parts of Eq. (A3) that rotation of the axis of polarization is produced by nonzero $\delta\beta z$, while the ellipticity is described by $\delta\alpha z$. The first-order expressions for $\delta\beta$ and $\delta\alpha$ derived from Eq. (A1), assuming $\epsilon_i \gg \epsilon_r$, ϵ_j, are

$$|\delta\beta| = k_0\epsilon_j/2 + k_0\epsilon_r/(8\epsilon_i)^{1/2}, \quad \text{(A6)}$$

$$|\delta\alpha| = k_0\epsilon_r/(8\epsilon_i)^{1/2}, \quad \text{(A7)}$$

where we assumed $\bar{\beta}/(\bar{\beta}^2+\bar{\alpha}^2) \cong \bar{\alpha}/(\bar{\beta}^2+\bar{\alpha}^2) \cong (k_0{}^2 8\epsilon_i)^{-1/2}$. Equation (A6) shows that both Hall terms cause a rotation but from Eq. (A7) we see that to first order only the ϵ_r term gives rise to ellipticity. The amount of this ellipticity is, moreover, comparable in magnitude to the rotation as evidenced by the equal magnitudes of $\delta\beta$ and $\delta\alpha$.

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Exchange Coupling and Conduction-Electron Polarization in Metals

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The exchange-coupling integral, $J(\mathbf{k},\mathbf{k}')$, between localized magnetic electrons and conduction electrons, treated as orthogonalized plane waves is investigated quantitatively for the case of a local moment which consists of the half-filled $4f^7$ shell of Gd^{3+} and for a range of $\mathbf{k}$ and $\mathbf{k}'$ values (the incident and scattered conduction-electron wave vectors). Ruderman-Kittel-Kasuya-Yosida (RKKY) theory is then employed, with and without an exchange-enhanced susceptibility, to obtain conduction-electron spin densities. For the special case of the rare-earth local moment, $J(\mathbf{k}, \mathbf{k}')$ is found to be well approximated by $J(Q)$ [where $Q \equiv |\mathbf{k}\text{-}\mathbf{k}'|$] but with a Q dependence which differs markedly from those traditionally assumed in RKKY theory. This severely affects spin-density predictions for a region extending several lattice sites away from the local-moment site. Use of the computed exchange coupling reduces the qualitative disagreement between theory and experiment.

I. INTRODUCTION

THE magnetic polarization of conduction electrons in alloys, pure metals, and intermetallic compounds containing local electronic magnetic moments, has been the object of extensive experimental investigation in recent years. Basic to the understanding of these observations is the familiar Ruderman-Kittel-Kasuya-Yosida (RKKY) theory[1] which in its original analytic form necessarily involved a number of important approximations. Since significant quantitative deviations have emerged between the predictions of the theory and experiment, questions concerning the validity of the approximations have been raised. In general, the susceptibility function has been considered to be chiefly responsible for these deviations and so attention has largely concentrated on this aspect of the theory.[2–4]

In this paper we inspect in detail the nature of the exchange coupling[5] between the local moment and the conduction electrons, i.e., the source of the conduction-electron polarization. The differences between the exact behavior of the coupling and that commonly assumed in the "simple" traditional theory will be seen to be as important for understanding the deviations between theory and experiment as are any refinements in the susceptibility. Indeed, an exact treatment of the exchange coupling *requires* abandonment of the utilization of the susceptibility function as used in the simple theory, a matter which will be inspected in a subsequent paper. A sampling of the exchange coupling will be made so that contact can be made with the traditional theory, Spin-density results will be reported for sus-

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[1] S. Vonsovskii, Zh. Eksperim. i Teor. Fiz. **16**, 981 (1946); **24**, 419 (1953); M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1965); A. H. Mitchell, Phys. Rev. **105**, 1439 (1957), and K. Yosida, *ibid.* **106**, 893 (1957). This list does not exhaust the early pertinent papers on the subject. The term "RKKY theory" represents a compromise with conventional usage.

[2] B. Giovannini, M. Peter, and J. R. Schrieffer, Phys. Rev. Letters **12**, 736 (1964).

[3] A. W. Overhauser and M. B. Stearns, Phys. Rev. Letters **13**, 316 (1964); the experiments relied on appear in M. B. Stearns and S. S. Wilson, Phys. Rev. Letters **13**, 313 (1964).

[4] T. Moriya, Progr. Theoret. Phys. (Kyoto) **34**, 329 (1965).

[5] A preliminary account appeared in R. E. Watson and A. J. Freeman, Phys. Rev. Letters **14**, 695 (1965).

ceptibilities with and without the enhancement[6] arising from a self-consistent accounting of the exchange interactions between conduction electrons. Throughout the paper, a local moment consisting of the half-filled $4f^7$ shell of Gd^{3+} will be utilized. Of interest in itself, it provides a particularly simple example for discussion since the local moment is spherical and there is a quite unique division (in low order) between what are "conduction" and "local moment" electrons. Also, the Gd ion-conduction electron exchange coupling is amenable to the sampling necessary for insertion into the traditional RKKY treatment—a situation which does not occur for an iron series local moment (a case which will be reported subsequently elsewhere.)

In the section which follows, we present a brief elementary review of the RKKY theory and the exchange enhanced susceptibility which has been applied[2,4] to it. The conventional assumptions concerning the local-moment–conduction-electron exchange coupling will be described. Some aspects of the experimental situation will be briefly inspected. The actual $4f^7$-shell–conduction-electron electrostatic exchange interaction is inspected in Sec. III. Because of its importance, the exchange-coupling results will be described in greater detail than is essential to the present spin-density investigation. For simplicity, we limit attention to the electrostatic exchange interaction ignoring effective exchange terms arising[7–10] from interband mixing. The interband matrix elements are less amenable to the sampling necessary for insertion into the traditional RKKY treatment; their role will be inspected elsewhere where this treatment is abandoned. The exchange integrals obtained in the body of the text are for conduction electron orbitals consisting of single plane waves orthogonalized to the $4f$ and closed shells of the rare-earth ion. Since the orthogonalization appreciably affects the results, both exchange and spin-density behavior for simple plane waves are inspected in an appendix.

Spin density results, with and without Wolff's exchange-enhanced susceptibility,[6] follow in Secs. IV and V. It is from these that we conclude that the differences between the actual and the traditionally assumed exchange coupling are significant to the character of the spin density predicted by RKKY theory and that utilizing the actual coupling appreciably reduces qualitative disagreement between theory and experiment. One does not find, and indeed cannot expect, quantitative agreement between an essentially free-electron treatment and experiments which almost exclusively involve transition metal hosts.

Our results show a tendency toward improved qualitative agreement between theory and experiment. This is perhaps surprising in view of the approximations which remain. The final test of RKKY theory awaits a more adequate accounting of a metal's conduction-band character[11] in all its aspects.

II. THE TRADITIONAL RKKY THEORY AND EXPERIMENT

In treating the spin density induced in conduction electrons by an exchange potential due to a local magnetic moment, one may expand the result in powers of the local-moment–conduction-electron exchange interaction. In RKKY theory, one deals entirely with the linear response, i.e., in terms linear in the exchange integral[12]

$$J_i(\mathbf{k},\mathbf{k}')\equiv\int\int d\tau_1 d\tau_2 \varphi_{\mathbf{k}}^*(\mathbf{r}_1)\psi_i(r_1)\frac{1}{r_{12}}\psi_i^*(\mathbf{r}_2)\varphi_{\mathbf{k}'}(\mathbf{r}_2) \quad (1)$$

involving conduction-electron orbitals $\varphi_{\mathbf{k}}$ and $\varphi_{\mathbf{k}'}$, and local moment orbitals ψ_i.[13] It should be noted that this is the appropriate expression for the exchange matrix element only when the φ and ψ are orthogonal. Two linear effects occur. First, diagonal ($\mathbf{k}=\mathbf{k}'$ and common spin) matrix elements lower the energy of conduction electrons of spin parallel to the local moment with respect to those with spin antiparallel thereby causing a depopulation of the latter (populating the former) across the Fermi surface. The result is a constant spin density throughout the metal.[14] Secondly, there is exchange mixing into the occupied Bloch states of the form

$$\varphi_{\mathbf{k},\pm}\rightarrow\varphi_{\mathbf{k},\pm}\mp\tfrac{1}{2}\sum_i\sum_{k'k>f}\frac{J_i(\mathbf{k},\mathbf{k}')}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}}\varphi_{\mathbf{k}',\pm}, \quad (2)$$

where k_F is the Fermi wave vector, the ϵ's are conduction-electron orbital energies, the i sum is over *unpaired* orbitals making up the local moment[13] and the $\pm$ subscript (and the $\mp$ of the sum) refer to spin parallel and antiparallel to the local moment. Cross terms involving $\varphi_{\mathbf{k}}\varphi_{\mathbf{k}'}$ which are linear in J, yield the familiar spatial spin distribution associated with RKKY theory. They

[6] P. A. Wolff, Phys. Rev. **120**, 814 (1960); **129**, 84 (1963).
[7] P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. **2**, 124 (1961); a few comments on this matter appear in P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[8] J. Kondo, Progr. Theoret. Phys. (Kyoto) **28**, 846 (1962).
[9] S. Koide and M. Peter, Rev. Mod. Phys. **36**, 160 (1964) and R. E. Watson, S. Koide, M. Peter, and A. J. Freeman, Phys. Rev. **139**, A167 (1965).
[10] A preliminary account, inserting interband terms into the traditional formulation was given in R. E. Watson and A. J. Freeman, J. Appl. Phys. **37**, 1444S (1966). A more detailed and rigorous account will be given by the same authors and S. Koide shortly.
[11] Energy band results for Pd have been obtained with this end in view by A. J. Freeman, A. M. Furdyna, and J. O. Dimmock, J. Appl. Phys. **37**, 1256S (1966).
[12] As already indicated, effective exchange-interaction terms (Refs. 7–10), arising from interband mixing are ignored in this paper. Their inclusion would add another term to the exchange integral which would be carried with it throughout the formalism.
[13] When dealing with a local moment of spin other than $\frac{1}{2}$, J will be taken to be an *average* over the ψ_i contributing to the moment. The $\frac{1}{2}\sum_i J_i$ of Eq. (2) then becomes SJ.
[14] C. Zener, Phys. Rev. **81**, 440 (1951); **83**, 299 (1951).

do not contribute to the net spin density; the constant-density Zener term[14] is entirely responsible for that.

Forming the cross product and summing over all occupied ($k=0$ to k_F) Block orbitals one obtains

$$\rho_{\pm}(\mathbf{r})=\mp S\sum_{k=0}^{k_F}\sum_{k'=0}^{\infty}\frac{J(\mathbf{k},\mathbf{k}')}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}}}\Big[\varphi_{\mathbf{k}}^{*}(r)\varphi_{\mathbf{k}'}(\mathbf{r})+\varphi_{\mathbf{k}}(r)\varphi_{\mathbf{k}'}^{*}(r)\Big], \quad (3)$$

where $\pm$ again refers to majority and minority spins and the odd symmetry (in k and k') of the energy denominator has been used to extend[1] the k' summation over all k space. At this point the traditional approximations are made. First, one assumes free-electron Bloch orbitals $\varphi_k=V_c^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}$ with free electron-like energies $\epsilon(\mathbf{k})\equiv k^2$ [where V_c is the volume of the lattice and units are used for which $\hbar^2/2m=1$]. Second, and more severe is the assumption that the exchange matrix elements are functions only of $\mathbf{Q}(=\mathbf{k}-\mathbf{k}')$. This is *not* correct for the nonlocal exchange interaction, although it is appropriate to a (local) Coulomb-potential matrix element between plane-wave states [such as enters the problem of the charge impurities in metals, dealt with by Friedel[15] and others]. Implementing these assumptions and going over to coordinates $\mathbf{k}$ and $\mathbf{Q}$, only the denominator of Eq. (3) explicitly involves $\mathbf{k}$. Doing the $\mathbf{k}$ summation over the free-electron Fermi sphere one obtains

$$\rho_{\pm}(r)=\mp S\int\chi(Q)J(Q)[e^{i\mathbf{Q}\cdot\mathbf{r}}+e^{-i\mathbf{Q}\cdot\mathbf{r}}]dQ, \quad (4)$$

where we have defined $\mathbf{r}$ with respect to the local-moment site and $\chi(Q)$ is the Qth Fourier component of the static free-electron susceptibility. The $Q\neq 0$ terms of the integral are the mixing terms of Eq. (3) while the $Q=0$ term is[1] the hitherto omitted constant-density Zener term.[14]

The advantages of assuming J to be a function of $\mathbf{Q}$ and in turn of dealing with Eq. (4) is that apart from numerical constants, $\chi(Q)$ is the static free-electron susceptibility which yields the electron response due to the Qth Fourier component $H(Q)$ of an applied magnetic field. Thus knowledge of higher order susceptibility terms, such as conduction-electron–conduction-electron interaction effects, can be immediately applied to RKKY theory. The recent development of the theory has been largely in this direction.[2–4]

The essential modification of the $\chi(Q)$ of Eq. (4) due to conduction-electron–conduction-electron exchange[6] is trivially, though superficially, understood in the following way. The electron gas is perturbed with a magnetic field $H(Q)$ yielding the response

$$\Delta(Q)=\chi(Q)H(Q). \quad (5)$$

[15] For example see J. Friedel, Nuovo Cimento **7**, 287 (1958).

Now if the response itself induces a field proportional to $\Delta(Q)$, say $v\Delta(Q)$, we have

$$\Delta(Q)\chi(Q)[H(Q)+v\Delta(Q)]. \quad (6)$$

Solving for $\Delta(Q)$,

$$\Delta(Q)=\frac{\chi(Q)H(Q)}{1-v\chi(Q)}\equiv\chi_v(Q)H(Q), \quad (7)$$

where

$$\chi_v(Q)=\chi(Q)/[1-v\chi(Q)] \quad (8)$$

is now the exchange-enhanced susceptibility. Such a denominator is a characteristic of the effect of self-consistency in linear response theory and has been obtained with proper rigor in the random-phase approximation by Wolff[6] for the problem at hand. The Fourier transform of the conduction-electron–conduction-electron exchange coupling, v, is a positive constant if one assumes a delta-function interelectronic interaction. Since the total moment induced in the conduction bands is entirely associated with the Zener, or $Q=0$, term, magnetization studies yield a measure of the enhancement occurring at $Q=0$. For Pd this appears to be better than an order of magnitude and falls off rapidly for higher Q because of the nonlinear character of the enhancement [and a $\chi(Q)$ which decreases with increasing Q].

Recently, Kim[16] has taken a Hamiltonian containing local moment conduction-electron and conduction-electron–conduction-electron terms and has transformed it to an effective conduction-electron–conduction-electron interaction Hamiltonian involving a new term which is of the exchange type and is repulsive in character. Its effect is to add a positive term (proportional to local moment concentration) to the v of Eq. (8), thus further enhancing the susceptibility. This Hamiltonian provides a particularly transparent prediction of the ferromagnetism of, for example, the dilute Fe-Pd alloys.

The penalty for dealing with Eq. (4) is, of course, its inexact treatment of the conduction electron-local mement exchange coupling and its inability[17] to account for local atomic Bloch-orbital character. The latter is readily incorporated into the evaluation of Eq. (3) and is of considerable interest when inspecting the hyperfine fields associated with RKKY spin distributions. It therefore becomes desirable to understand what RKKY theory predicts in the contexts of both Eqs. (3) and (4). In the present paper we limit attention to Eq. (4) and to a case where an assumed Q dependence of J happens not to be bad. The effect of going to $\chi_v(Q)$ will be considered but we will not inspect the effect of the spin-density wave enhanced susceptibility studied by Over-

[16] D. J. Kim, Phys. Rev. **149**, 434 (1966).

[17] Using analytically simpler functions and integrals, Kaplan [T. Kaplan, Phys. Rev. Letters **14**, 499 (1965)] obtained a $\mathbf{k}$ and $\mathbf{Q}$ expansion of $\mathbf{k}$ and $\mathbf{k}'$ dependent orbital behavior for insertion into Eq. (4). The present intermediate results were not amenable to such a fit.

hauser and co-workers.[3,18] This effect, if any, may, of course, also be incorporated into the χ of Eq. (4).

For some purposes, Eq. (4) becomes more transparent if one does the angular integrations, assuming J to be a function only of the magnitude of Q (as has always been done). In this case, one obtains

$$\rho(\mathbf{r})=\frac{8\pi S}{r}\int_0^\infty (\sin Qr)J(Q)\chi(Q)QdQ. \qquad (9)$$

The factor $(Q/2k_F)\chi(Q)$ is independent of k_F and is plotted in Fig. 1. As is well known, there is a singularity at $Q=2k_F$ and we see that the Q space in the immediate vicinity of the singularity is most heavily weighted when obtaining $\rho(r)$. The fact that $J(Q)$ may differ in sign from traditional assumptions, for Q's in this region, will be important to the results we report. The singularity occurs at the Q value where zero valued energy denominator contributions [see Eq. (3)] cease to be made to $\chi(Q)$, i.e. $\mathbf{k}'$ must lie off of the Fermi surface.

Considerable direct and indirect experimental information is available concerning the induced conduction-electron spin density, $\rho(0)$, at the local moment nucleus. One of the most serious shortcomings of "traditional" RKKY theory has been its inability to rationalize these data. Crudely speaking, the experimental densities at the local-moment nucleus are of the order of, to one order of magnitude larger than the densities, $\rho(NN)$, seen at near-neighbor ion sites, i.e.

$$1\gtrsim|\rho(0)/\rho(NN)|\lesssim 10.$$

In the interest of obtaining analytic results, the original RKKY estimates assumed a constant $J(Q)$ which led to an infinitely valued $\rho(0)$. This nonphysical result is associated with too heavy a weighting of the high Q components. $J(Q)$ must go to zero at $Q\to\infty$. Recently, Overhauser has[19] approximated the exchange parameter by the form factor

$$J_{FF}(Q)\equiv\int e^{i\mathbf{Q}\cdot\mathbf{r}}|\psi_{1oc}(r)|^2 d\mathbf{r}, \qquad (10)$$

a result obtained by replacing $1/r_{12}$ in Eq. (1) by a delta function. The approximation thus assumes strong shielding, within an atomic volume, of the conduction electron-local moment interaction. Utilizing J_{FF} with the unenhanced $\chi(Q)$ of Eq. (4) leads to

$$500\lesssim|\rho(0)/\rho(NN)|\lesssim 5000$$

and the exchange-enhanced χ_v would further worsen disagreement with experiment. Overhauser and Stearns[3] concluded that spin-density wave contributions to χ were responsible for the decreased ratio inferred experimentally for metallic iron. The results of Sec. IV suggest a more important reason, namely, that the differences between $J_{FF}(Q)$ and the actual exchange coupling are very important to the predicted ratio. The use of the latter greatly improves the possibility of having theory agree with experiment without any severe modification of χ.

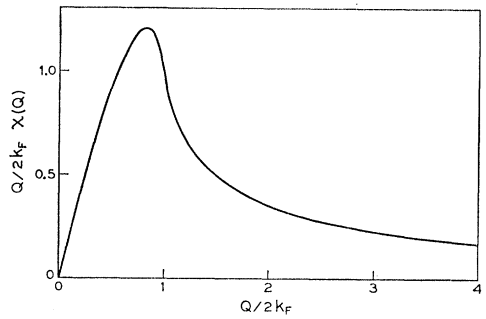

FIG. 1. The Q dependence of $Q/2k_F\chi(Q)$, where $\chi(Q)$ is the simple conduction-electron susceptibility.

The other outstanding feature of RKKY theory is the attendant "Friedel oscillations." For the asymptotic region of large r values, it is traditionally argued that the exponentials of Eq. (4) [or the sine function of Eq. (9)] oscillate so rapidly that only the singularity in the integrand at $Q=2k_F$ (see Fig. 1) makes a nonzero contribution to the spin density. The result is a density involving that one Fourier component which oscillates as $1/2k_F$. When evaluating Eq. (4), one discovers that the oscillations occur even at smaller r values where it is completely inappropriate to invoke asymptotic arguments. Such r values would typically include nearest-neighbor and next-nearest-neighbor ion sites—the regions most heavily sampled in many experiments. From Fig. 1 we see that the Q space in the vicinity of $2k_F$ is heavily weighted and, from our experience in integrating Eq. (4), it appears that the integrand in this region may act *cooperatively* to preserve the oscillations into this small r region. One expects the detailed behavior of the oscillations at such r values to be particularly sensitive to details of $J(Q)$ and $\chi(Q)$ and indeed this is the case. There is experimental evidence indicating such oscillations. Low and Collins have directly observed[20] sign reversals in $\rho(r)$ in neutron-diffraction investigations of impurities in iron and nickel alloys. While the resolution is such that the detailed behavior of $\rho(r)$ cannot be obtained, the sign reversal is a necessary feature of the oscillations. Spin-density oscillations have also been inferred from hyperfine data.[21] Finally, it must be emphasized that most of the data is for transition metal hosts with band structures and Fermi surfaces that are far more complicated than the free-electron model utilized in the RKKY theory described

[18] See also A. W. Overhauser, Phys. Rev. **128**, 1437 (1962), and D. R. Hamann and A. W. Overhauser, *ibid.* **143**, 183 (1966).
[19] A. W. Overhauser, J. Appl. Phys. **34**, 1019S (1963).
[20] G. G. Low and M. F. Collins, J. Appl. Phys. **34**, 1195S (1963); M. F. Collins and G. G. Low, J. Phys. Radium **25**, 596 (1964); and A. Arrott, M. G. Collins, T. M. Holden, G. G. Low, and R. Nathans, J. Appl. Phys. **37**, 1194S (1966).
[21] For example, see Ref. 3, and M. Rubinstein, G. H. Stauss and M. B. Stearns, J. Appl. Phys. **37**, 1334S (1966).

here. Therefore, theory should not be in quantitative agreement with experiment.

III. THE EXCHANGE INTEGRAL

We are interested in the exchange-integral coupling between Bloch orbitals and the spherical half-filled $4f$ shell of Gd. The effects arising from the coupling with an aspherical moment are of interest,[22] but as there is much to be learned from the spherical case, and since added aspherical complications would only obscure such observations, they will be ignored here. A few details of the explicit evaluation of the integrals are given in Appendix I. In this section we are primarily interested in the behavior of the coupling with particular emphasis on the appropriateness of replacing $J(\mathbf{k},\mathbf{k}')$ by $J(Q)$. It is desirable to inspect the exchange coupling appropriate to both a rare-earth- and an iron- series ion. It happens that the Gd coupling is reasonably approximated by a $J(Q)$ and hence is amenable to insertion into Eq. (4). This is not the case for Fe and hence its inspection will await a later paper when Eq. (3) is evaluated.

It is convenient to expand the Bloch orbitals at the magnetic-moment site as

$$\varphi_{\mathbf{k}}(r)=\sum_{l,m}\langle lm|\mathbf{k}\rangle \Xi_{l,m}{}^{k}(r)Y_l{}^{m}(\theta,\varphi), \tag{11}$$

where the Ξ would be spherical Bessel functions if the φ's were simple plane waves. One may evaluate the spin-dependent exchange coupling in Hartree-Fock theory for φ's which are not orthogonal to the Gd^{3+} ion, but this involves using more complicated expressions than the $J(\mathbf{k},\mathbf{k}')$ of Eq. (1) which, as noted, holds only for orthogonal orbitals. There are two sources of the complications: nonorthogonality with the closed shells of the ion and with the open $4f$ shell. The effect of the closed-shell nonorthogonality on the exchange coupling can be accounted for quite rigorously by first orthogonalizing the φ to the closed shells and then evaluating Eq. (1) with the orthogonalized φ. This effect is very important to the results of this section. The same orthogonalization will be done also with the open $4f$ shell, although this procedure does not have strong justification. This open-shell process is unimportant to the results and we will not consider either its shortcomings or its proper extension, a matter perhaps best inspected when simultaneously considering interband mixing.[7–9] We will therefore evaluate Eq. (1) for single plane waves orthogonalized to the Gd^{3+} ion core (OPW's). [Exchange integrals obtained without this orthogonalization, and with the then incorrect Eq. (1), appear in Appendix II along with the resulting predictions for $\rho(r)$.] For our OPW's we have

$$\langle lm|\mathbf{k}\rangle=(i)^{l}N_kY_l{}^{-m}(\theta_k,\varphi_k) \tag{12}$$

and[23]

$$\Xi_l{}^{k}(r)=j_l(kr)-\textstyle\sum_n S_{nlk}R_{nl}(r), \tag{13}$$

where $R_{nl}(r)$ is the radial function of the core shell with principle quantum numbers l and n, and S_{nlk} is the radial integral between that radial function and the Bessel function $j_l(kr)$. The n summation spans all core shells of given l and normalization is accounted for by the factor

$$N_k=\frac{4\pi}{\sqrt{V}}\left\{1-\frac{4\pi}{V}\sum_{n,l}(2l+1)S_{nlk}{}^{2}\right\}^{-1/2}, \tag{14}$$

where V is the atomic volume associated with a lattice site. The n, l summation of Eq. (14) spans all ion core shells including the $4f$. In writing Eq. (14) we have normalized to a single site volume in order to avoid questions of different types of lattice sites in our metal or alloy. Unnormalized exchange integral and $\rho(r)$ results will be reported so as to avoid results specific to a specific lattice (via the V) and to specific ion cores (via the S's) at particular ion sites.

Given φ_k of the form of Eq. (11), the exchange integral of Eq. (1) is trivially evaluated, yielding:

$$J(\mathbf{k},k')=\sum_{\substack{l,l'm\\ \mathfrak{L}\mathfrak{M}}}(i)^{l-l'}N_kN_{k'}(2L+1)[(2l+1)(2l'+1)]^{1/2}Y_l{}^{-m}(\theta_k\varphi_k)Y_{l'}{}^{m}(\theta_{k'}\varphi_{k'})$$
$$\times\begin{pmatrix}l & \mathfrak{L} & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l' & \mathfrak{L} & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l & \mathfrak{L} & L\\ m & -\mathfrak{M} & -M\end{pmatrix}\begin{pmatrix}l' & \mathfrak{L} & L\\ -m & \mathfrak{M} & M\end{pmatrix}\mathfrak{F}^{\mathfrak{L}}(k,k'), \tag{15}$$

where L and M are the quantum numbers associated with the local orbital ψ, brackets ( ) denote $3j$ coefficients.

$$\mathfrak{F}^{\mathfrak{L}}(k,k')\equiv\int\int R_L(r)R_L(r')\Xi_l{}^{k}(r)\times\Xi^{k'}{}_{l'}(r')\frac{r_<{}^{\mathfrak{L}}}{r_>{}^{\mathfrak{L}+1}}r^2dr\,r'^2dr', \tag{16}$$

where R_L is the local-moment radial function. For the case of a spherical local moment, where we average J over local-moment orbitals (i.e., over M), one obtains

$$J(\mathbf{k},\mathbf{k}')=\frac{N_kN_{k'}}{4\pi}\textstyle\sum_l P_l(\cos\Omega)\mathcal{G}_l(k,k'), \tag{17}$$

where Ω is the angle between $\mathbf{k}$ and $\mathbf{k}'$ and

$$\mathcal{G}_l(k,k')\equiv(2l+1)\sum_{\mathfrak{L}}\mathfrak{F}^{\mathfrak{L}}(k,k')\begin{pmatrix}l & \mathfrak{L} & L\\ 0 & 0 & 0\end{pmatrix}^{2}. \tag{18}$$

[22] For example see T. A. Kaplan and D. H. Lyons, Phys. Rev. **129**, 2072 (1963).

[23] Note the omission of the m subscript on the radial Ξ function. Orthogonalization to a spherical ion core causes Ξ to be independent of m.

J depends only on the magnitudes of $\mathbf{k}$ and $\mathbf{k}'$ and on the angle between them—a result expected for a spherical moment. Equation (17) suggests that extraordinary circumstances are required for it to even approximately obey the simple Q dependence assumed in deriving Eq. (4). This is very different from the case of a direct Coulomb interaction.

We wish to sample $J(k,k')$ behavior with an eye to insertion into Eq. (4) despite the fact that it seems unlikely that Eq. (17) will yield a simple Q dependence. Emphasis will be placed on that choice of $\mathbf{k}$ and $\mathbf{k}'$ yielding the minimum energy denominator in Eq. (3), hence the maximum contribution to χ, for a given Q. This choice is indicated in Fig. 2. For $Q<2k_F$ the two k vectors simply trace the Fermi surface while for $Q>2k_F$ the two k vectors are antiparallel with $\mathbf{k}'$ moving off the surface. Results for this choice, *defined* as J_Q, utilizing Hartree-Fock Gd^{3+} wave functions[24] for the $4f$ shell and the ion core are given in Fig. 3. The methods used to evaluate the $\mathfrak{F}^{\mathfrak{L}}$ integrals are indicated in Appendix I. [As noted, these and subsequent results of this section are given without the $N_kN_{k'}/4\pi$ factor of Eq. (17) so that they are not specific to a specific metal environment.] The l summation[25] is cut off at $l=3$. The form factor, $J_{FF}(Q)$ also appears in Fig. 3 and we see strong, and important, differences between it and J_Q. For example, J_Q is negative in the region $Q\sim 2k_F$ and this is due to significant $l=1$ contributions. Not only is $J_Q(2k_F)$ negative, but its magnitude is substantial when compared with $J_Q(0)$. The susceptibility function of Fig. 1 suggests that this will be important. Note that while the sign reversal on going from $Q=0$ to $2k_F$ is associated with odd-l components, the angular factors remain constant for $Q>2k_F$ and the outer oscillations in J_Q are associated with the $\mathcal{G}^l(k,k')$ factors. We will return to this matter shortly. If one accounts for the normalization appropriate to the rare-earth metal lattice, one discovers that the diagonal integrals, $J(0)$, are of the right order of magnitude to account for the conduction-band spin moment appearing in ferromagnetic Gd metal. [The $J(0)$'s actually run small, a fact to be wished for when one goes on to account for the effect of the metal's band character on the coupling.]

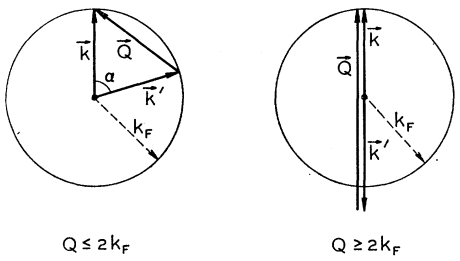

FIG. 2. The $\mathbf{k}$ and $\mathbf{k}'$ choice for given Q employed in the exchange-coupling sampling J_Q. Note that this choice involves the minimum-energy denominator in Eq. (3) for which $|k|=k_F$ and $|k'|$ takes the minimum value possible for a given Q.

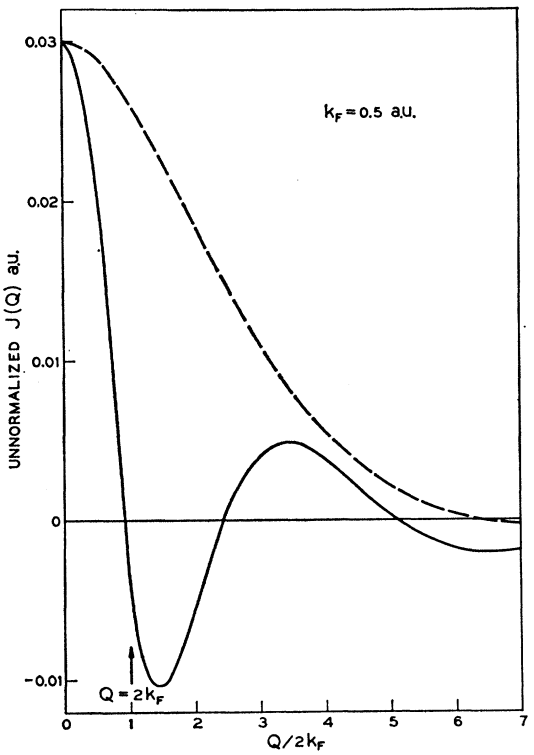

FIG. 3. Un-normalized exchange couplings: the OPW J_Q (solid line) and J_{FF} (dashed line) for Gd^{3+} and $k_F=0.5$ a.u.

Results for other Q samplings, with $k_F=0.5$ atomic units (a.u.), appear in Fig. 4. In both cases $\mathbf{k}$ is kept on the Fermi surface and $\mathbf{k}'$ moves off as indicated. While quantitative differences occur, there is a strong qualitative agreement between the curves. The integral goes negative in the vicinity of $2k_F$ and thereafter oscillates with substantial magnitude in all three cases.

A k_F value of 0.5 a.u. represents the lower range of values expected from free electron sphere arguments and 1.0 a.u. represents the upper limit which is normally encountered. Results for $k_F=1.0$ appear in Fig. 5. J_Q is again negative at $2k_F$, and shows a discontinuity in slope at that point, which reflects the $\mathbf{Q}$ choice of Fig. 2. A similar, but less discernable discontinuity occurs in the $k_F=0.5$ result. The curvature for $0\leq Q\leq 2k_F$ betrays small but observable $l=2$ contributions to J_Q in that range. The samplings in Fig. 5, have $\mathbf{k}$ fixed at values of 0, 0.5 or 1.0 a.u. while $\mathbf{k}'(\geq k_F)$ moves. All curves except the case $\mathbf{k}'$ parallel to $\mathbf{k}$, display negative values in the vicinity of $2k_F$ and there appears an over-all tendency for this negative $J(\mathbf{k},\mathbf{k}')$ region to center on Q values smaller than those characteristic of the J_Q sampling alone. This contrasts with the results of Fig. 4, where a reverse tendency is seen. The curve for $\mathbf{k}'$ parallel to $\mathbf{k}$, which stays positive for $Q<2k_F$, is associ-

[24] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).
[25] The omission of terms $l>3$ in Eq. (17) does not significantly affect the results for the range of $\mathbf{k}$ and $\mathbf{k}'$ for which J was evaluated.

ated with the maximum energy denominator, for given Q, in Eq. (3). However, the results of Fig. 6 suggest that the region of k-Q space contributing to that curve is relatively unimportant to $\chi(Q)$. In Fig. 6 plots of $J(\mathbf{k},\mathbf{k}')$ are given for $k=k_F$ and with $\mathbf{k}'$ vectors of constant magnitude. Thus, any one curve is associated with a fixed-energy denominator. The tendency for J to go negative for $Q\sim 2k_F$ is seen to hold out to $|k'|$ values well off the Fermi surface. We therefore conclude that J_Q offers a fair qualitative sampling of $J(\mathbf{k},\mathbf{k}')$ behavior, but errs by having its first negative region slightly too contracted for $k_F=0.5$, and too expanded for $k_F=1.0$ a.u.

The results of Figs. 3 to 6 show strong exchange-integral oscillations which cannot be blamed on the angular dependence of the $P_l(\cos\Omega)\mathcal{G}_l$ terms of odd l. While oscillations occur for $J(\mathbf{k},\mathbf{k}')$ evaluated for simple plane waves (see Appendix II), the OPW results of the above figures are strongly affected by the $S_{nlk}R_{nl}$ orthogonalization terms of Eq. (13). There exist closed $5s^2$ and $5p^6$ shells in a rare-earth ion which the conduction electrons must penetrate in order to overlap, and, in turn, have an exchange interaction with the open $4f$ shell. The orthogonalization terms of these shells are particularly important to the exchange coupling; the associated S_{nlk} integrals are plotted in Fig. 7. They display oscillations which reflect the relative phases of the plane waves when in the region of the $5s$ and $5p$ shells (having defined a common phase at the rare-earth nucleus). Note also, how $5p$ overlap effects are most important in the region $0.5\leq k\leq 1.0$ a.u. For any case of given $\mathbf{k}$ and $\mathbf{k}'$ where $S_{nl''k}$ and $S_{nl''k'}$ differ in sign, one has a negative contribution to the associated $\mathcal{G}_{l''}(k,k')$ integrals; such terms are responsible for much of the oscillatory character seen in Figs. 3 to 7. Even in the one case where $J(\mathbf{k},\mathbf{k}')$ did not go negative at $Q\sim 2k_F$ i.e., $\mathbf{k}\|\mathbf{k}'$ in Fig. 5, these terms can be seen to be trying to drive it negative. There is, of course, no intrinsic connection between k_F values, the overlap integrals, and, in turn, the orthogonalization contributions to the oscilllations. Negative terms at $Q\sim 2k_F$ reflect the accident of the spatial distributions of the $4f$, $5s$, and $5p$ shells versus characteristic free-electron k_F values.

In this section we have inspected the $4f$-shell local-moment conduction-electron exchange-integral coupling in its own right, with an eye to assuming the pure Q dependence required by Eq. (4). We will utilize the J_Q choice indicated by Fig. 2 in the sections which follow. The choice is associated with the minimum-energy denominator of Eq. (3) and it appears to give a good qualitative representation for much of $\mathbf{k}$, $\mathbf{k}'$ space. It seems to err by being slightly too contracted (in its

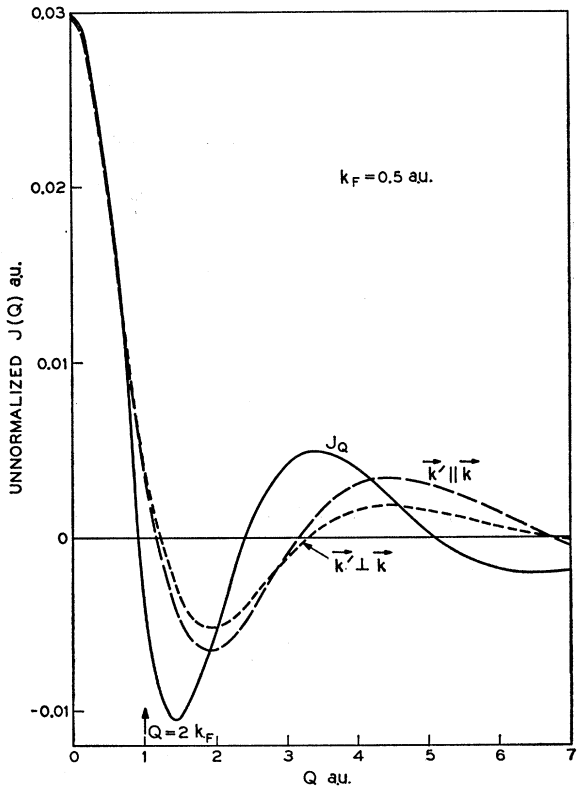

FIG. 4. Un-normalized OPW-Gd^{3+} exchange integrals, $J(Q)$ for various choices of $\mathbf{k}$ and $\mathbf{k}'$ with $k_F=0.5$ a.u. $=|\mathbf{k}|$ and, of necessity, $|\mathbf{k}'|\geq k_F$.

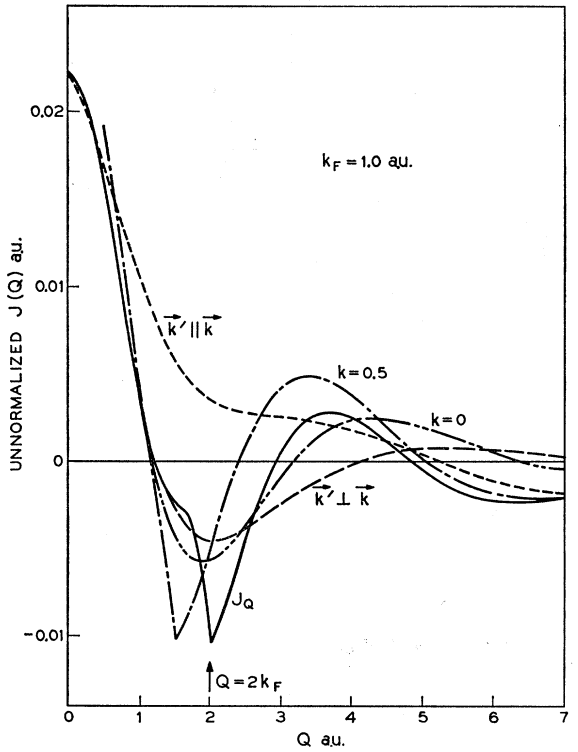

FIG. 5. Un-normalized OPW-Gd^{3+} exchange integrals, $J(Q)$ for various choices of $\mathbf{k}$ and $\mathbf{k}'$. Except where otherwise indicated $|\mathbf{k}|=k_F=1.0$ a.u.

first negative region) for small k_F and too expanded for larger k_F. Accounting for this would further enhance some of the most interesting features of the $\rho(r)$ given in the next sections. Integration of Eq. (3) with the full $J(\mathbf{k},\mathbf{k}')$ further indicates that the assumption of a $J_Q(Q)$ yields qualitatively correct results. It must be emphasized that this is largely a matter of accident, relying as it does on the orthogonalization terms, and that a similar lucky accident does not occur when dealing, for example, with iron-series moments.

IV. SPIN-DENSITY RESULTS OBTAINED WITH THE UNENHANCED SUSCEPTIBILITY

Equation (4) has been integrated, using J_Q, out to values of Q equal to $[7+k_F]$ a.u.[26] The results we will report are un-normalized, the missing normalization factor being

$$S_z/\pi^2\left\{\left[1-\frac{4\pi}{V}\sum_{n,l}(2l+1)S_{nlk}{}^2\right]^{1/2}\times\left[1-\frac{4\pi}{V}\sum_{n,l}(2l+1)S_{nlk'}{}^2\right]^{1/2}\right\}, \quad (19)$$

where the { } is in some sense an average over k, and k'

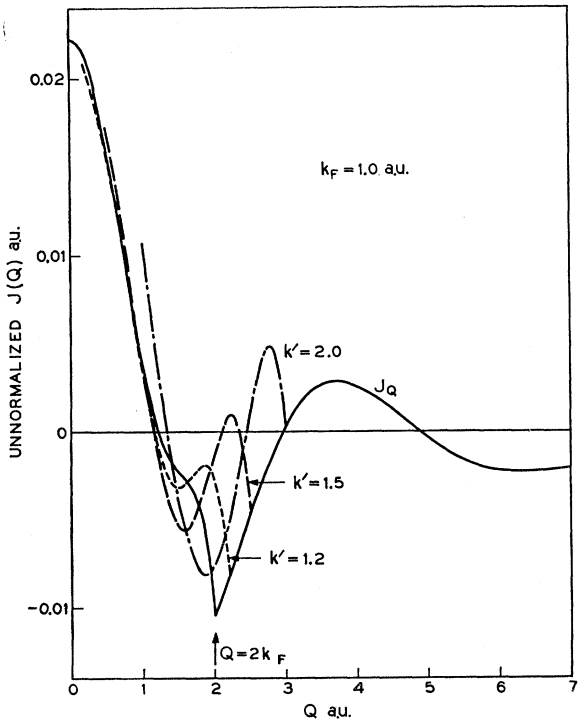

FIG. 6. Additional un-normalized OPW-Gd^{3+} exchange integrals for k_F=1.0 a.u. Except for J_Q, $|\mathbf{k}'|$ take the fixed values indicated and in all cases $|\mathbf{k}|=k_F$.

[26] $J(\mathbf{k},\mathbf{k}')$ was evaluated out to k' values equal to 7 a.u. and since $Q_{\max}=k_F+k_{\max}'$ one has Q max$=7+k_F$. Maintenance of numerical accuracy in J (see Appendix I) led to this cutoff.

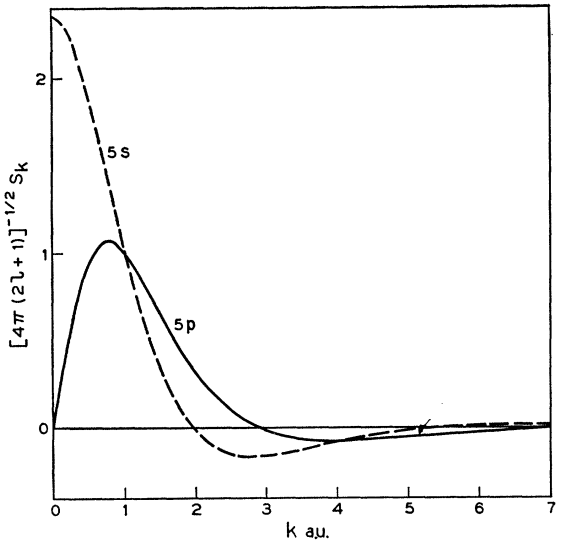

FIG. 7. Plane wave—5p and 5s shell overlap integrals [see Eq. (13) and text which follows] as a function of k.

values.[27] In utilizing Eq. (4) and in writing this normalization factor we have, of course, accounted for orthogonalization effects when evaluating J_Q. As observed earlier, the OPW exchange integral represents the proper evaluation starting with either a plane wave not orthogonal to the ion core or an OPW. We have employed simple plane-wave Bloch orbitals in the density expression. There are computational reasons for this choice. We are interested in the simple plane-wave density in order to avoid detailed behavior specific to specific environments. Computationally, we found it impossible[17] to extract the simple Q dependence for either the normalization factor or the density terms specifically involving ion-core character[28] necessary to allow their insertion into Eq. (4). Such factors will be inspected in a subsequent paper where the predictions of Eq. (3) will be viewed.

Spin-density results appear in Fig. 8. Also shown is the result of integrating the form factor coupling, J_{FF}, for a k_F=0.5 a.u. Its amplitude is adjusted so that its average induced spin density equals that obtained for J_Q and the same k_F. The J_Q results have two features which are characteristic of the traditional theory. First, for larger r values, they display Friedel oscillations. Second, their average density is positive, reflecting the sign of $J(0)$ which drives the Zener term. Of greater interest, are the differences. The bulk of induced positive density is not centered on the nucleus, but in a region some 2 a.u. away. We find that $\rho(0)$ can be positive or negative and of the order of, larger than, or

[27] The curly bracket is a sufficiently slowly varying function of k and k', thus, in turn, of Q, so that its omission from the integrand of Eq. (4) is of no importance to the qualitative results obtained here.

[28] One is especially interested in the spin density at a nuclear site (rather than simple normalization) and it was this that Kaplan was considering.

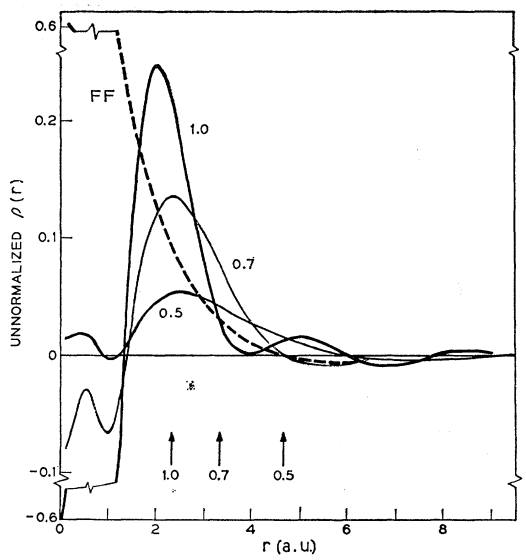

FIG. 8. Un-normalized spin-density predictions employing the unenhanced susceptibility $\chi(Q)$ with J_Q for $k_F=0.5$, 0.7 and 1.0 a.u. and with J_{FF} for $k_F=0.5$ a.u.

smaller than $\rho(NN)$ in magnitude. [Near-neighbor distances are typically 4 to 6 a.u.] This is in striking contrast with the FF and the more traditional results where $\rho(0)$ is always large and positive [for positive $J(0)$]. The behavior of $\rho(0)$ and the associated outward shift of the region of net induced density is also reflected in increased radii for the onset of normal looking Friedel oscillations. Given negative J_Q, for $Q=2k_F$, asymptotic theory would suggest oscillations which were 180° out of phase with traditional results. The situation is more complicated for the spatial region plotted. The vertical arrows in Fig. 8 indicate where traditional or FF densities first go negative. The equivalent nodes for the present results are those bounding the positive-density regions to the outside. These fall at significantly larger radii than do the arrows and the differences are not simple half multiples of the periods of the Friedel oscillations. The $k_F=1.0$ curve shows an oscillation in the region $r=3$ to 4 a.u. but does not go negative until about 6 a.u. This sort of behavior is reminiscent of the exchange-enhanced, χ_v, results of Giovannini and coworkers[2] (and of the section which follows), but here the behavior is entirely associated with the local-moment–conduction-electron exchange-integral coupling. The exchange coupling conspires to make the $k_F=1.0$ results, which would normally be of shortest "range," to actually be of longest "range" in the sense of viewing where $\rho(r)$ first goes negative once off the ion site.[29]

[29] The word range has taken on two distant meanings in the literature: range in the sense used here and range as a measure of the rate at which the Friedel oscillations die out (i.e., the power of r). The near region is of interest to us and only the former meaning is used throughout the paper.

V. SPIN-DENSITY RESULTS WITH $\chi_v(Q)$

Conduction-electron–conduction-electron exchange-enhanced results (the dashed curves) appear in Fig. 9 for a choice of the exchange constant v, such that

$$\chi_v(0)=7\chi(0).$$

Unenhanced results (solid curves) also appear in the figure. A sevenfold enhancement of $\chi(0)$ is the upper limit expected for most metals. For Pd, which is an exception to the rule, a larger enhancement, say a factor of ten, is anticipated.

A sevenfold increase in $\chi(0)$ implies a sevenfold increase in the net induced spin density which, we see from the figures, is lifted like a rug. increasing the range by partially or completely washing out the first negative oscillation.[30] For $k_F=1.0$, where the first oscillation was already driven positive by the exchange coupling, the range is relatively unaffected. $\chi_v(0)/\chi(0)$ ratios significantly greater than ten are necessary to wipe out the second negative-density oscillation.[31] Results scale rather simply, from those plotted, for other choices of v. In particular, the net density, concentrated in the main peak centered at $r=2$ to 3 a.u., scales roughly linearly with the enhancement (as it must) since the Zener term is associated with $Q=0$. The dependence of $\rho(0)$ on the enhancement is least simple; the effect is relatively minor for $k_F=1.0$ and major for $k_F=0.5$. The value of $\rho(0)$ arises from the competition of different regions of Q space with $J(Q)$'s of differing sign. The χ_v enhancement is greatest for $Q\sim0$ where $J(Q)$ is (of necessity) positive, and thus all $\rho(0)$ values become increasingly positive with increased v.

Results obtained with J_{FF} are embarassed by the effect of the enhancement since $\rho(0)$ is most strongly increased by the "rug lifting" which, crudely speaking, raises the most positive density regions most strongly. Since this makes the form factor $\rho(0)/\rho(NN)$ ratios even poorer[31], Overhauser and Stearns[3] were led to invoke an enhancement in $\chi(Q)$ in the region $Q\sim2k_F$. It is our opinion that shortcomings in J_{FF} were almost totally responsible for this result. We should again note that J_{FF} is a very reasonable choice granting that one neglects OPW effects and assumes Coulomb screening for dimensions small compared with the local-moment region. Both factors are important to the differences seen here with the form-factor results. Omitting orthogonalization effects, the simple plane-wave results of Appendix II still differ significantly from those obtained by using J_{FF}.

With or without the enhancement, the induced

[30] Moriya (Ref. 4) has considered the dependence of this range on exhange enhancement in some detail (in particular inspect his Fig. 13). Having made the traditional assumption concerning the exchange coupling, his results are only qualitatively comparable with what has been obtained here.

[31] The traditional, constant $J(Q)$, result would be similarly embarassed if it were not for the fact that $\rho(0)$ was already infinite.

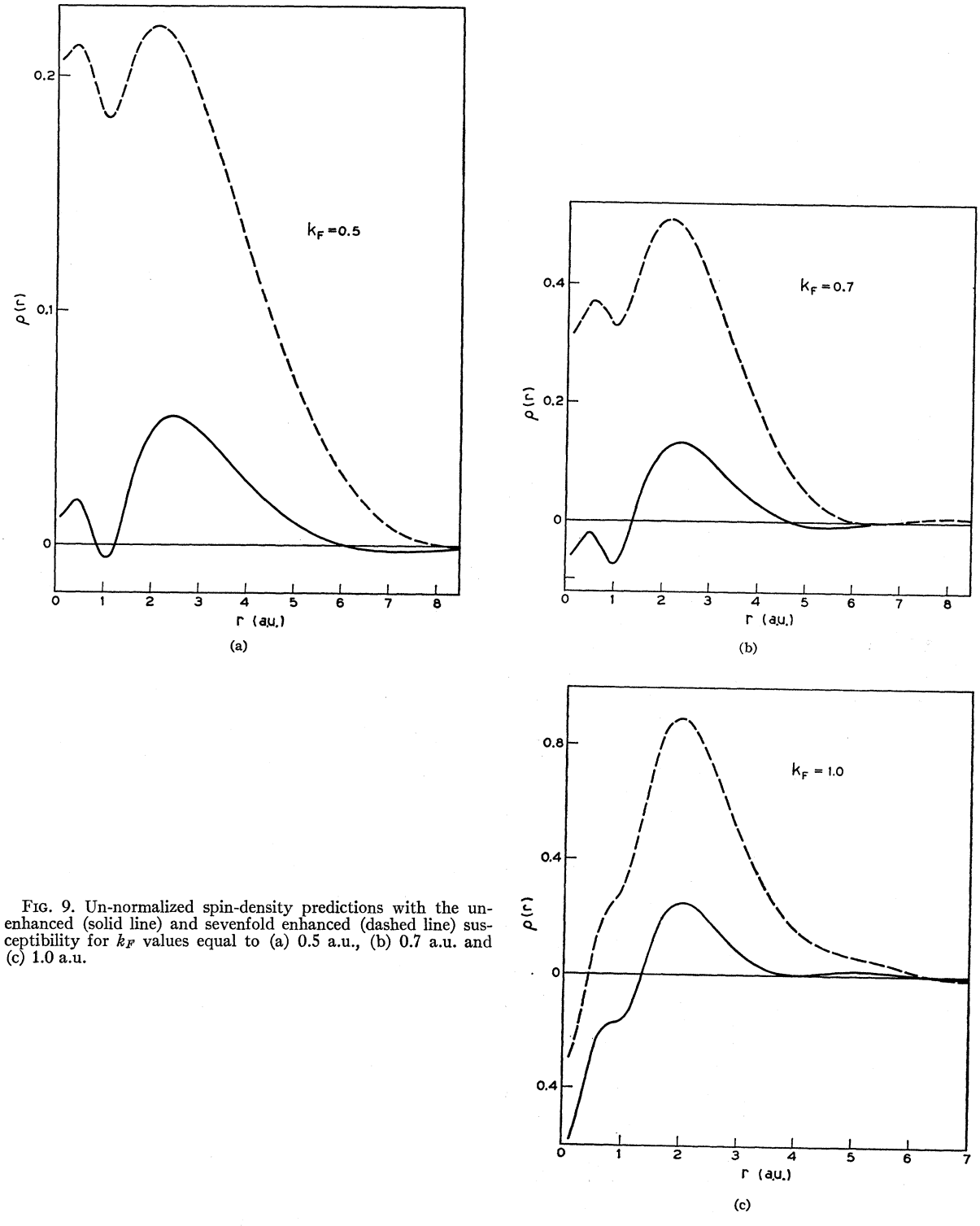

FIG. 9. Un-normalized spin-density predictions with the unenhanced (solid line) and sevenfold enhanced (dashed line) susceptibility for k_F values equal to (a) 0.5 a.u., (b) 0.7 a.u. and (c) 1.0 a.u.

spin density looks very "atomic" with its tendency to concentrate in the outer radial reaches of the ion. This particular behavior is an accident due to details of the exchange coupling and of the k_F values of interest and is not "ionic" in origin. Accounting for OPW ion-core behavior in the density, will, of course, perturb it further but will not, we believe, shift it significantly out of this region and in particular, not back in on the origin.

VI. DISCUSSION

We have inspected the exchange-integral coupling between local moments and free-electron-like conduction electrons in rare earths, and the resulting (lowest-order) spin density induced in the conduction band. The exchange coupling was examined in greater detail than is essential to our purposes here because it is of interest in itself and in anticipation of further work. The interaction was seen to differ significantly from the various traditional assumptions concerning its behavior. The results of Sec. III and Appendix II indicate that the orthogonalization of the free electrons as they penetrate the ion has severe effects. The rare-earths with closed $5s$ and $5p$ shells exterior to the magnetic $4f$ shell provide unique examples of this in that the relative roles and behavior of the s and p-like exchange components [$l=0$ and 1 in Eq. (17)] are substantially affected. [Transition-metal ions with their magnetic d shell located in the exterior of the ion site are differently affected as will be seen in a subsequent paper.]

Since most of the available experimental information is about the spin density in the near-neighbor ion regions and at the magnetic ion's nucleus (via the Fermi-contact hyperfine interaction), or concentration has been with these regions. The center of the bulk of the spin density was seen to be shifted from the magnetic nucleus radially out to the outer reaches of the ion site. The reduced $\rho(0)/\rho(NN)$ ratios which result greatly improve the theory's qualitative position with respect to experiment. While details of the density distributions, such as a particular negative $\rho(0)$, hinge on approximations and computational detail, we believe that the outward shift in the density and the reduced $\rho(0)/\rho(NN)$ ratios are essential features associated with the actual coupling features which will remain when one goes on to an ultimate treatment of the problem.

Associated with the shift in the density away from $r=0$, is a substantial increase in the range of the positive-density region. On first inspection, one might be tempted to associate this with the negative value of $J(Q)$ for $Q=2k_F$, implying a 180° phase shift in the asymptotic Friedel oscillations. The r space inspected is *not* in the asymptotic region and the outward shift is *not* simply associated with a negative $J(Q)$ for $Q=2k_F$. Actually, negative J behavior for any of k-Q space where χ is of significant magnitude contributes to the outward shift. Anything causing a depression of $\rho(0)$ to small positive, or better yet to negative, values necessitates an increase in the range.

There has been one notable example of large-range density distributions, namely, for magnetic impurities in Pd. This was first inferred from spin-resonance results[32] and, more recently, more directly by neutron diffraction.[33] The experiments yield ranges of 15 to 20 a.u., ranges which are well outside the predictions of traditional free-electron theory with traditional free-electron Fermi spheres. The RKKY work[2,4] with the exchange enhanced χ_v was directed, at understanding these results. While the enhancement appears very important, more important still is the occurence on a "jungle gym" d-band Fermi-hole surface, which is primarily responsible for the metal's high density of states. This surface has an unusually small $2k_F$ value ($\sim$0.2 a.u.) as found both experimentally[34] and in band calculations.[11] Given the exchange enhancement, and more importantly the Fermi-surface dimensions, Pd appears to yield an oustanding qualitative success of RKKY theory—a case which in the recent past seemed to represent its most notable failure.[35] Unfortunately, because of its transition-metal character Pd represents the outstanding case where the present and previous[2,4] χ_v work is not really applicable since essentially free-electron band behavior was assumed. Any rigorous treatment of the problem promises to be formidable.

ACKNOWLEDGMENTS

We wish to acknowledge valuable discussions with S. Koide and the programming and computational assistance of B. B. Cetlin, E. Salamin, R. Sheshinski, and E. Wolfson.

APPENDIX I: EVALUATION OF THE $\mathfrak{F}^l(k,k')$ INTEGRALS

Equation (16) was evaluated with $R_L(r)$ and $\Xi_l^k(r)$ constructed from analytic Hartree-Fock Gd^{3+} radial orbitals[24] of the form

$$R_i(r)=\sum_j C_{ij} r^n j e^Z j^r, \tag{20}$$

Given analytic functions it was decided to evaluate the integrals analytically in hopes of accuracy and machine economy. This was only partially successful, as is indicated below.

Equation (16) then became weighted sums of integrals of the form

$$\int\int r^m j_l(kr) e^{-Sr} \frac{r_<^{\mathcal{L}}}{r_>^{\mathcal{L}+1}} (r')^{m'} e^{-S'r'} j_l(k'r') dr dr', \tag{21}$$

$$\int\int r^m j_l(kr) e^{-Sr} \frac{r_>^{\mathcal{L}}}{r_<^{\mathcal{L}+1}} (r')^{m'} e^{-S'r'} dr dr', \tag{22}$$

[32] D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. **135**, A1346 (1964).

[33] G. G. Low, *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and the Physical Society, London, 1965), p. 133.

[34] N. E. Alekseevskii, G. E. Karstens, and V. V. Mozhaev, Zh. Eksperim. i Teor. Fiz. **46**, 1979 (1964) [English transl.: Soviet Phys.—JETP **19**, 1333 (1964)].

[35] It should be noted that any negative-density region, outside the main positive peak, has yet to be observed experimentally. This may simply reflect the dominance of the main peak.

and integrals involving only exponentials (no Bessel functions) which are trivially evaluated. The S's are real and consist of one, or a sum of two, of the Z_j's of Eq. (20). Breaking up Eq. (22) into inner and outer integrals

$$\left[\int_0^\infty dr \int_0^r dr' \text{ or } \int_0^\infty dr \int_r^\infty dr'\right],$$

keeping the Bessel function in the outer $[\int_0^\infty dr]$ integral and integrating the inner by parts, the integral becomes a sum over N of terms like

$$\int_0^\infty r^N j_l(kr) e^{-(S+S')r} dr. \tag{23}$$

Such integrals may be expressed as hypergeometric functions[36] which in turn may be evaluated analytically in closed form if $N \geq l+1$. For $N<l+1$, power series expansions were used and of the several available, one always converged rapidly. As a result, Eq. (22) could always be evaluated economically and accurately.

When dealing with Eq. (21), the Bessel function appearing in the inner integral was expanded in exponentials of imaginary argument [the standard sine and cosine expressions which are good for all but near-zero-valued arguments]. The inner integrals were then integrated by parts again yielding Eq. (23), but with an exponential of complex argument. The closed form expressions for $N \geq l+1$ could again be straightforwardly and accurately evaluated but the power-series expansions for complex argument did not necessarily converge. Significant errors crept into the $\mathfrak{F}^4$, $\mathfrak{F}^5$ and $\mathfrak{F}^6$ integrals contributing to $\mathcal{G}_2$ and $\mathcal{G}_3$ [see Eq. (17)] by the time k or k' was of the order of 7 a.u. Integral evaluation therefore was terminated at k values of 7 a.u. In this range, the resulting $J(\mathbf{k},\mathbf{k}')$ integrals are more accurate than is required for our purposes. This is in part because the the most important $\mathcal{G}_0$ and φ_1 integrals were not affected and the $\mathcal{G}_2$ only moderately so.[37] Termination of the integration of the spin-density expressions, Eqs. (3) or (4), at k values of 7 a.u. does not significantly affect their evaluation (a fact verified by several more extended integrations).

[36] For the definition and properties of hypergeometric functions, see *Higher Transcendental Functions*, edited by A. Erdelyi (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, A; W. Gröbner and N. Hofreiter, *Bestimmte Integrale* (Springer-Verlag, Vienna, 1958); I. S. Gradshteyn and I. M. Ryshik, *Tables of Integrals, Series and Products* (Academic Press Inc., New York, 1965).

[37] While the methods used here have been adequate for our purposes, they are clearly insufficient if one wished to evaluate core-conduction electron exchange rigorously for an OPW band calculation because one would then require results for very large k values. In Such a case one has, of course, lattice periodicity. By exploiting this feature (where $1/r_{12}$ goes over to $1/Q^2$), Brinkman and Goodman, Phys. Rev. **149**, 597 (1966) have obtained a result involving integrals of the form of Eq. (23), all of powers of r such that they may be evaluated analytically.

APPENDIX II: PURE-PLANE-WAVE EXCHANGE-INTEGRAL RESULTS

In order to better indicate the role played by OPW character in the results reported in the body of this paper, exchange integrals evaluated for simple plane waves and the resulting spin-density predictions will be inspected here.

J_Q results for $k_F=0.5$ and 1.0 appear in Fig. 10. They neither display the strong oscillatory character seen in Figs. 4 and 5 nor go negative in the vicinity of $Q=2k_F$. They do go negative at significantly smaller Q values and oscillate more stronlgy then does J_{FF} [whose $Q=0$ value has been arbitrarily scaled to match the $k_F=0.5$ curve]. These curves may be compared quantitatively with Figs. 4 and 5. The $J(0)$'s, and hence the net induced spin densities, seen here are twice the $k_F=0.5$, and three times the $k_F=1.0$ OPW counterparts.[38] The $\mathcal{G}_0$ is strongly reduced, the $\mathcal{G}_1$ significantly increased [see Eq. (17)] on going from Fig. 10 to Figs. 4 or 5. These effects are largely associated with $5s$ and $5p$-shell orthogonalization [$4s$, $4p$, $4d$ and $4f$ orthogonalization is significant to $\mathcal{G}_l$ behavior as well].

Spin-density results appear in Fig. 11. The plane-wave results, ρ_{PW}, have been scaled so as to have the same net spin densities as the OPW results. The ρ_{FF}

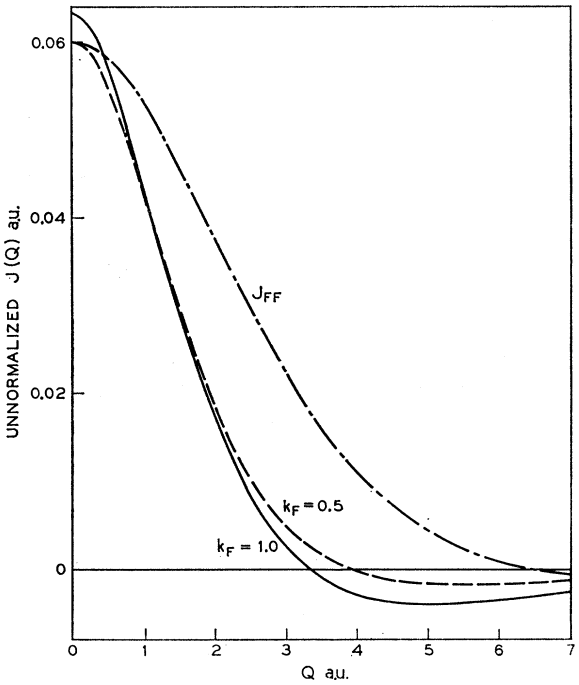

FIG. 10. J_Q exchange integral results evaluated with simple plane waves for $k_F=0.5$ and 1.0 a.u. Also shown is J_{FF}. Apart from the { } of Eq. (14), the missing normalization of these J_Q is identical to that of Figs. 3–6.

[38] The curly bracket entering OPW normalization [see Eq. (14)], modifies these observations to an insignificant extent.

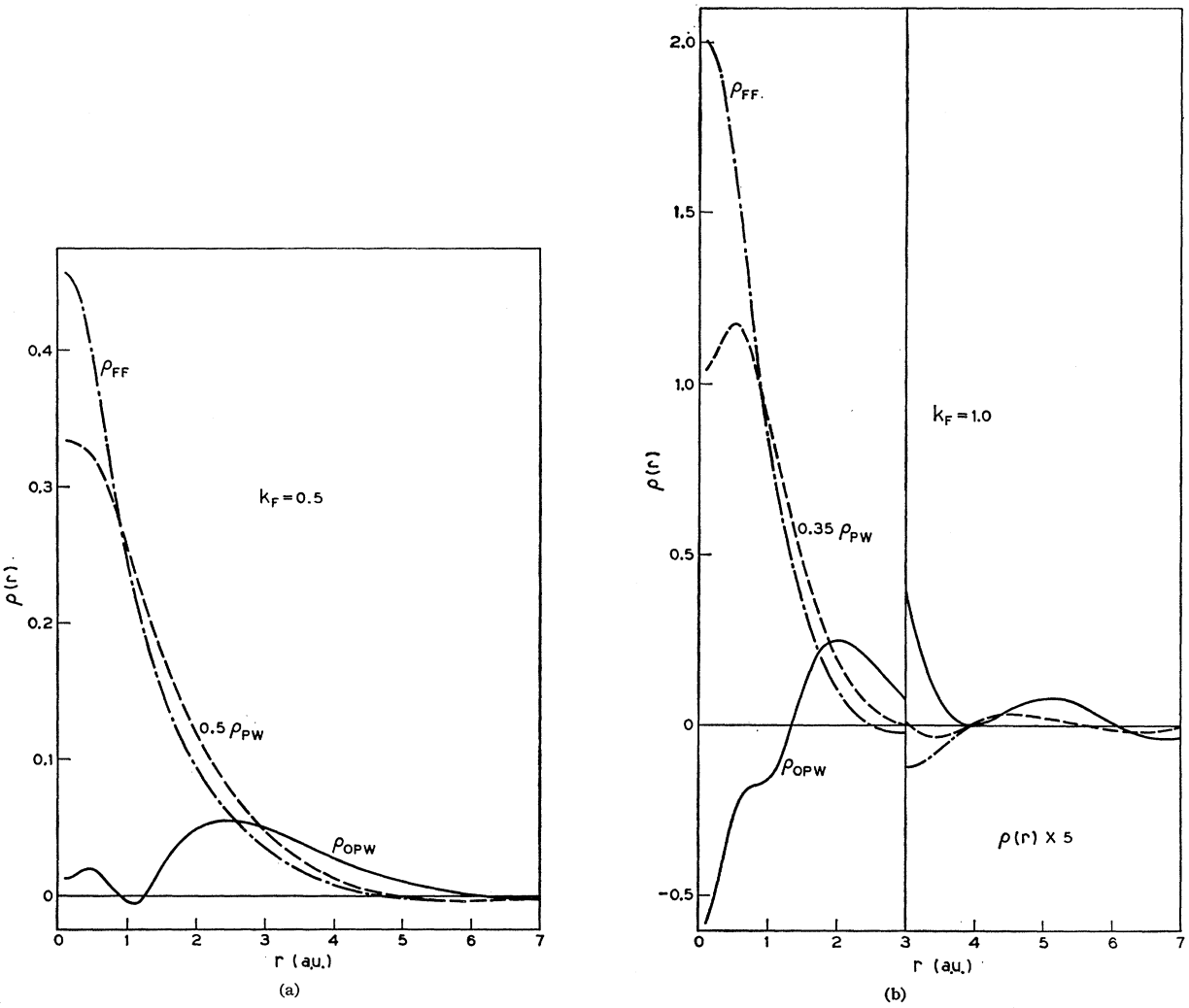

FIG. 11. Simple plane-wave, OPW and J_{FF} predictions of the spin density $\rho(r)$ for k_F values equal to (a) 0.5 a.u. and (b) 1.0 a.u. [For their respective normalizations see the text.]

are, in turn, scaled to match the amplitudes of the outer Friedel oscillations of the ρ_{PW}. While the plane wave $\rho(0)/\rho(NN)$ ratios represent an improvement over form-factor predictions we see that the results of the body of this paper are associated primarily with OPW effects of the exchange coupling.