{ex}}$ [Eq. (4)] summed over occupied states, where $J_{\vec{k}',\vec{k}}$ is taken from Eq. (6) (modified to include the mixing-exchange contribution in the $l = 2$ term). In the absence of conduction-band exchange one finds the Curie susceptibility to be corrected by a factor[11,12]

$$\chi_{\text{imp}}(T)/\chi_S(T) = [1 + \tfrac{1}{2}\rho(E_F) J_{\vec{k}_F,\vec{k}_F}]^2 \, , \tag{19}$$

where $\chi_S(T)$ is the free-spin Curie susceptibility and $J_{\vec{k}_F,\vec{k}_F}$ denotes evaluation for $\vec{k}'=\vec{k}$ on the Fermi surface.

In order to take account of band enhancement, we must at this point draw a physical distinction between the effects of direct and mixing contributions to $J_{\vec{k},\vec{k}}$ on the impurity susceptibility. It is noted that the direct-exchange terms in Eq. (19) represent an actual host-band polarization effect, which is therefore enhanced by the $q=0$ enhancement factor $(1-\alpha)^{-1}$. On the other hand, the mixing term in Eq. (19) represents a reduction in the saturation moment due to the finite width of the virtual d states [see, e.g., Eq. (12)]. By the Anderson-Clogston compensation theorem[4,6] the associated net band polarization is small. Moreover, Moriya[36] has shown that only the net polarization is enhanced by band exchange. To a good approximation, then, the impurity-moment reduction due to mixing in Eq. (19) is not affected by band enhancement in free-electron-like metals. This picture holds for $V_{\vec{k}d}\,\rho(E_F)\ll 1$.

Considering only $l=0$, 1, and 2 terms to be important for the present work, we therefore express the impurity susceptibility as

$$\chi_{\rm imp}(T)/\chi_S(T)\cong\{1+\tfrac{1}{2}\rho(E_F)[(J_0+3J_1+5J_2)/(1-\alpha)+5J_\chi^m]\}^2\,, \tag{20}$$

where J_χ^m is the mixing exchange as reflected by the impurity-state moment. Combining Eqs. (3) and (12) and putting the result in the form of $g\mu_B S[1+5\rho(E_F)J_\chi^m/2]$, we find

$$J_\chi^m=-[1/\pi\rho(E_F)S]\sin^{-1}\{\Delta(E_d^- - E_d^+)\times[(E_d^- - E_F)^2+\Delta^2]^{-1/2}[(E_F-E_d^+)^2+\Delta^2]^{-1/2}\}\,. \tag{21}$$

J_χ^m is seen to coincide with $J_{\rm SDO}^m$ [Eq. (15)] in the limit of small Δ.

B. EPR linewidth and high-temperature spin-lattice relaxation of the impurity nucleus

The EPR linewidth T_{1e}^{-1} reflects the exchange parameters of Eq. (6) in the single-impurity ("unbottlenecked") limit. Direct measurements of T_{1e} are not available in the case of *Cu*Mn. However, T_{1e} has been measured indirectly for *Cu*Mn through the high-temperature spin-lattice relaxation of the ^{55}Mn nuclei.[10,41] For noninteracting electrons this quantity is related to the s-d exchange parameters through the Korringa[42] expression

$$1/T_{1e}=\pi\rho(E_F)^2\langle J_{\vec{k},\vec{k}'}^2\rangle_{\rm av}k_B T/\hbar\,, \tag{22}$$

where the average is taken over $\vec{k},\vec{k}'$ values on the Fermi surface. To include band exchange effects in Eq. (22) we modify Moriya's RPA-model theory by using Eq. (16) for the dynamic susceptibility. Thus the quantity $\langle J_{\vec{k},\vec{k}'}^2\rangle_{\rm av}$ in Eq. (22) is replaced, using Eq. (6), by

$$\langle J_{\vec{k},\vec{k}'}^2\rangle\to 2\sum_{l,l'}(2l+1)(2l'+1)J_l'J_{l'}'\times\int_0^1\frac{P_l(1-2x^2)P_{l'}(1-2x^2)x\,dx}{[1-\alpha\bar{I}(x)G(x)]^2}\,, \tag{23}$$

where

$$x=q/2k_F\,,$$

$$G(x)=\tfrac{1}{2}\{1+(1-x^2)\ln[\,|(1+x)/(1-x)|\,]/2x\}\,,$$

and

$$J_l'=J_l+\delta_{l2}J_{T_{1e}}^m\,.$$

For the dynamic exchange parameter due to mixing $J_{T_{1e}}^m$, we take the Kondo, Schrieffer-Wolff expression,[3]

$$J_{T_{1e}}^m=-S^{-1}\langle V_{\vec{k}d}^2\rangle_{\rm av}[(E_d^- - E_F)^{-1}+(E_F-E_d^+)^{-1}]\,. \tag{24}$$

From Eq. (23) we see that not only are the J_l^2 terms enhanced, but also there now appear cross terms $\propto J_l'J_{l'}'$, $l\neq l'$, with nonvanishing coefficients. In order to interpret T_{1e} data one must calculate the components of the enhancement tensor,

$$\mathcal{K}_{l,l'}(\alpha)=2(2l+1)(2l'+1)(1-\alpha)^2\times\int_0^1\frac{P_l(1-2x^2)P_{l'}(1-2x^2)x\,dx}{[1-\alpha\bar{I}(x)G(x)]^2}\,, \tag{25}$$

as a function of α. For this purpose it is necessary to choose a form for $\bar{I}(x)$. As noted by Shaw and Warren,[18] the quantity $\mathcal{K}_{0,0}(\alpha)$ is relatively insensitive to the variation of $\bar{I}(x)$ at large x ($x\sim 1$). Thus, using somewhat different functions $\bar{I}(x)$, both these authors[18] and Bhattacharyya *et al.*[19] found good agreement with NMR T_1 data on the alkali metals. The results are therefore not critically dependent on this choice.

For mathematical convenience, then, we choose the potential function given by Shaw and Warren,[18] taking $\gamma=0.25$ (exchange only):

$$\bar{I}(x)=(1/4\gamma x^2)[1-(\beta/x)D(x/\beta)]\,, \tag{26}$$

with $\beta^2=1/6\gamma$ and where $D(y)$ is the Dawson integral.[43] Combining Eqs. (25) and (26), we have carried out numerical evaluations of the $\mathcal{K}_{l,l'}(\alpha)$ as a function of α. These are shown in Fig. 1. For $l=l'$ [Fig. 1(a)] the $2l+1$ scale factor is suppressed to facilitate comparison of different $\mathcal{K}_{l,l}(\alpha)$'s. The $\mathcal{K}_{0,0}(\alpha)$ values coincide with results given in Ref. 18.

Finally, for convenient reference, we rewrite Eq. (22) as

$$\frac{1}{T_{1e}}=\frac{\pi}{\hbar}\rho(E_F)^2k_BT(1-\alpha)^{-2}\sum_{l,l'}J_l'J_{l'}'\mathcal{K}_{l,l'}(\alpha)\,. \tag{27}$$

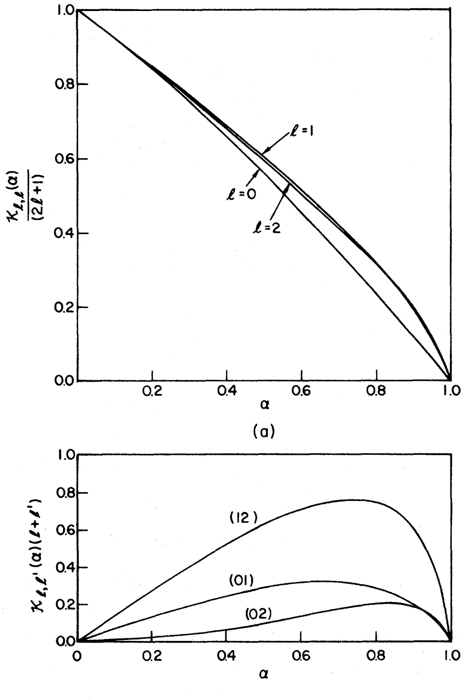

FIG. 1. (a) Diagonal and (b) off-diagonal terms of the T_{1e} enhancement tensor $\kappa_{l,l'}(\alpha)$ as a function of α, calculated using the Shaw potential Eq. (26) in Eq. (25).

V. INTERPRETATION OF HOST NMR LINEWIDTHS AND OTHER EXCHANGE-RELATED DATA FOR *Cu*Mn AND *Ag*Mn

In this section we discuss the interpretation of experimental data for dilute *Cu*Mn and *Ag*Mn in terms of *s*-*d* exchange parameters. In a preliminary subsection (V A) detailed formulas are developed for the interpretation of host NMR linewidths using the results of Secs. II and III and of Ref. 9. With these and the results of Sec. IV we then proceed to discuss measures of *s*-*d* exchange for *Cu*Mn (V B) and *Ag*Mn (V C).

A. Host NMR linewidth formulation

It was established very early[24] that experimental magnetic-impurity-induced NMR line shapes are very nearly Lorentzian in shape. This has been affirmed by the theory of Ref. 9, where the half-width at half-height in the case of RKKY broadening in an fcc lattice was calculated to be

$$\langle \Delta H\rangle = 16\pi A c/3a^3 \ , \tag{28}$$

where c is the atomic fraction of impurities present and a is the fcc lattice constant. A is the RKKY amplitude coefficient defined by writing the induced hyperfine field shift at distance r from the impurity

$$\Delta H(r) \cong A\cos(2k_F r + \varphi)/r^3 \ . \tag{29}$$

It is to be noted that the dilute linewidth is independent of the net SDO phase φ.

$\Delta H(r)$ in Eq. (29) is related to the spin density [Eq. (10)] by

$$\Delta H(r) = \Delta n(r)\Omega H_{\rm hf}^s \gamma(2k_F)^2 \ , \tag{30}$$

where $H_{\rm hf}^s$ is the host-band hyperfine coupling field (in gauss per μ_B of polarization per atom), and $\gamma(2k_F)$ is taken from Eq. (18). $H_{\rm hf}^s$ can be expressed in terms of the s-contact NMR shift K_s and spin-susceptibility-enhancement factor $(1-\alpha)^{-1}$ as

$$H_{\rm hf}^s = K_s(1-\alpha)/2\mu_B\rho(E_F) \ , \tag{31}$$

where K_s and α are taken from experiment. Combining Eqs. (29)–(31) one has

$$A = -\langle S_z\rangle \Omega\gamma(2k_F)^2 K_s J_{\rm SDO}(1-\alpha)/8\pi\mu_B \ , \tag{32}$$

with the over-all SDO exchange constant $J_{\rm SDO}$ defined by

$$J_{\rm SDO}\cos(2k_F r+\varphi) = \left| \sum_l (-1)^l (2l+1) J_l' \times \cos(\delta_l^+ - \delta_l^-)\cos(2k_F r + \delta_l^+ + \delta_l^-)\right| \ . \tag{33}$$

In discussing experimental linewidth data we define the broadening coefficient

$$W = \langle \Delta H\rangle / c\,\langle S_z\rangle \ . \tag{34}$$

In terms of W, $J_{\rm SDO}$ may be written via Eqs. (28) and (32) as

$$J_{\rm SDO} = \frac{6\mu_B W}{K_s\gamma(2k_F)^2(1-\alpha)} \ , \tag{35}$$

where $\Omega_0 = a^3/4$ has been inserted for the fcc lattice. Equations (33)–(35) are used to tabulate and interpret NMR linewidth data in Secs. V B and V C.

B. Measures of *s*-*d* exchange in *Cu*Mn

For *Cu*Mn we employ data on host NMR linewidths, high-temperature ^{55}Mn spin-lattice relaxation, and impurity susceptibility to assess the *s*-*d* exchange properties of the impurity state. At the outset we specify the values of $\rho(E_F)$ and α to be used for Cu metal. For $\rho(E_F)$ we adopt the band-structure density of states ($m^*/m = 1.27$) recently calculated by O'Sullivan *et al.*,[44] giving $\rho(E_F) = 0.135$ states/(eV atom) for one direction of spin. α is obtained from recent measurements of the de Haas–van Alphen *g* factor as a function of position on the Fermi surface.[45] These results lead to the estimated spin susceptibility $\chi_s = 1.45\ \chi_{\rm free\ el}$ for Cu metal. Combining this with $\rho(E_F)$ above gives $\alpha = 0.12$. It is noted that this value for α is considerably smaller than that deduced from the experimental Korringa product K^2T_1T.[16,46] A resolution of this discrepancy has recently been suggested in terms of residual Van Vleck susceptibility and NMR shift in Cu metal.[15] We shall adopt the viewpoint

TABLE I. Broadening coefficients W [Eq. (34)] for dilute *Cu*Mn, derived from various sources of NMR linewidth data as described in the text.

Source	W (kG)
Behringer[a]	83
Chapman and Seymour[b]	100
Sugawara[c]	89
Heeger, Klein, and Tu[d]	140
Alloul and Bernier[e]	104
Karnezos and Gardner[f]	74

[a] Reference 22.
[b] Reference 23.
[c] Reference 24.
[d] Reference 25.
[e] Reference 26.
[f] Reference 27.

of Ref. 15 in this paper, in which the experimental shift of Cu metal $K = 0.24\%$ is presumed to be partitioned into an s-contact part $K_s = 0.18\%$ and an orbital part $K_d^{\mathrm{orb}} = 0.06\%$.

Turning to the question of s-d exchange parameters, we analyze first the susceptibility data since the numbers obtained will be required for the other analyses to follow. Early measurements of the Mn-impurity susceptibility χ_{Mn} in *Cu*Mn have been reviewed by van den Berg.[47] He arrives at a consensus value for $p_{\mathrm{eff}}\{\equiv g[S(S+1)]^{1/2}\} \sim 4.9$. Subsequent measurements give $p_{\mathrm{eff}} = 4.92$[48] and at high temperatures, $p_{\mathrm{eff}} = 5.16$.[49] Whether the indicated temperature dependence of p_{eff} is real is a matter of conjecture. It is also noted that the temperature dependences of $\rho(E_F)$ and α argued by El Hanany and Zamir[46] are open to question in view of the analysis of Ref. 15. In the present work we shall adopt $p_{\mathrm{eff}} = 4.9$ and ignore any temperature variation of the $\rho(E_F)$ and α values cited in the previous paragraph.

Attributing the deviation of p_{eff} from the $S = \frac{5}{2}$ free-spin value ($p_{\mathrm{eff}} = 5.92$) to the correction factor $\{\ \}$ in Eq. (20), one is led to conclude that the negative J_χ^m term is predominant. Substitution of the appropriate parameters yields

$$5|J_\chi^m| - 1.13(J_0 + 3J_1 + 5J_2) = 2.55 \text{ eV} . \qquad (36)$$

Next, we tabulate ^{63}Cu NMR linewidth data for *Cu*Mn, i.e., the quantity W from Eq. (34), in Table I. W values were obtained from various sources[22–27] as derived from the slope of a plot of linewidth against $\langle S_z\rangle$ and corrected for dipolar broadening effects.[24] $\langle S_z\rangle$ was calculated from Eq. (20) using the correction factor discussed in the previous paragraph. Values of W obtained in this way are seen to vary quite widely, rather surprisingly so for such an apparently straightforward experimental quantity. This may reflect internal oxidation effects as suggested by Howling.[50] For the present discussion we extract from Table I a mean value $W = 9.8\times10^4$ G ± 15%.

The SDO exchange parameter is obtained by substituting appropriate parameter values into Eq. (35). From Eq. (26) we have $\bar{I}(1) = 0.59$, which, combined with $\alpha = 0.12$ in Eq. (18) gives $\gamma(2k_F) = 1.04$. With $K_s = 0.18\%$[15] and W from above, Eq. (35) gives $J_{\mathrm{SDO}} = 2.00$ eV.

To express J_{SDO} in terms of the J_l's we assume $|J_{\mathrm{SDO}}^m|$ [Eq. (15)] is large and develop Eq. (33) to first order in the J_l's. Second-order corrections $\sim(J_l/J_{\mathrm{SDO}}^m)^2$ are of the order of a few percent and therefore negligible compared with the error limits of available data. To first order, then, Eq. (33) gives

$$\begin{aligned} J_{\mathrm{SDO}} &\cong 5|J_{\mathrm{SDO}}^m| - J_0\cos(2\delta_0) + 3J_1\cos(2\delta_1) - 5J_2 \\ &\cong 2.00 \text{ eV} , \end{aligned} \qquad (37)$$

where we take $\delta_2^+ + \delta_2^- \cong \pi$.

The third source of s-d exchange data is high-temperature ^{55}Mn nuclear relaxation measurements,[10] which we interpret using the Moriya enhancement model for EPR spin-lattice relaxation as discussed in Sec. IV. From Ref. 10 the nuclear relaxation rate is written

$$1/T_1 = \tfrac{2}{3}(\gamma_n \alpha_d \mu_B N_0 p_{\mathrm{eff}})^2 T_{1e} , \qquad (38)$$

where γ_n is the nuclear gyromagnetic ratio, $\alpha_d = -11.8(\mathrm{emu/mole})^{-1}$ is the d-spin hyperfine coefficient,[10] N_0 is Avogadro's number, $p_{\mathrm{eff}} = 4.9$ from above, and T_{1e} is the local-moment spin-lattice relaxation time. From $T_1^{-1} = 2.3\times10^5$ sec^{-1},[10] we find $T_{1e}^{-1} = 1.32\times10^{13}$ sec^{-1} at 1200 K. T_{1e} is then related to the exchange by Eq. (27). Using the values of α and $\rho(E_F)$ from above and the appropriate values of $\mathcal{K}_{l,l'}(\alpha)$ from Fig. 1, Eq. (27) yields

$$5|J_{T_{1e}}^m| - 0.02J_0 - 0.19J_1 - 5J_2 = 2.46 \text{ eV} , \qquad (39)$$

where again only first-order terms in J_0 and J_1 are retained.

1. Discussion

Equations (36), (37), and (39) are now examined to compare s-d exchange parameters reflected by these three experimental measurements. Two important features are noted immediately. First, the direct-exchange constants J_l are known to be $\lesssim 0.1$

TABLE II. Configurations of mixing exchange parameters from Eqs. (36), (37), and (39) for three possible sets of J_l parameters. The second set of J_l's corresponds closely to the values deduced for *Ag*Mn in Ref. 2. All values are in eV.

Estimated direct exchange			Corresponding mixing exchange		
J_0	J_1	J_2	$\langle S_z\rangle_{\max}\lvert J_{\mathrm{SDO}}^m\rvert/S$	$\lvert J_{T_{1e}}^m\rvert$	$\lvert J_\chi^m\rvert$
0.10	0.05	0	0.36	0.49	0.57
0.09	0.06	0.03	0.38	0.52	0.60
0.05	0.05	0.05	0.40	0.54	0.60

eV, as borne out by recent work on *Ag*Mn.[2] Thus, it is clear that the mixing terms predominate strongly in these equations.

Secondly, we note that the Anderson-model theory gives

$$J_\chi^m \cong J_{T_{1e}}^m \cong \langle S_z \rangle_{\max} J_{\mathrm{SDO}}^m / S \tag{40}$$

as embodied in Eqs. (15), (21), and (24). Equation (40) holds asymptotically as $\Delta \to 0$. However, it is clear from Eqs. (36)–(39) that there are discrepancies between these quantities which cannot be accounted for with reasonable values of the J_l's. In particular one appears to have the ordering

$$\langle S_z \rangle_{\max} J_{\mathrm{SDO}}^m / S < J_{T_{1e}}^m < J_\chi^m \ , \tag{41}$$

with a range of roughly ± 20%. This relationship is further illustrated in Table II, where J^m's are listed for three hypothetical sets of J_1 parameters. Although it is difficult to establish error limits on these determinations, there is the possibility here of a real discrepancy, for example, between J_χ^m and $\langle S_z \rangle_{\max} J_{\mathrm{SDO}}^m / S$. This point can only be resolved by more accurate data.

Ignoring these discrepancies for the moment, it is interesting to consider the implications of these results for the Anderson-model parameters of *Cu*Mn. We take, for example, the equation for J_{SDO}^m [Eq. (15)] and rewrite it as

$$y(1+x^2)^{-1/2}[(y-x)^2+1]^{-1/2} = j \ , \tag{42}$$

with $x = (E_d^- - E_F)/\Delta$, $y = (E_d^- - E_d^+)/\Delta$, and $j = \pi \rho(E_F) \times |J_{\mathrm{SDO}}^m| \langle S_z \rangle_{\max}$. With $|J_{\mathrm{SDO}}^m| \sim 0.4$ eV and $\rho(E_F) = 0.135\ \mathrm{eV}^{-1}\,\mathrm{atom}^{-1}$ we find $j = 0.35$. The total number of d electrons n_d at the Mn site is then written [Eq. (14)]

$$n_d = 5 + (5/\pi)\{\tan^{-1}(x^{-1}) - \tan^{-1}[(y-x)^{-1}]\} \ . \tag{43}$$

Noting that only the case $x, y > 0$ need be considered, we make the following observations on Eqs. (42) and (43). First, the minimum value of y, $y_{\min} = 11.1$, occurs for $y = 2x$, giving $n_d = 5$. Thus, for $E_d^- - E_d^+ \sim 5$ eV,[51] one has $\Delta \sim 0.45$ eV, in good agreement with estimates based on spin-flip scattering cross sections of $3d$ impurities in *Cu*[51] as well as with band-structure calculations for pure $3d$ metals[52] as interpreted by Heine.[53]

However, the latter remarks presume $n_d = 5$, which may be incorrect. Five d electrons requires two band electrons per Mn site for charge neutrality. One may argue that this costs too much energy and therefore $n_d > 5$, with correspondingly fewer band electrons. Equation (42) offers an interesting insight on this point. Considering x to be the independent variable, the only applicable solution of this equation is

$$y = (x^2+1)/[x - (1-j^2)^{1/2}/j] \ . \tag{44}$$

Equation (44) gives the condition $x \leq (1-j^2)^{1/2}/j = 2.66$, which with Eq. (43) leads to the condition $n_d \leq 5.6$. Since $\Delta \to 0$ at the singularity, one has more realistically $\Delta \geq 0.3$ eV,[51,53] placing the limit at $n_d \leq 5.46$. The measured J_{SDO}^m therefore places a rather stringent upper limit on the number of impurity-site d electrons which are consistent with the Hartree-Fock theory.

C. *Ag*Mn

We proceed now to comment on measurements of impurity susceptibility[47] and host NMR linewidths[28] in *Ag*Mn, using the formulas of Secs. II and IV. It is of special interest to compare our interpretation of these data with the s-d exchange parameters recently obtained from ESR data by Davidov *et al.*[2] The interpretation given in Ref. 2 is based on the assumption of negligible exchange enhancement in Ag metal. We shall proceed on the same basis.

Impurity-susceptibility data[47] give $p_{\mathrm{eff}} \cong 5.8$, corresponding to only a slight reduction of the free-spin moment ($p_{\mathrm{eff}} = 5.92$). Reference 2 gives the parameters $J_0 = 0.13$ eV, $J_1 = 0.09$ eV, and $J_2' = -0.13$ eV [notation of Eq. (23)]. Expressing the mixing parameter in Eq. (20) as $J_2' - J_2$ we find

$$p_{\mathrm{eff}} = 5.92\left[1 + \tfrac{1}{2}\rho(E_F)\left(\frac{J_0 + 3J_1 + 5\alpha J_2}{1-\alpha} + 5J_2'\right)\right] \ . \tag{45}$$

With $\rho(E_F) = 0.131\ \mathrm{eV}^{-1}$,[2] Eq. (45) gives $p_{\mathrm{eff}} = 5.82$. This is in good agreement with experiment.

The host NMR linewidth data present a more difficult situation to interpret. These data are plotted in Fig. 2 against measured $\langle S_z \rangle = N^{-1}\sum_i \langle S_{zi} \rangle$, just as in Mizuno's original paper.[28] The linewidth is seen to exhibit a curious feature, namely, a large decrease of slope with increasing $\langle S_z \rangle$, which causes us to suggest that there is more than one line-broadening agent in the *Ag*Mn alloy used. This conjecture is based on the following argument. In Ref. 9 it was shown that the host NMR line width for a single species of impurity is proportional to $N^{-1}\sum_i |\langle S_{zi} \rangle|$, i.e., to the average magnitude of $\langle S_z \rangle$ for impurity spins. At high temperatures (small $\langle S_z \rangle$) we have $N^{-1}\sum_i |\langle S_{zi} \rangle| \cong \langle S_z \rangle$, since the spins are polarized primarily by the external field. As T is lowered, however, one obviously has $\sum_i |\langle S_{zi} \rangle| \geq \sum_i \langle S_{zi} \rangle$. Thus as $T \to 0$ the linewidth must increase with $\langle S_z \rangle$ at least as fast as determined by the high-temperature slope, contrary to what is observed in Fig. 2.

We therefore interpret the behavior in Fig. 2 as stemming from two types of magnetic impurities, as follows. At high temperatures the linewidth is dominated by a broadening agent which is very strong, but which "freezes out" just above helium temperatures. Below this point in temperature $\langle S_z \rangle$ is dominated by a much weaker broadening

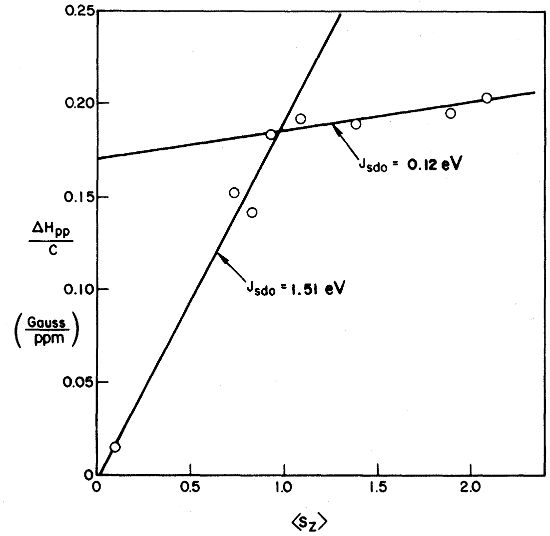

FIG. 2. ^{109}Ag NMR linewidth data for 25- and 42-ppm Mn in Ag plotted as a function of impurity-spin expectation values $\langle S_z \rangle$ obtained from measured susceptibilites. Stated exchange parameters are derived from Eq. (35) as discussed in text. Data taken from Mizuno (Ref. 28).

agent, very likely isolated Mn impurities. Whether either of these slopes represents a useful value of W from which to evaluate J_{SDO} with Eq. (35) is a debatable question.

For completeness, let us examine the range of possibilities here. Again taking $\alpha = 0$, we also adopt $K_S = 0.37\%$ as determined from the nuclear spin-lattice relaxation rate using the Korringa relation.[15,16] These parameters yield $|J_{\mathrm{SDO}}| \sim 1.5$ eV from Eq. (35) using the high-temperature data of Fig. 2 and about an order of magnitude smaller than that at low temperatures. By comparison, the exchange parameters of Ref. 2 give via Eq. (33) a range of values $0.2 < J_{\mathrm{SDO}} < 0.7$ eV, depending on the choice of phase angles. Here we assume five d electrons, with two more bound in the s and p waves. The lower end of this range is in fair agreement with the low-temperature data of Fig. 2. In any case, agreement at high temperatures leaves the puzzling question of the low-temperature slope. Further study with alloys having a variety of metallurgical treatments will probably be needed to resolve this question.

VI. CONCLUSIONS AND DISCUSSION

The theoretical machinery for extracting s-d exchange parameters from data on host NMR linewidths, impurity-state susceptibilities, and single-impurity EPR linewidths has been assembled and summarized in Secs. II, III, IV and V A. The formulation given is restricted to S-state ions reasonably near to a free-spin configuration, since (a) the Anderson-model formulas are limited to such a case and (b), for non-S ionic states other interaction terms between the localized and band electrons become important.[54] Within the above restriction the generalization of this formulation to rare-earth ions is obvious and will not be discussed in detail.

The application of these analyses to the case of dilute *Cu*Mn yields results of only moderate consistency for the mixing-exchange parameter, presenting thereby an apparent inconsistency with the Hartree-Fock solution of the Anderson model. The most serious disparity seems to concern the rather low value found for J^m_{SDO} [Eq. (37)] as compared with J^m_χ and $J^m_{T_{1e}}$ (see Table II). Unfortunately, the large scatter in host NMR linewidth data (Table I) for *Cu*Mn generates some doubt as to whether this disparity is real. This scatter suggests the possibility that internal oxidation effects noted by Howling[50] as well as other metallurgical problems may affect *Cu*Mn alloy samples in a relatively uncontrolled way without special precautions. In contrast, *Cu*Mn impurity susceptibilities reported in the literature show an excellent consistency.[47,48] These observations drive home the fundamental point that, while susceptibility is a bulk property and would be expected to correlate with chemical analyses of impurity concentration, the host NMR linewidth is a truly microscopic quantity sensitive only to those impurities which are randomly distributed throughout the host metal. The number of such impurities is clearly more difficult to measure and control.

It must be pointed out that the negative magnetoresistance studies of *Cu*Mn by Monod[13] lead also to a somewhat smaller value of mixing exchange ($|J^m_{\mathrm{MR}}| \sim 0.36$ eV) when interpreted with second-order perturbation theory assuming potential scattering to be large compared with the exchange effect. As emphasized in Ref. 14, however, this interpretation is not fully quantitative. There is uncertainty about the importance of the higher-order terms (which lead to smaller $|J^m_{\mathrm{MR}}|$ values) as well as the approximation of large potential scattering, which, if invalid, makes $|J^m_{\mathrm{MR}}|$ appear smaller than its true value.[14] We therefore do not attempt to draw a quantitative conclusion about this measure of s-d exchange at the present time.

The single-electron localized state width Δ obtained for *Cu*Mn ($\Delta_{\max} \sim 0.45$ eV) was seen to correspond well with the spin-orbit scattering value given by Yafet[51] as well as the s-d band gaps in $3d$ transition-metal band structures[52] using a picture developed by Heine.[53] In the latter work it was shown that the energy scale of a given $3d$ band is determined essentially by a single parameter closely related to V_{kd}. The semiquantitative correspondence found for *Cu*Mn may be fortuitous, however, since one would also expect such a correspondence to hold for the *Ag*Mn case where V_{kd} appears to be smaller by a factor ~ 2. Thus V_{kd} for the Mn ion appears to show a strong dependence on the metallic-host environment. One might speculate that more d character occurs in the local conduction-band states of *Cu*Mn because of the proximity of the filled $3d$ band to the Fermi surface in Cu as compared with Ag metal.

For the *Ag*Mn case the host NMR linewidth data[28] again highlight the occurrence of metallurgical problems, where the line-broadening theory of Ref. 10 enables one to conclude that something other than isolated Mn impurities is playing an important role. Without the benefit of further experimental work (which is clearly needed) one can only guess that pairs or clusters of Mn ions are occurring in numbers far beyond their statistical probabilities. Again, in contrast to the linewidth data, the bulk susceptibility appears well behaved.[28,47]

Finally, we note that a correction is in order regarding the interpretation of the discontinuity in *Cu*Mn impurity susceptibility between the liquid and solid phases[49] as developed in Ref. 10. There a model of isotropic ($l=0$) exchange was used, and the observed change in T_1 from liquid to solid was interpreted with Eq. (38) and Eq. (27) (for $l=0$, $\alpha=0$) to indicate a corresponding change in "J." The latter quantity was then inserted into Eq. (19), yielding a jump in χ_{imp} in reasonable agreement with experiment. The foregoing picture changes when one attributes this effect to the $l=2$ term as we do here. Now, the derived increase (~ 50%) in $J^m_{T_{1e}}$ on going from liquid to solid is about twice as large as needed to explain the change in χ_{imp} with Eq. (19). Working the argument backward, the discontinuity in $J^m_{T_{1e}}$ is evidently smaller than 50%, so that $J^m_{T_{1e}}$ may actually be smaller than the value given in Table II.

APPENDIX A

The object here is to derive Eq. (10) using the first-order Green's-function expansion of Eq. (8), where G_0 is the Green's function for an impurity with a spherically symmetric potential $V(r)$ embedded in a free-electron gas [Eq. (9)]. Our discussion closely parallels that of Anderson,[7] to which the reader is referred for further details on the derivation of $G_0(\vec{r},\vec{r}\,')$.

Because of the spherical symmetry of V, $G_0(\vec{r},\vec{r}\,')$ may be expanded as

$$G_0(\vec{r},\vec{r}\,')=\sum_{l,m} G_l(r,r')\Psi_{lm}(\hat{r})\Psi^*_{lm}(\hat{r}') \ , \tag{A1}$$

where $G_l(r,r')$ satisfies the radial equation

$$\frac{\hbar^2}{2m}\nabla^2_r G_l(r,r')+\left(\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)-E\right)G_l(r,r') = \delta(r-r')/r^2 \ . \tag{A2}$$

In the following we take $E=\hbar^2k^2/2m$. The correctly normalized solution to (A2) is then[7]

$$G_l(r,r')=-(2mk/\hbar^2)\left[\mathfrak{N}_l(r_>)+i\mathcal{J}_l(r_>)\right]\mathcal{J}_l(r_<) \ , \tag{A3}$$

where $\mathcal{J}_l(r)$ is the solution of the homogeneous equation which is finite at the origin, and $\mathfrak{N}_l(r)$ is the other linearly independent solution. $V(r)$ is considered to be localized, i.e., to vanish outside a certain radius $r_{\max}$. For $r>r_{\max}$ we have

$$\begin{aligned}\mathcal{J}_l(r)&=\cos\delta_l j_l(kr)-\sin\delta_l n_l(kr) \ , \\ \mathfrak{N}_l(r)&=\sin\delta_l j_l(kr)+\cos\delta_l n_l(kr) \ ,\end{aligned} \tag{A4}$$

where j_l and n_l are the Bessel functions of half-integral order and the δ_l's are the phase shifts caused by $V(r)$.

Exchange is properly a two-body potential; however, we consider the impurity here to remain in the manifold of total spin S and therefore take the exchange operator in the $\vec{r}$ representation from Eqs. (4) and (5) to be

$$J_{\text{op}}(\vec{r},\vec{r}\,')=\sum_{\mu}\frac{\varphi_{d\mu}(\vec{r}\,')\varphi_{d\mu}(\vec{r})}{5|\vec{r}-\vec{r}\,'|}\begin{bmatrix} S_z & \frac{1}{2}S_- \\ \frac{1}{2}S_+ & -S_z\end{bmatrix} \ . \tag{A5}$$

Combining Eqs. (7), (8), (A3), and (A5) and keeping only the leading term in the expansion of $j_l(kr)$ and $n_l(kr)$ for $kr\gg 1$, we obtain

$$\Delta n(r)=\frac{m\Omega_0\langle S_z\rangle}{4\pi^3\hbar^2r^2}\sum_l(-1)^l(2l+1) \times\int_0^{k_F}dk\,k\,J_l(k,k)\sin(2kr+2\delta_l) \ , \tag{A6}$$

where S_z is replaced by its thermal average to obtain the $\omega=0$ component of $\Delta n(r)$, and where

$$J_l(k,k)=\frac{64\pi^2}{5\Omega_0}\int_0^{\infty}dr\,r^2\mathcal{J}_l(r)f_d(r) \times\int_r^{\infty}dr'r'^2\mathcal{J}_l(r')f_d(r')\left|\sum_L\frac{r^L}{r'(L+1)}\,\frac{c(2Ll;000)^2}{2L+1}\right. . \tag{A7}$$

In (A7) $f_d(r)$ is the radial part of $\varphi_{d\mu}(\vec{r})$, and $c(2Ll;000)$ is a Clebsch-Gordan coefficient. The identification of $J_l(k,k)$ is made by expanding Eq. (5) in the form of Eq. (6), whereupon Eq. (A7) is obtained with $J_l\to j_l$. Note, however, that Eq. (A7) gives the exchange integral in terms of the actual eigenfunction of $\mathcal{H}=T+V$.

By partial integration Eq. (A6) may be developed in a series of increasing inverse powers of r, the leading (r^{-3}) term of which is the desired result. A straightforward generalization to the case of different phase shifts for up- and down-spin electrons leads to Eq. (10) in the text. We may recover Yosida's result[11] by letting $\delta_l \to 0$ and identifying $J(0) = \sum_l (-1)^l (2l+1) J_l(k_F, k_F)$.

APPENDIX B

We derive the enhancement of the long-range (r^{-3}) term of the SDO using Eq. (16) for $\chi(q)$ and assuming, for simplicity, that the SDO range function is given by

$$f(\vec{r}) = \int d\vec{q}\, e^{i\vec{q}\cdot\vec{r}} \chi(q) \quad . \tag{B1}$$

Equation (B1) corresponds to a δ-function scattering potential and yields the RKKY range function[11,37] when $\chi(q)$ is taken to be the unenhanced free-electron susceptibility

$$\chi_0(q) = \tfrac{1}{2}\mu_B^2 \rho(E_F)\left(1 + (1-x^2)\ln\left|\frac{1+x}{1-x}\right| \Big/ 2x\right) \quad , \tag{B2}$$

with $x = q/2k_F$. It is assumed that the enhancement factor of the r^{-3} term obtained from Eq. (16) and (B1) will also hold for the r^{-3} term of the more general range function derived in Sec. II and Appendix A.

To evaluate Eq. (B1) we expand the denominator of $\chi(q)$ [Eq. (16)] in a power series about the (singular) point $q = 2k_F$ as follows:

$$[1 - I(x)\chi_0(x)]^{-1} = (1-\beta)^{-1} \sum_{n=0}^{\infty} (\alpha/2)^n \times \frac{\left(\bar{I}'(x) + \bar{I}(x)(1-x^2)\left|\ln\frac{1+x}{1-x}\right| \Big/ 2x\right)^n}{(1-\beta)^n} \quad , \tag{B3}$$

where $I(x)$ is assumed to be well behaved in the vicinity of $|x| = 1$, and where $\alpha = I(0)\chi_0(0)$, $\beta = \frac{1}{2}\alpha \bar{I}(1)$, $\bar{I}(x) = I(x)/I(0)$, and $\bar{I}'(x) = \bar{I}(x) - \bar{I}(1)$. Performing the angular integration in (B1) and combining with (B3), one finds

$$f(r) = -\frac{4\pi\mu_B^2 k_F^2 \rho(E_F)}{ir(1-\beta)} \int_{-\infty}^{\infty} dx\, x e^{2\pi i x y} \times \left(1 + (1-x^2)\ln\left|\frac{1+x}{1-x}\right| \Big/ 2x\right) \sum_{n=0}^{\infty} \frac{\alpha^n}{2^n (1-\beta)^n} \times \left(\bar{I}'(x) + \bar{I}(x)(1-x^2)\ln\left|\frac{1+x}{1-x}\right| \Big/ 2x\right)^n \quad , \tag{B4}$$

where $y = k_F r/\pi$.

The Fourier transform in (B4) can be calculated by a simple extension of Lighthill's Theorem 19.[38] This theorem, as applied to the present problem, is stated as follows. If the function to be transformed is expanded in a series about the singular points at $x = \pm 1$ as

$$F_{\pm 1}(x) = \sum_{m=1;\,n=0}^{\infty}\sum^{\infty} A_{nm}^{\pm}(x \pm 1)^m (\ln|x \pm 1|)^n \quad , \tag{B5}$$

then the Fourier transform in (B4) is simply the Fourier transform $\mathcal{T}$ of $F_{+1}(x) + F_{-1}(x)$. Transforms of the functions in (B5) can be obtained from the result[38]

$$\mathcal{T}|x|^{\alpha} = \mathcal{T}\sum_{n=0}^{\infty} \frac{\alpha^n}{n!}(\ln|x|)^n = 2\cos\left[\tfrac{1}{2}\pi(\alpha+1)\right]\alpha!\,(2\pi|y|)^{-(\alpha+1)} \quad , \tag{B6}$$

e.g., with

$$\mathcal{T}(\ln|x|)^n = \lim_{\alpha\to 0}\frac{d^n}{d\alpha^n}(\mathcal{T}|x|^{\alpha}) \tag{B7}$$

and the relation

$$\mathcal{T}x^m(\ln|x|)^n = \frac{i^m}{(2\pi)^m}\frac{d^m}{dy^m}[\mathcal{T}(\ln|x|)^n] \quad . \tag{B8}$$

The algebraic operations in (B7) and (B8) can be justified by the methods of Lighthill.[38] One sees from (B6) that the full expression for $f(r)$ consists of a series of ascending inverse powers of y (i.e., of r). The leading terms of (B5),

$$[F_{+1}(x) + F_{-1}(x)]_{m=n=1} = A_{11}^{+}(x+1)\ln|x+1| + A_{11}^{-}(x-1)\ln|x-1| \quad , \tag{B9}$$

give rise to the r^{-3} term of $f(r)$ which we seek:

$$f(r)\big|_{r^{-3}} = -\frac{\pi^2\mu_B^2\rho(E_F)}{(1-\beta)^2}\frac{\cos(2k_F r)}{r^3} \quad . \tag{B10}$$

That no other term of (B5) yields an r^{-3} term in $f(r)$ can be seen as follows. First, the $n = 1$, $m > 1$ terms in (B5) cannot contribute by (B8) and second, examination of (B4) reveals $m \geq n$ for $n > 1$ as well. It follows from this and from (B6) and (B8) that there are no further y^{-2} terms in $\int_{-\infty}^{\infty} dx$ of (B4), and thus the full result for the leading term is given by (B10).

The principal result (B10) shows that band exchange enhances long-range SDO by the factor $(1-\beta)^{-2}$, where we note that $(1-\beta)^{-1}$ is the static susceptibility enhancement [Eq. (18)] for $q = 2k_F$.

---

[1] We do not attempt to enumerate the vast literature on this subject, but refer the reader to such review articles as appear in *Magnetism*, edited by H. Suhl (Academic, New York, 1973), Vol. V, and in *Solid Physics*, edited by F. Seitz, D. Turnbull, and A. Ehrenreich (Academic, New York, 1969), Vol. 23.

[2] Such a determination has been carried out for *Ag*Mn by combining EPR and resistivity data. D. Davidov *et al.*, Phys. Rev. B (to be published).

[3] J. Kondo, Prog. Theor. Phys. 28, 846 (1962); J. R. Schreiffer and P. A. Wolff, Phys. Rev. 149, 491 (1966).

[4] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[5] Throughout the paper, the discussion is restricted to the r^{-3} term in the spin-density oscillations.

[6] T. Moriya, in *Theory of Magnetism in Transition Metals*, edited by W. Marshall (Academic, New York, 1967).

[7] P. W. Anderson, in *Theory of Magnetism in Transition Metals*, edited by W. Marshall (Academic, New York, 1967).

[8] D. Davidov, K. Maki, R. Orbach, C. Rettori, and E. P. Chock, Solid State Commun. 12, 621 (1973).

[9] R. E. Walstedt and L. R. Walker, Phys. Rev. B 9, 4857 (1974).

[10] R. E. Walstedt and W. W. Warren, Jr., Phys. Rev. Lett. 31, 365 (1973).

[11] K. Yosida, Phys. Rev. 106, 893 (1957).

[12] D. J. Scalapino, Phys. Rev. Lett. 16, 937 (1966).

[13] P. Monod, Phys. Rev. Lett. 19, 1113 (1967).

[14] M-T. Béal-Monod and R. A. Weiner, Phys. Rev. 170, 552 (1968).

[15] R. E. Walstedt and Y. Yafet, Solid State Commun. 15, 1855 (1974).

[16] A. Narath and H. T. Weaver, Phys. Rev. 175, 373 (1968).

[17] R. Lobo, K. S. Singwi, and M. P. Tosi, Phys. Rev. 186, 470 (1969); K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B 1, 1044 (1970).

[18] R. Shaw and W. W. Warren, Jr., Phys. Rev. B 3, 1562 (1971).

[19] P. Bhattacharyya, K. N. Pathak, and K. S. Singwi, Phys. Rev. B 3, 1568 (1971).

[20] T. Moriya, Prog. Theor. Phys. 18, 526 (1963).

[21] J. B. Boyce and C. P. Slichter, Phys. Rev. Lett. 32, 61 (1974).

[22] R. E. Behringer, J. Phys. Chem. Solids 2, 209 (1957).

[23] A. C. Chapman and E. F. W. Seymour, Proc. Phys. Soc. Lond. 72, 797 (1958).

[24] T. Sugawara, J. Phys. Soc. Jpn. 14, 643 (1959).

[25] A. J. Heeger, A. P. Klein, and P. Tu, Phys. Rev. Lett. 17, 803 (1966).

[26] H. Alloul and P. Bernier, in *Low Temperature Physics-LT* 13, edited by W. J. O'Sullivan, K. D. Timmerhaus, and E. F. Hammel (Plenum, New York 1973), Vol. 2.

[27] N. Karnezos and J. A. Gardner, AIP Conf. Proc. 10, 801 (1972).

[28] K. Mizuno, J. Phys. Soc. Jpn. 30, 742 (1971).

[29] W. Kohn and S. H. Vosko, Phys. Rev. 119, 912 (1960).

[30] A. Blandin and E. Daniel, J. Phys. Chem. Solids 10, 126 (1959).

[31] For a potential not perfectly spherical, there may be small contributions to other even-parity phase-shifts.

[32] Note that Eq. (4) corresponds to the form $J\vec{S}\cdot\vec{s}$ for the coupling of two spins $\vec{S}$ and $\vec{s}$.

[33] R. E. Watson, A. J. Freeman, and S. Koide, Phys. Rev. 186, 625 (1969).

[34] P. Jena and D. J. W. Geldart, Phys. Rev. B 7, 439 (1973).

[35] P. A. Wolff, Phys. Rev. 120, 814 (1960).

[36] T. Moriya, Prog. Theor. Phys. 34, 329 (1965).

[37] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954); T. Kasuya, Prog. Theor. Phys. 16, 45 (1956).

[38] M. J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge U.P., Cambridge, England, 1959).

[39] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959).

[40] A. Blandin, thesis (Paris, 1961) (unpublished).

[41] R. E. Walstedt and A. Narath, Phys. Rev. B 6, 4118 (1972).

[42] J. Korringa, Physica 16, 601 (1950).

[43] See, e.g., *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. GPO, Washington, D. C., 1964).

[44] W. J. O'Sullivan, A. C. Switendick, and J. E. Schriber, in *Electronic Density of States*, edited by L. H. Bennett, Natl. Bur. Stand. (U.S.) Special Publ. 323 (U.S. GPO, Washington, D. C., 1971).

[45] D. L. Randles, Proc. R. Soc. A 331, 85 (1972).

[46] U. El Hanany and D. Zamir, Phys. Rev. B 5, 30 (1972).

[47] G. J. van den Berg, *Progress in Low Temperature Physics*, edited by C. J. Gorter, (North-Holland, Amsterdam 1964), Vol. 4.

[48] H. P. Myers and R. Westin, Philos. Mag. 8, 1969 (1963); C. M. Hurd, J. Phys. Chem. Solids 30, 539 (1968).

[49] J. A. Gardner and C. P. Flynn, Philos. Mag. 15, 1233 (1967).

[50] D. W. Howling, Phys. Rev. Lett. 17, 253 (1966).

[51] Y. Yafet, J. Appl. Phys. 39, 853 (1968).

[52] L. F. Mattheiss, Phys. Rev. 134, A970 (1964).

[53] V. Heine, Phys. Rev. 153, 673 (1967).

[54] B. Coqblin and J. R. Schrieffer, Phys. Rev. 185, 847 (1969); L. L. Hirst, Z. Phys. 244, 230 (1971); 258, 284 (1973).