CONDUCTION-ELECTRON POLARIZATION IN METALS

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Mössbauer, nuclear-magnetic-resonance, electron-spin-resonance, neutron-diffraction, and other measurements have supplied both direct and indirect information concerning the magnetic polarization of conduction electrons in alloys, pure metals, and intermetallics containing local (electronic) magnetic moments. Our understanding of these observations is based mainly on the familiar Ruderman-Kittel-Kasuya-Yosida (RKKY) theory[1] of conduction-electron exchange polarization. In addition to treating the conduction electrons as free electrons, applications of this theory commonly make drastic simplifying assumptions concerning the analytic character of the local moment–conduction electron exchange coupling $J(Q)$. Any observed discrepancy between theory and experiment is usually[2,3] ascribed to the susceptibility function which appears in the theory. We have investigated the character of $J(Q)$ and find strong differences from any previously assumed Q dependence. This causes spin-density distributions which differ severely from the traditional RKKY predictions. In particular, significant spin densities may occur at near-neighbor ion sites without the huge densities at the origin predicted by conventional application of RKKY theory. In some senses these changes are more severe than the spin-density modifications recently ascribed[2,3] to the susceptibility function in order to obtain agreement between theory and experiment.

RKKY theory commonly starts with the spin density induced by a magnetic ion moment, centered at the origin, of the form

$$\rho(\vec{r}) = \frac{2C}{\pi k_F}\int_0^\infty d\vec{k}'\int_0^{k_F} d\vec{k}\,\frac{J(\vec{k},\vec{k}')}{k^2-k'^2}\{\exp[i(\vec{k}-\vec{k}')\cdot\vec{r}]+\exp[-i(\vec{k}-\vec{k}')\cdot\vec{r}]\}, \tag{1}$$

where C is a negative constant, k_F is the Fermi vector, and $J(\vec{k},\vec{k}')$ is the exchange integral coupling plane-wave states with wave vectors $\vec{k}$ and $\vec{k}'$, respectively, i.e.,

$$J(\vec{k},\vec{k}') \equiv \frac{1}{2S}\sum_i \int d\vec{r}_1 \int d\vec{r}_2\, \varphi_i^*(\vec{r}_1)\exp(i\vec{k}\cdot\vec{r}_1)\frac{1}{r_{12}}\varphi_i(\vec{r}_2)\exp(-i\vec{k}'\cdot\vec{r}_2), \tag{2}$$

where the sum is over all unpaired ion orbitals, φ_i, comprising the local moment. It is then assumed that J is only a function of the magnitude of $\vec{Q}(=\vec{k}-\vec{k}')$, and on changing integration variables and doing the k integration one obtains the familiar spin-density function

$$\rho(\vec{r}) = C\int_0^\infty J(\vec{Q})\chi(\vec{Q})[\exp(i\vec{Q}\cdot\vec{r})+\exp(-i\vec{Q}\cdot\vec{r})]d\vec{Q}, \tag{3}$$

$\chi(Q)$ being the susceptibility function. Equation (3) is then evaluated by assuming that $J(Q)$ is either a constant (RKKY approximation) or the form factor[3] appropriate to the local moment (the "FF" approximation). In the latter case, J is of one sign, and falls off slowly, out to quite large Q values.[4]

We have made a study of $\rho(r)$ based on a more realistic treatment of the exchange integral using Ge^{3+} $4f$ wave functions to represent the local spin distribution and plane waves orthogonalized to the Gd core to represent the conduction electrons. Since J is, in fact, a function of $\vec{k}$ and $\vec{k}'$, this involves a sampling of J behavior. For a spherical moment, as in Gd, the directions of $\vec{k}$ and $\vec{k}'$ (other than with respect to one another) do not enter, and for a given Q one wishes a sampling of J, over k magnitude (0 to k_F) and $\vec{Q}$ direction, weighted

by such factors as the denominator of Eq. (1). In this paper we have made what we think is the best choice of a single integral for this, namely the integral associated with the smallest denominator in Eq. (1) for the given Q. This choice is indicated in the upper corner of Fig. 1, where $k = k_F$ and $k' \geq k_F$ such that k' takes on the minimum magnitude consistent with the particular Q. While obtained for the minimum denominator, it provides a fair sampling of J behavior for k-Q space in the vicinity of that minimum. We thus have sampled the region making the leading contributions to $\chi(Q)$. The smaller the magnitude of Q, the more inclusive is the sampling, and it is small Q values (say 0 to $2k_F$) which are most important in determining $\rho(r)$ in the regions of greatest interest to us (except at the origin). Whatever the shortcomings in the present choice of $J(Q)$, it represents a substantially more realistic treatment than the use of a constant or a form factor. (The detailed dependence of J on $\vec{k}$ and $\vec{Q}$ and its implications for a more careful estimate of the spin density will be reviewed in subsequent fuller publications.) The $J(Q)$, obtained for $k_F = 0.5$ (and plane waves orthogonalized[5] to the Gd core), and plotted as a function of Q in Fig. 1, is seen to oscillate in sign, first going negative for $Q < 2k_F$, i.e., inside the singularity in $\chi(Q)$. These oscillations,[6] with their substantial amplitude, change the character of $\rho(r)$ from that of traditional predictions. The oscillations are associated with the relative phases of the pair of conduction-electron orbitals involved in the exchange integral and, in turn, with the fact that the p-, d-, and f-like components of these orbitals make substantial contributions to the exchange coupling. The angular dependence associated with the lth component is the $P_l(\cos\alpha)$ Legendre function, where α is the angle between $\vec{k}$ and $\vec{k}'$. The negative $J(Q = 2k_F)$ is the consequence of the fact that the odd-phased p- and f-like terms are greater than the s and d for the case plotted in Fig. 1. The fact that the local moment is made up of one-electron functions with $l \neq 0$ is important to this behavior.

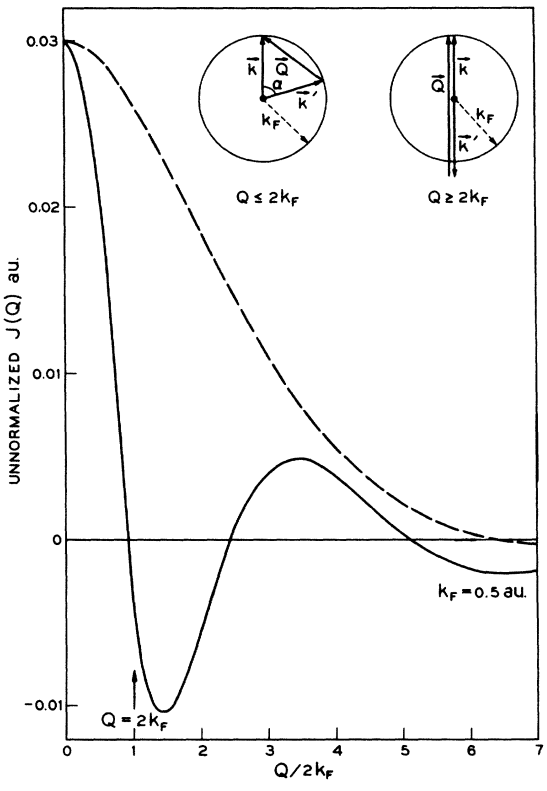

FIG. 1. The Q dependence of the exchange integral $J(Q)$ [solid curve] obtained for the Q sampling indicated in the corner of the figure [see text] and the form factor $F(Q)$ [dashed curve]. Both are obtained for the Gd $4f$ shell and a $k_F = 0.5$ [orthogonalized plane waves were used[5] in evaluating $J(Q)$]. The scale is arbitrary because a specific conduction-electron volume normalization has not been assumed.

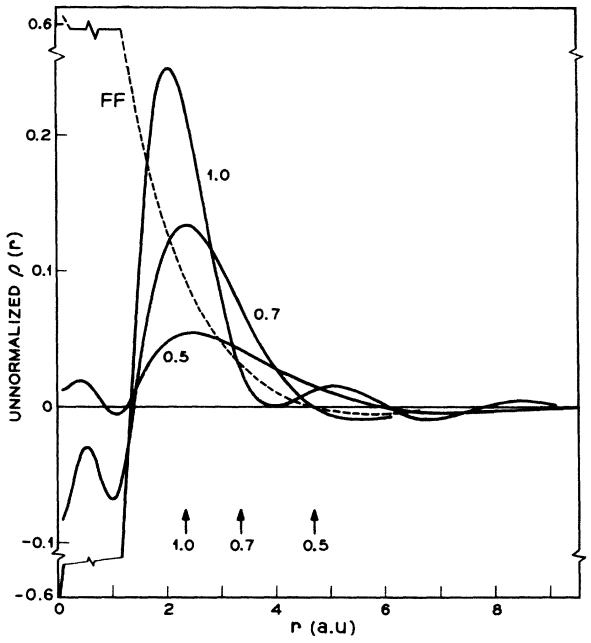

FIG. 2. The spin density,[8] $\rho(r)$, as a function of r resulting from the integration of Eq. (3) for $k_F = 0.5$, 0.7, and 1.0, and the $J(Q)$ choice indicated in Fig. 1. Also shown is the FF result [dashed curve] for $k_F = 0.5$ normalized to the same integrated density as the $J(Q)$ result.

For comparison, $J(Q)$, as based on the form factor, is also plotted in Fig. 1.

Figure 2 shows the result of integrating Eq. (3) with the above choice of $J(Q)$ and the conventional $\chi(Q)$ [arising from the integration of Eq. (1)]. For computational reasons, the integrations have not been carried out to infinity, but instead to $Q = 15k_F$, $11k_F$, and $8k_F$ for the k_F values of 0.5, 0.7, and 1.0 a.u., respectively.[7] Inspection of $\rho(r)$ as a function of the upper limit of integration suggests that, despite this approximation, the qualitative, and the crude quantitative, features of the plotted[8] $\rho(r)$ are well established for $r > 3$ a.u. (Near-neighbor distances in metals are typically 4.5 to 6.5 a.u.) We estimate[9] that a complete integration would yield densities at the origin, $\rho(0)$, which lie in the ranges -0.01 to 0.05, -0.25 to 0.04, and -0.8 to -0.4 for the k_F values 0.5, 0.7, and 1.0, respectively.

The important feature of the present results is their striking deviation from conventional RKKY and FF theory [the FF result for $k_F = 0.5$ also appears in Fig. 2]. In agreement with these theories [as is necessary when $J(0) > 0$], the average spin density, $V^{-1}\int\rho(\vec{r})d\vec{r}$, is always positive in the sense of having a spin direction parallel to that of the local moment; however, in disagreement with these theories, the spin density at the origin may be either parallel or antiparallel to that moment [i.e., $\rho(0)$ may be positive or negative]. Further, a $\rho(0)$ may be larger, of the same order, or even smaller than the density, $\rho(r_{nn})$, appropriate to a near-neighbor ion radius, whereas the RKFF prediction is for a $\rho(0)$ which is some two orders of magnitude greater than $\rho(r_{nn})$ [cf. Fig. 2]. The present tendency towards higher $|\rho(r_{nn})|/|\rho(0)|$ ratios represents a distinct improvement in agreement between theory and experiment. We believe that the inability of FF theory to produce such ratios was a significant and spurious contributor to the Overhauser-Stearns iron susceptibility function.[3] Admittedly, the present results were not obtained for an iron moment, but this does not affect this observation significantly. (Results for iron will be given in a future publication.) This case involves a transition-metal host for which it is overoptimistic to presume that free-electron RKKY theory has great relevance (despite its almost universal application for transition metals). Relatively little experimental data exist which allow a comparison of $\rho(0)$ with the spin density away from the magnetic ion site for a host which is more free-electron–like.

Another important feature of the present results is that the node outside the dominant positive spin-density region (which is, incidentally, the first node outside the impurity ion region), occurs at an appreciably larger radius than it does in RKKY-FF theory (the RKKY radii are indicated by the ↑ markers in Fig. 2). Such an increased "range" is also associated with Wolff's exchange-enhanced $\chi(Q)$.[2,10] Finally, we should note that at large radii, $\rho(r)$ oscillates with the characteristic period proportional to $(2k_F)^{-1}$. In some situations the onset of these oscillations occurs in the near-neighbor region with an amplitude which is more significant, when compared with $\rho(0)$, than that predicted by RKKY-FF theory.

The present work attempts to provide a more accurate knowledge of the predictions of free-electron theory—predictions which are of interest in their own right and which are needed as a preliminary step towards going on to understand the transition metals. A number of factors have been omitted in this Letter, including (i) the role of interband mixing[11] in contributing to an exchange parameter and in turn to $\rho(r)$; (ii) the role of the conduction-electron–conduction-electron exchange enhancement[2] of the polarization. These matters have been investigated. They are experimentally significant and will be reported on in a subsequent fuller publication.

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[4]The FF approximation is valid in the limit of strong conduction-electron screening of the interelectronic in-

teraction, for which the r_{12}^{-1} of Eq. (2) may be replaced by $\delta(r_{12})$. We employ the unscreened interaction because we do not anticipate strong screening over dimensions small with respect to those of the local moment.

[5]An exchange integral, evaluated for simple plane waves as in Eq. (2), does not display such strong oscillations as seen in Fig. 1. The evaluation (as we have done) of Eq. (3) with exchange integrals based on plane waves orthogonalized to the Gd ion's shells is in some senses inconsistent with Eq. (3) and its simple plane-wave functional character, though one may argue its appropriateness when viewing ρ away from the Gd site. Orthogonalization effects on J and elsewhere must be accounted for in an ultimate treatment of the problem, and in anticipation of such a treatment we have chosen to use $J(Q)$ based on orthogonalized functions. The effect of inserting orthogonalized plane-wave functions into Eq. (1) is significant and will be reported in a further publication.

[6]Two observations should be made concerning the Q dependence of J. First, there is a singularity at $2k_F$ (barely observable in the present case) due to the Q sampling. Second, J oscillates with decreasing amplitude with increasing Q. These oscillations are of much more significant magnitude than the oscillations in the tail of the form factor (see Fig. 1).

[7]Free-electron theory normally yields a choice of k_F between 0.5 and 1.0 a.u. for most metals.

[8]The $\rho(r)$ are plotted for unnormalized conduction-electron orbitals, but assuming common normalization, the three $\rho(r)$ are scaled appropriately for direct comparison.

[9]These were obtained by observing the range in which $\rho(0)$ oscillates [due to the varying sign of $J(Q)$] as the upper limit of integration is varied. In addition, we have crudely estimated the effect on $\rho(0)$ of going from our $J(Q)$ sampling to a suitably averaged $J(Q)$.

[10]For the experimental situation considered by Giovannini, Peter, and Schrieffer,[2] see, for example, D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. 135, A1346 (1964); G. Low, Proceedings of the International Conference on Magnetism, Nottingham, England, 1964 (Institute of Physics and the Physical Society, University of Reading, Berkshire, England, 1965); P. Craig, B. Mozer, and R. Segnan, to be published.

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DENSITY-OF-STATES EFFECTS IN THE MAGNETIC STIFFNESS OF 3*d*-3*d* TRANSITION-METAL ALLOYS

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In Figs. 1(a) and 1(b) we give neutron-scattering results for the spin-wave stiffness constant [$D(0)$ in the spin-wave energy term $D(T)q^2$] of bcc 3*d*-3*d* transition-metal alloys, and compare them with a quantity obtained from an approximate density-of-states curve of these materials. Bearing in mind the uncertainties that attend a derivation of the density-of-states function, the qualitative resemblance of the two figures is rather remarkable. We give below what we believe to be the explanation of it.

A year ago we published results for both bcc and fcc phases of the Fe-Ni system, and interpreted them with apparent success in terms of the Heisenberg Hamiltonian.[1] According to that discussion the stiffness may be computed from the mean spin $\bar{S}$ and an effective exchange parameter which is such that $\mathcal{J}_{\mathrm{eff}}(\vec{r}-\vec{r}')\bar{S}^2 = \langle \mathcal{J}_{\vec{r}\vec{r}'} S_{\vec{r}} S_{\vec{r}'} \rangle$, where $\mathcal{J}_{\vec{r}\vec{r}'}$ can be any of the three types of coupling AA, AB, and BB. We

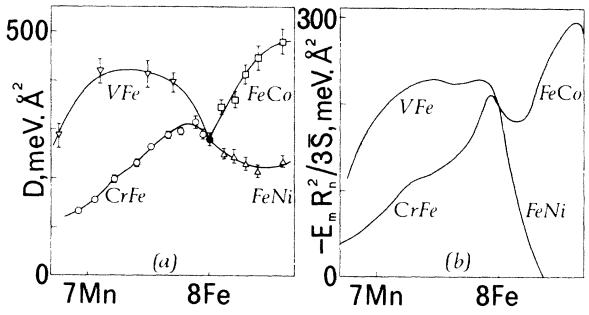

FIG. 1. (a) The observed spin-wave stiffness parameter $D(0°\mathrm{K})$ for 3*d*-3*d* alloys; (b) an approximate prediction of this parameter using the total magnetic energy E_m deduced from the density of states.

now find that the same interpretation cannot be made for the Cr-Fe system, and it therefore appears that our previous fit may have been due merely to the fact that we were matching in each phase a three-parameter quadratic form to a smoothly varying set of only six or