Realistic Calculation of the Indirect-Exchange Interaction in Metals

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It is shown that the indirect-exchange interaction, or Ruderman-Kittel-Kosuya-Yosida (RKKY) interaction, between localized moments in metals can be evaluated numerically for realistic band structures. The numerical method gives results in excellent agreement with the analytical RKKY results for free-electron bands and is applied to the calculation of the indirect-exchange interaction between nuclear moments in Cu. We find the nearest-neighbor exchange-interaction constant to be $J=-22.6$ nK compared to the free-electron RKKY value of $J=-8.2$ nK with the same normalization procedure.

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The indirect-exchange interaction between either localized spin moments or nuclear moments, together with the direct interaction, leads to cooperative phenomena and ordered phases in metals, semiconductors, and alloys. Of recent interest is the observation of nuclear cooperative phenomena at temperatures below 1 μK in Cu.[1] If the indirect interaction between the moments is mediated by band electrons, the interaction is often known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[2] The RKKY interaction has usually been calculated for a free-electron model of the bands of the solid under consideration with the matrix element of the interaction between the localized moments and the electrons taken to be constant. These approximations yield an interaction which is oscillatory and decays as the fourth power of the moment separation. In this Letter we describe a numerical method for the evaluation of this interaction which employs both realistic energy bands and the variation of the matrix elements throughout the Brillouin zone (BZ). It is shown first that the numerical technique accurately reproduces the RKKY result for free-electron bands. The method is then applied to the calculation of the indirect-exchange energy between nuclear moments in Cu by use of realistic energy bands.

There have been several previous attempts at the use of less idealized band structures to calculate the indirect-exchange interaction and these have indicated that deviations from a free-electron band structure may have a significant effect upon the strength and form of the interaction. Roth, Zeiger, and Kaplan[3] showed that parallel and cylindrical portions of the Fermi surface can considerably extend the range of the interaction, with the decay becoming linear in the former case for intermoment vectors perpendicular to the parallel surfaces. Investigations of the role of the band structure[4] and the matrix elements[5] in the RKKY theory have shown that the assumptions of the original RKKY model are inadequate. However, failure to quantify these effects adequately for realistic band structures throughout the BZ has meant that the interpretation of many experimental data must still be based on the free-electron model or other model band structures.[6,7] For comparison with experiment in some cases, it is sufficient to calculate only the Fourier transform of the indirect interaction and this calculation has been done for realistic bands in a few cases.[8,9] The real space dependence of the interaction is required in order to calculate thermodynamic properties of the solid. In the case of Cu a result for the interaction in real space was obtained by fitting an eight-nearest-neighbor (NN) model to the Fourier-transform values at fourteen points in the Brillouin zone.[9] The results of the direct numerical calculation using the realistic band structure given below are in much better agreement with experimental results for the indirect interaction than either the free-electron–based RKKY result or the fit to the Fourier transform for Cu. The improvement appears to be due to two factors: first, the development of the numerical method so that realistic band structures and matrix elements can be used directly, and second, the inclusion of higher-energy bands which we show make a significant contribution to the indirect interaction.

If off-diagonal scattering terms between different multiplets of the spins are neglected,[10] the indirect-exchange interaction between localized moments can be described by a Heisenberg-type interaction

$$\mathcal{H}=-\sum_{\substack{i>j\\ i,j}} J(\mathbf{R}_{ij})\mathbf{S}_i\cdot\mathbf{S}_j,$$

where $\mathbf{R}_{ij}$ is the vector joining localized moments. The interaction constants $J(\mathbf{R})$ can be written

$$J(\mathbf{R})=\Omega^{-2}\sum_{\mathbf{k},\mathbf{k}'}\sum_{n,n'}\frac{f_n(\mathbf{k})[1-f_{n'}(\mathbf{k}')]\,|\mathcal{J}_{nn'}(\mathbf{k},\mathbf{k}')|^2\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}]}{E_{n'}(\mathbf{k}')-E_n(\mathbf{k})}, \tag{1}$$

where $f_n(\mathbf{k})$ is the Fermi function corresponding to the band energy $E_n(\mathbf{k})$ for wave vector $\mathbf{k}$ in the first BZ, $\mathcal{J}_{nn'}(\mathbf{k},\mathbf{k}')$

is the exchange matrix element whose form depends on the type of moment being considered, Ω is the volume of the real-space unit cell, and the summation extends over all bands n,n'. The main obstacle to a direct numerical calculation of Eq. (1) is the convergence of the double summation over reciprocal space of the rapidly varying function. The problem is more difficult than the calculation of similar quantities such as the susceptibility[11] or the Fourier transform of the indirect-exchange interaction which require only a single summation.

The method we have used to evaluate the double, reciprocal-space summation of Eq. (1) is based on the linear tetrahedron method.[11,12] A mesh of 256 tetrahedra is established in the irreducible wedge of the BZ and at each of the grid points the energy eigenvalues and eigenfunctions are calculated. After the summation of the exponential term over the star of $\mathbf{k}$ and the star of $\mathbf{k}'$, to give $g(\mathbf{k},\mathbf{k}',\mathbf{R})$, Eq. (1) can be rewritten as a double summation over tetrahedra t and t' in the irreducible wedge of the first BZ of a double integration over each pair of tetrahedra:

$$J(\mathbf{R})=(2\pi)^{-6}\sum_{n,n'}\sum_{t,t'}\int_t d^3k\int_{t'}d^3k'\,g(\mathbf{k},\mathbf{k}',\mathbf{R})[E_n(\mathbf{k})-E_{n'}(\mathbf{k}')]^{-1}|\mathcal{J}_{nn'}(\mathbf{k},\mathbf{k}')|^2. \tag{2}$$

Within each tetrahedron, the integral is treated as the product of the integral of each of the three terms separately. This allows the rapidly varying term $g(\mathbf{k},\mathbf{k}',\mathbf{R})$ to be integrated exactly and this greatly increases the overall convergence obtained.[13] After the energies $E_n(\mathbf{k})$ and $E_{n'}(\mathbf{k}')$ are linearized within their respective tetrahedra, the resulting expression for the integral of the energy denominator over the tetrahedra can be evaluated in the general case, but this procedure is not practicable because of the proliferation of computationally slow terms. For tetrahedra away from the Fermi surface, it is sufficient to integrate over one tetrahedron and average over the vertices of the second. For cases in which each tetrahedron has at least one vertex on the Fermi surface, singularities in the integrand may remain after the first integration. In these cases the second integration is also dealt with analytically. The integration of the slowly varying matrix element $\mathcal{J}_{nn'}(\mathbf{k},\mathbf{k}')$ is obtained by averaging over the four vertices of each tetrahedron which is equivalent to the assumption of linearity within each tetrahedron.

It is important to realize that a significant contribution to the RKKY interaction comes from bands well above the Fermi energy. The RKKY result for free-electron bands below an energy E_m corresponding to a wave vector $k_m > k_F$, where k_F is the wave vector at the Fermi energy, is given by

$$I(E_m,R)=(2\pi^2R)^{-2}|\mathcal{J}|^2\int_0^{k_F}k\sin(kR)dk\int_{k_F}^{k_m}k'\sin(k'R)[E_{n'}(k')-E_n(k)]^{-1}dk'. \tag{3}$$

Numerical integration of Eq. (3) shows that for Cu having a free-electron Fermi energy of 7.04 eV,

$$I(E_m,R_{nn})-I(\infty,R_{nn})=0.52I(\infty,R_{nn})$$

for $E_m=23$ eV and R_{nn} equal to the NN distance. Unlike the analytical expressions for the RKKY result, many previous calculations of the indirect interaction have ignored higher bands and therefore those results may have been more indicative of the cutoff chosen than of the quantity being calculated. The approach that we shall adopt is to show that the contribution to the indirect exchange from higher bands tends to the free-electron band contributions, so that these can be summed analytically.

The numerical method described above can be easily tested by application of it to a free-electron band structure and comparison of the results with the analytical expressions first derived by Ruderman and Kittel.[1] A direct comparison was achieved by inclusion of only energies up to 23 eV in our numerical program and comparison of the result to $I(E_m,R)$ from Eq. (3) with $E_m=23$ eV. Figure 1 shows that the agreement achieved is very good out to at least the tenth-nearest neighbors. The value of $|\mathcal{J}|^2$ used for Fig. 1 is for the case described below of nuclear moments in Cu. Separate confirmation of convergence was obtained by varying the mesh size.

Having tested the accuracy of our method, we investigated the effect of a nonspherical Fermi surface, by constructing an artificial band structure yielding a cubic Fermi surface with rounded corners in the ⟨111⟩ directions. The calculated indirect interaction showed very strong anisotropy and decayed very slowly in the ⟨100⟩ directions. This result is in agreement with the results of Ref. 3.

Recent interest in low-temperature ordering of nuclear moments in Cu,[1] along with experimental data from which the indirect-exchange interaction can be deduced,[14] make Cu an interesting example for the application of the present method. The band structure of Cu was calculated by use of atomic d state and orthogonalized plane-wave (OPW) basis states.[15] This band-structure method has been found to reproduce well the band structure, momentum density, and Compton-profile anisotropy of Cu, as determined by experiment or first-principles calculations. The isotropic indirect-exchange interaction between Cu nuclei is a result of the Fermi contact interaction between the s-like band electrons and the nuclear spins. The expression for the matrix element in Eq. (1) in this case is

$$|\mathcal{J}_{nn'}(\mathbf{k},\mathbf{k}')|^2 = \Omega^2(8\pi g g_N\beta\beta_N/3)^2|\psi_{n\mathbf{k}}(0)|^2|\psi_{n'\mathbf{k}'}(0)|^2, \tag{4}$$

where g and g_N are the electron and isotope-averaged

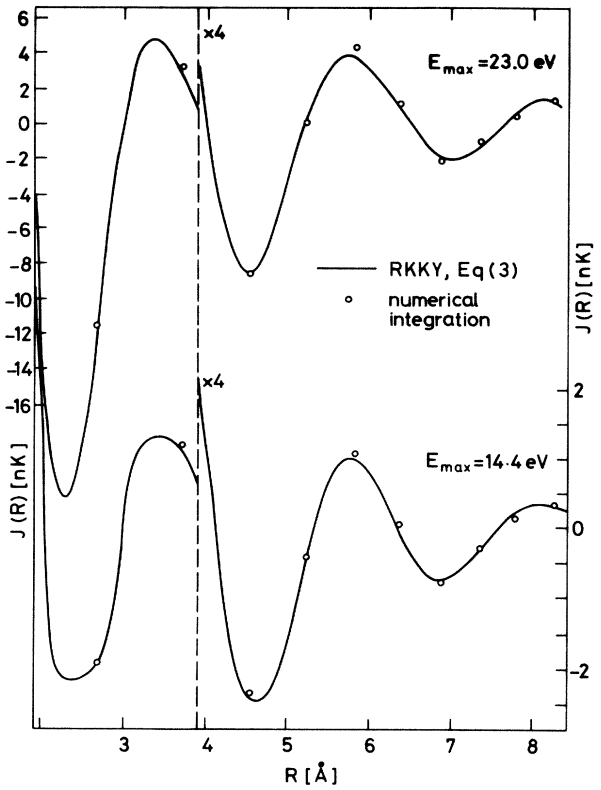

FIG. 1. Indirect-exchange interaction constant $J(\mathbf{R})$ as a function of the inter-moment separation R for the free-electron band structure of Cu, obtained by inclusion of bands up to an energy $E_{max}=E_m$ as indicated. There is excellent agreement between the results of the numerical integration (circles) and the RKKY result for each energy range.

nuclear g values, β and β_N are the Bohr and nuclear magnetons, and $|\psi_{n\mathbf{k}}(0)|^2$ is the electron number density at the nucleus for electrons in band n with wave vector $\mathbf{k}$. Since the d-orbital component of the wave function does not contribute to the Fermi contact term, we have

$$|\psi_{n\mathbf{k}}(0)|^2=|c_{n\mathbf{k}}|^2|\psi_{\mathrm{OPW}}(0)|^2,$$

where $|c_{n\mathbf{k}}|^2$ is the fraction of OPW content in the wave function with wave vector $\mathbf{k}$. The value of the OPW contribution $|\psi_{\mathrm{OPW}}(0)|^2$ was obtained from the experimental value of the Knight shift for Cu as follows. The average of the contact-term part of band-state wave function over the Fermi surface is

$$\langle|\psi(0)|^2\rangle_{E_F}=\langle|c_{n\mathbf{k}}|^2\rangle_{E_F}|\psi_{\mathrm{OPW}}(0)|^2,$$

and a value of $\langle|c_{n\mathbf{k}}|^2\rangle_{E_F}=0.75$ was found for our band structure. With use of

$$\langle|\psi(0)|^2\rangle_{E_F}=3(\Delta H/H)/8\pi M\chi_s,$$

where, for ^{63}Cu, the atomic mass $M=63$, the Knight shift[16] $\Delta H/H=2.32\times10^{-3}$, and the electron-spin susceptibility[17] $\chi_s=1.08\times10^{-7}$ emu/g, one obtains

TABLE I. The indirect-exchange interaction constants $J(\mathbf{R})$ for the nth-nearest neighbors in Cu. The standard free-electron RKKY result is compared with our result obtained from a realistic band structure for Cu.

Neighbor n		$J(\mathbf{R})$ (nK)	
n	Direction	RKKY	This Work
1	$(\frac{1}{2},\frac{1}{2},0)$	−8.20	−22.60
2	(1,0,0)	+3.65	+10.87
3	$(1,\frac{1}{2},\frac{1}{2})$	−2.03	−3.27
4	(1,1,0)	−0.26	+4.38
5	$(\frac{3}{2},\frac{1}{2},0)$	+1.04	+2.93
6	(1,1,1)	+0.17	−0.14
7	$(\frac{3}{2},1,\frac{1}{2})$	−0.58	−0.56
8	(2,0,0)	−0.34	−2.07
9	$(\frac{3}{2},\frac{3}{2},0)$	+0.19	+0.25
9	$(2,\frac{1}{2},\frac{1}{2})$	+0.19	+0.43
10	(2,1,0)	+0.37	+0.65

$\langle|\psi(0)|^2\rangle_{E_F}=2.44\times10^{-31}$ m^{-1} and therefore

$\langle|\psi_{\mathrm{OPW}}(0)|^2\rangle=3.24\times10^{-31}$ m^{-1}.

As remarked above, it is necessary to include bands up to a very high energy to obtain a result for $J(\mathbf{R})$ in Eq. (1) that has converged. We find that the contributions from bands above the ninth Cu band are very close to those from the corresponding free-electron bands. Therefore, we have obtained the final result by adding the analytical RKKY result for the infinite energy range to the difference, from our numerical calculations, between the contributions from the first nine realistic Cu bands and from the first nine free-electron Cu bands.

The values of the indirect-exchange interaction for the first ten nearest neighbors in Cu are given in Table I and compared with the free-electron RKKY values which were obtained from Eq. (3) with $E_m=\infty$ after inclusion of the matrix element contribution from Eq. (4). The value of $|\psi_{n\mathbf{k}}(0)|^2$ for the free-electron bands was also obtained by comparison with the Knight shift for Cu.

The results obtained for $J(\mathbf{R})$ can be compared with experiment by use of the dimensionless quantity $R=\sum_i J(\mathbf{R}_i)/\mu_0(g_N\beta_N)^2\rho$ which has been determined from low-temperature nuclear magnetic resonance measurements[14] on Cu where ρ is the atomic number density. The advantage of the use of the quantity R is that it depends only on the indirect exchange interaction and not the direct interaction between the nuclear spins. The values of the individual values of the $J(\mathbf{R}_i)$ have not been determined from experiment but R is a sensitive test because it depends on the differences between the large positive and negative values of the $J(\mathbf{R}_i)$ for the different neighbors. A previous theoretical value[9] of R for Cu, which was obtained by summation of over eight nearest neighbors and only the lowest energy bands, was $R=-0.34$. We obtain $R=-0.43$ for eight nearest neighbors and all energies compared with the experimen-

tal value[14] of -0.42 ± 0.05. The corresponding RKKY value is $R = -0.28$. Since the indirect exchange is oscillatory and falls off with distance, and since eight nearest neighbors completes the second cycle of oscillation, we expect that our value would remain within the experimental error of the experimental result if all NN interactions were included. The agreement with experiment is very satisfactory but the inclusion of more NN shells and the effect of improved band-structure models needs to be investigated. It may also be important to consider the effect of many-electron interactions both on the magnitude of $J(\mathbf{R})$ as calculated in its dependence on $|\psi_{n\mathbf{k}}(0)|^2$ and on the mechanism of the interaction itself[18] as expressed in Eq. (1). For each of the values quoted above, the normalization via the Knight shift may have compensated for the former effect.

We have shown that it is possible to calculate the indirect-exchange interaction for real band structures. Since the technique reproduces the analytical result for free-electron bands with high precision, the results for other band structures can be accepted with confidence. One important result is that $J(\mathbf{R})$ is dependent on the direction as well as the magnitude of the intermoment distance $\mathbf{R}$ with the possibility of enhancement of the interaction in certain directions. As Table I demonstrates for Cu, the consequences of the real band structure in metals will include changes in the relative magnitudes of the interactions as well as the overall magnitude of the interaction for all neighbors. It has been shown here that the overall magnitude calculated from the real band structure for Cu is in better agreement with experiment than the RKKY result. The values of $J(\mathbf{R})$ found herein partially determine the ordering temperature and the arrangement of the nuclear spins in Cu. The increased overall magnitude of the effect might be expected to lead to a higher ordering temperature but the ground-state properties are sensitive functions of the space dependence of the interaction[19] which we find to be significantly different from the RKKY result used in the past to predict the ordering temperature and ground-state configurations.

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