Indirect-exchange interaction between localized moments in semiconductors

Steven J. Frisken and D. J. Miller
School of Physics, University of New South Wales, P.O. Box 1, Kensington, New South Wales, Australia 2033
(Received 2 January 1986)

A numerical technique is described for calculating the indirect-exchange interaction in semiconductors. Calculations have been performed for localized moments in a narrow-band-gap semiconductor and the results show that the indirect interaction alternates in magnitude as the distance between magnetic moments is increased. It is suggested that the formation of a spin-glass phase in diluted magnetic semiconductors may not be due to the frustration mechanism alone.

I. INTRODUCTION

In a wide range of materials which contain localized moments, the indirect-exchange interaction between the moments is much more significant than the direct-exchange interaction between them. In the case of metals, the indirect interaction is mediated by the electrons in the partially filled conduction bands and is known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[1] In the case of nonmetals, the main contributions to the interaction involve a virtual transition across the band gap between the filled and empty bands. Examples in nonmetals include the exchange interaction of the nuclear spins in insulators[2] and of the localized moments of the $4f$ shell electrons in magnetic semiconductors such as EuTe.[3] Interest in the indirect-exchange interaction in semiconductors has been stimulated recently by reports of magnetic ordering and spin-glass phenomena in a new class of semiconductors, for example $Hg_{1-x}Mn_xTe$, which have been called diluted magnetic semiconductors,[4] or semimagnetic semiconductors.[5] Since the indirect exchange between the Mn ions has been taken to be antiferromagnetic at all separations between the ions,[4] it has been concluded that the formation of a spin glass in the semimagnetic semiconductors is due to the frustration mechanism. In metals, the indirect interaction alternates in sign with increasing distance between the localized moments and the alternation in sign can itself lead to the formation of a spin glass. Therefore it is necessary to examine carefully whether the indirect-exchange interaction in semimagnetic semiconductors must indeed be negative for all spin separations, with the consequence that the frustration mechanism alone must determine the spin orientations. The purpose of the present work is to describe an improved calculation of the indirect-exchange interaction in semiconductors to provide information about these and other questions.

The calculation of the indirect exchange in both nonmetals and metals is difficult, and in previous work a number of approximations which have significant effects have been made. In probable decreasing order of importance, the approximations have usually included the replacement of the real Brillouin zone by a spherical one, the use of unrealistic energy bands, and the neglect of matrix element terms which occur in the expression for the interaction. For example, Bloembergen and Rowland[2] calculated the indirect exchange between nuclei in an insulator using a spherical Brillouin zone, a flat valence band, and a parabolic conduction band. Although results were obtained in this approximation, it was later pointed out that had the correct, nonspherical Brillouin zone been used in the calculation, the result would have been identically zero for the case of interest, namely moments occupying the lattice sites.[6] This shows that the approximations required to obtain results for the indirect-exchange interaction in analytical form can lead to incorrect results. Other analytical calculations of the indirect-exchange interaction in semiconductors have involved the neglect of matrix elements and the use of parabolic bands and either a spherical or an infinite Brillouin zone.[2,7–10] Lewiner and Bastard have calculated the indirect exchange for $Hg_{1-x}Mn_xTe$ using a Kane model of the band structure in the parabolic and extreme nonparabolic limits.[9,10] They included the relevant matrix elements in their calculations but assumed an infinite Brillouin zone with cutoff factors to obtain convergence for the interaction.

In all the above approaches, the models of the semiconductors were constructed so that the indirect-exchange interaction could be obtained in analytical form. A different approach would be to use the correct Brillouin zone and a realistic band structure and use a numerical technique to calculate the exchange interaction. The ultimate need for a numerical approach was pointed out previously.[7] We show below that it is possible to perform the integrations that are required in the calculation numerically using the linear tetrahedron method.[11–13] The results are quite different from previous analytical approximations.

In the next section we briefly outline the theory of the interaction and develop the numerical method used to evaluate the theoretical expressions. In the Results section, we apply the method to a model case similar to that first considered by Bloembergen and Rowland.[2] Firstly, it is shown that the numerical results are in good agreement with the analytical results for a spherical Brillouin zone. Secondly, it is shown that the numerical technique gives the correct zero result for a real Brillouin zone. Finally, we calculate the indirect exchange for the model band structure proposed by Lewiner and Bastard.[10]

II. THEORY

In the absence of spin-orbit coupling and using second-order perturbation theory, the indirect-exchange interaction between localized moments is given by a Heisenberg-type interaction,

$$H=\sum_{\substack{i>j\\ i,j}} J(\mathbf{R}_i-\mathbf{R}_j)\mathbf{S}_i\cdot\mathbf{S}_j\ , \tag{1}$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spin operators of the localized moments located at $\mathbf{R}_i$ and $\mathbf{R}_j$, respectively. The interaction $J(\mathbf{R}_i-\mathbf{R}_j)$ can be written

$$J(\mathbf{R}_i-\mathbf{R}_j)=\frac{2}{\Omega^2}\sum_{\mathbf{k},\mathbf{k}'}\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_i-\mathbf{R}_j)]}{E_n(\mathbf{k})-E_{n'}(\mathbf{k}')}\times|j(\mathbf{k},\mathbf{k}')|^2\ , \tag{2}$$

where Ω is the volume of the crystal, $\mathbf{k}$ ($\mathbf{k}'$) is the wave vector of states in the n (n')th conduction (valence) band and $E_n(\mathbf{k})$ [$E_{n'}(\mathbf{k}')$] is the corresponding energy. The summation over $\mathbf{k}$ and $\mathbf{k}'$ extends over the entire zone for each band. The above expression represents the interband contribution to the indirect-exchange interaction, and it is assumed that the valence-band states are all full and the conduction-band states are all empty. In the absence of spin-orbit coupling in the band states, the matrix element is given by

$$|j(\mathbf{k},\mathbf{k}')|^2=\Omega^2|\langle\phi_{n'}(\mathbf{k}')|j(\mathbf{r})|\phi_n(\mathbf{k})\rangle|^2\ , \tag{3}$$

where $\phi_{n'}(\mathbf{k}')$ and $\phi_n(\mathbf{k})$ are the normalized valence- and conduction-band wave functions and $j(\mathbf{r})$ is the exchange interaction between a localized moment and a band electron at a distance $\mathbf{r}$ from it. A summation over the twofold spin degeneracy of each band state has already been made to obtain the above form.

If the bands are modified by a spin-orbit interaction, the band states still have twofold Kramer's degeneracy but each state is composed of admixtures of both electron-spin orientations. Therefore the band states can be written

$$|\phi_n^\sigma(\mathbf{k})\rangle=|\phi_{n,+}^\sigma(\mathbf{k})\rangle|\tfrac{1}{2}\rangle+|\phi_{n,-}^\sigma(\mathbf{k})\rangle|-\tfrac{1}{2}\rangle\ ,$$

where $\pm\frac{1}{2}$ refers to the m_s value of the components of wave function and $\sigma=\pm1$ identifies the two states of the Kramer's doublet. With the inclusion of spin-orbit coupling, the quantity in Eq. (3) is therefore a dyadic and the exchange interaction is anisotropic. If only the isotropic part is retained, the above formalism is preserved with the matrix element given by

$$|\langle j(\mathbf{k},\mathbf{k}')\rangle|^2=\Omega^2\sum_{\sigma,\sigma'=\pm1}|\langle\phi_{n'}^{\sigma'}(\mathbf{k}')|j(\mathbf{r})s_z|\phi_n^\sigma(\mathbf{k})\rangle|^2\ ,$$

where s_z operates on the m_s values of the components of the wave function.

We have used a modification of the linear tetrahedron method to evaluate the summation of Eq. (2). In the method, the Brillouin zone, or an irreducible wedge of the zone if appropriate, is divided up into tetrahedra and the variable of integration is linearly interpolated throughout each tetrahedron. The method is most advantageous when analytical expressions can be obtained for the integral of the function of the linearized variable. In that case, the value of the integral can be obtained in terms of the values of the function at the vertices of the tetrahedra. The advantage of using tetrahedra is that an integral number fills the irreducible wedge of the Brillouin zone. The method was first applied to the calculation of the density of states and related functions[11,12] and later extended to the calculation of magnetic susceptibility.[13]

To proceed with this method in the present application, Eq. (2) is rewritten as a double summation over tetrahedra t and t', in the irreducible wedge of the first Brillouin zone, of a double integration in each pair of tetrahedra:

$$J(\mathbf{R})=(2\pi)^{-6}\sum_t\sum_{t'}\int_t d^3\mathbf{k}\int_{t'}d^3k'\,g(\mathbf{k},\mathbf{k}',\mathbf{R})f(\mathbf{k},\mathbf{k}')\times|j(\mathbf{k},\mathbf{k}')|^2\ , \tag{4}$$

where

$$g(\mathbf{k},\mathbf{k}',\mathbf{R})=48^2\cos k_xR_x\cos k_yR_y\cos k_zR_z\cos k_x'R_x\times\cos k_y'R_y\cos k_z'R_z$$

and $f(\mathbf{k},\mathbf{k}')=[E_n(\mathbf{k})-E_{n'}(\mathbf{k}')]^{-1}$ and R_x,R_y,R_z are the Cartesian components of $\mathbf{R}=\mathbf{R}_i-\mathbf{R}_j$ which has been taken to be in the ΓL direction. There are two difficulties in applying the tetrahedron method to Eq. (4). Firstly, a double summation is required and , secondly, the function to be summed is a product of three factors, one of which is rapidly varying and should be dealt with as accurately as possible. It was decided to treat the three terms separately, that is, replace within any one tetrahedron the integral of the product of the three terms, by the product of the integral of each term separately. The advantage of doing this is that the integrals within tetrahedra of the rapidly varying exponential term and of the energy denominator can then be performed analytically.

The integration of $g(\mathbf{k},\mathbf{k}',\mathbf{R})$ in each tetrahedron is readily obtained using the result

$$\int_t\cos(u)du=-6v\sum_{i=1}^4\sin(u_i)\left[\prod_{\substack{j=1\\ j\neq i}}^4(u_i-u_j)\right]^{-1}\ ,$$

where v is the volume of the tetrahedron t and the u_i are the values at the vertices of the tetrahedron of any quantity, u, which is linear within the tetrahedron.

The result of the integration of $f(\mathbf{k},\mathbf{k}')$ in Eq. (4) in one tetrahedron is given by Rath and Freeman.[13] The energy $E(\mathbf{k}')$ could be linearly interpolated in tetrahedron t' and integrated, but it is shown below that sufficient accuracy is achieved by approximating the second integration by the average of the values of the first integration at the vertices of tetrahedron t'.

The integral of the matrix element term in Eq. (4) was taken as the average of the values at the vertices of the tetrahedron t for each t'. The results which follow were obtained using the above results for 107 tetrahedra in the irreducible wedge of Brillouin zone.

III. RESULTS

In order to test the accuracy of the above scheme it was applied to a model for which exact results can be obtained analytically if matrix elements are taken to be constant: $j(\mathbf{k},\mathbf{k}')=\alpha$. In the model, one band was taken to be flat, $E_n(\mathbf{k})=E_{\text{gap}}$, and the other to be parabolic, $E_{n'}(\mathbf{k}')=\hbar^2(k')^2/2m^*$, where $\hbar$ is Planck's constant h divided by 2π and m^* is the effective mass. There are two ways of using the model to test the numerical scheme. Firstly, for a real Brillouin zone, the strength of the exchange interaction given by Eq. (2) is zero when the localized moments are separated by lattice vectors. Secondly, for a spherical zone, the results for the model can be obtained analytically for all intermoment spacings and compared with the numerical results.

The results for the numerical calculation were obtained for a cubic crystal with a cubic unit cell dimension of 0.3 nm, for localized moment separations R in the ΓL direction and for an effective mass of 5 times the free electron mass, m_e. In the following, R is expressed in multiples of 0.52 nm, the nearest-neighbor distance in the ΓL direction. Firstly, the results in Fig. 1 show that for the real Brillouin zone, the result is indeed zero for localized moments separated by multiples of the lattice vectors, that is, for $R=1$, 2, or 3. The latter value corresponds to over 7 times the nearest-neighbor distance. Figure 1 also shows that the correct result is obtained for different values of the band gap, E_{gap}. Secondly, the results in Fig. 2 show excellent agreement between the numerical results and the analytical results for a spherical Brillouin zone with radius $k_m=\pi/\sqrt{3}$ which is the radius of a sphere inscribed in the first Brillouin zone in the above case. The analytical result for the matrix element independent quantity, $I(\mathbf{R})=J(\mathbf{R})/\alpha^2$, is obtained from

$$I(\mathbf{R})=-(2\pi)^{-6}\int d^3\mathbf{k}\int d^3\mathbf{k}'\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}]}{\hbar^2(k')^2/2m^*}$$

$$=\frac{2m^*}{\pi^2R^3h^2}\left[k_m\cos(Rk_m)-\frac{\sin Rk_m}{R}\right]\text{Si}(Rk_m)\ ,$$

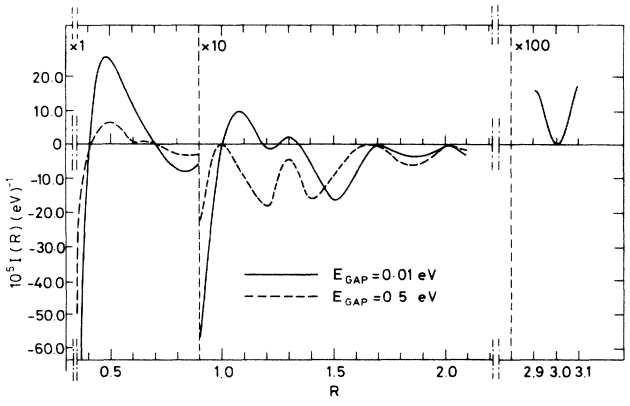

FIG. 1. Indirect-exchange interaction between localized moments as a function of moment separation for the case of a flat valence band and a quadratic conduction band. The prediction of the zeros at integral values of R is observed for two different values of the energy gap.

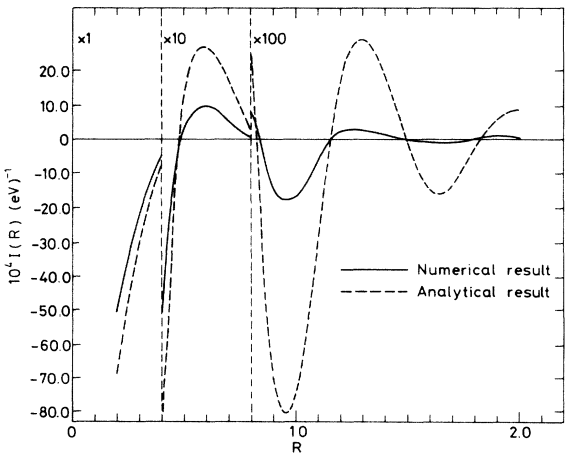

FIG. 2. Numerical and analytical results for the indirect-exchange integral, calculated using a spherical Brillouin zone of radius $k_m=\pi/\sqrt{3}$.

where $\text{Si}(x)=\int_0^x[\sin(t)/t]dt$ and the integrals are performed within spheres of radii k_m. The numerical results were obtained by taking the contribution from a tetrahedron through which the Fermi surface passed to be equal to the contribution of that tetrahedron times the fraction of the volume of the tetrahedron that was occupied. Because this calculation was performed only as a check on the method, it seemed unnecessary to divide the occupied volume up into several smaller tetrahedra to obtain a more accurate result for the contribution from the partially occupied tetrahedra. Thus the results of the numerical method for the full zone in Fig. 1, and in the following, should be more accurate than the numerical results in Fig. 2 for the spherical zone.

Since the numerical scheme gives correct results for the above example, it can be applied with confidence to cases for which it is not possible to obtain an analytical result without making approximations. A recent example of importance is the calculation of the indirect interaction in $Hg_{1-x}Mn_xTe$ for a composition x corresponding to zero band gap. An analytical result was obtained after the Brillouin zone was assumed to be spherical and infinite.[10] The contribution to $J(\mathbf{R})$ from virtual transitions between the conduction band and the heavy-hole valence band is given[10] in terms of a function $\varphi(\delta)$:

$$J(R)=-(m_v\beta^2/96\pi^2\hbar^2R^4)\varphi(\delta)\ ,$$

where β is a matrix element involving the components of the band wave function, m_v is the effective mass in the parabolic valence band, and $\delta=R/1.13$ (for R in Å). The function $\varphi(\delta)$ from Ref. 10 is shown in Fig. 3. For comparison, we also show the values of $\varphi(\delta)$ which we have extracted from our calculation of $J(\mathbf{R})$ for exactly the same model, namely $E_n(\mathbf{k})=-\hbar^2k^2/2m_v$ with $m_v=0.5m_e$ and $E_{n'}(\mathbf{k}')=\hbar k'(2E_p/3m_e)^{1/2}$ where $E_p=18$ eV. The matrix elements in Eq. (4) were calculated using the wave functions given in Ref. 10 and the results are for $\mathbf{R}$ in the ΓL direction. For the analytical result,[10] the direction of $\mathbf{R}$ is immaterial because the solution is spherically symmetric.

It is clear from Fig. 3 that the analytical and numerical

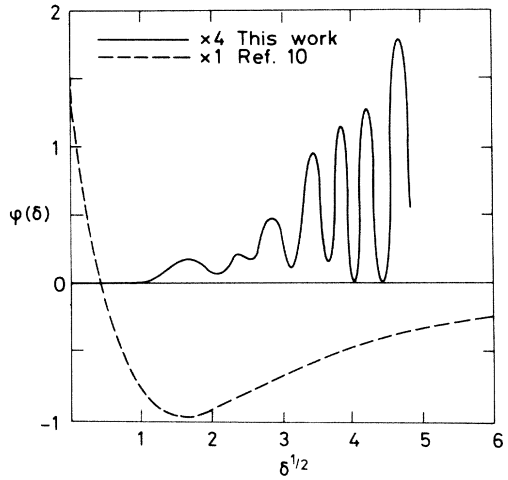

FIG. 3. Comparison of the numerical calculation of the indirect-exchange interaction, employing a real Brillouin zone, with analytical results obtained using an infinite Brillouin zone (Ref. 10).

results for $\varphi(\delta)$ and hence $J(\mathbf{R})$ differ in three respects. The numerical result is oscillatory, has a different sign and a different dependence on localized moment separation R than the analytical result. In view of the excellent agreement between the numerical method and an exact analytical result shown in Figs. 1 and 2, we would suggest that the differences shown in Fig. 3 are a result of the approximations used to obtain the analytical result in the latter case.

IV. CONCLUSION

The most important conclusion to be drawn from the numerical results is that the indirect-exchange interaction is oscillatory and not a monotonic decreasing function of distance between spins for spins separated by multiples of the lattice constant. It has been argued[10] that oscillations in the indirect interaction predicted previously[2,3] were mostly unphysical and a result of the use of a spherical Brillouin zone with a finite radius. The present work shows that oscillations are characteristic of the interaction even when the correct Brillouin zone is used. Indeed, one would expect the indirect-exchange interaction to oscillate because in the case of a flat conduction band, a quadratic valence band, and constant matrix elements, the interaction must go to zero when the localized moments are separated by lattice vectors. While it is not unreasonable that the inclusion of matrix elements and dispersion of the conduction band would change the details of the interaction, it seems unlikely that the oscillations of the former case would be removed altogether in the latter one.

Figure 3 illustrates the difference between the numerical and analytical results for the same model band structure. It may be that neither result indicates the correct variation of the exchange interaction involving the upper valence band and lower conduction band in $Hg_{1-x}Mn_xTe$. This is because the band structure has an important influence on $J(\mathbf{R})$ but the bands used in both calculations do not correspond closely to the real bands of $Hg_{1-x}Mn_xTe$. Apart from the idealized dispersion of the bands, the separation of the bands at the edge of the zone L is 19.7 eV compared with an expected value of less than 3 eV. Since the difference in the band energies appears in the denominator of Eq. (2), this distortion has the effect of overemphasizing the relative contribution to $J(\mathbf{R})$ of the part of the Brillouin zone near Γ. Because this part of the zone corresponds to small $\mathbf{k}$, it makes a ferromagnetic contribution to the overall interaction. Therefore the numerical results are likely to be more antiferromagnetic for the real band structure than for the model band structure. Thus the oscillations shown in Fig. 3 for the numerical results would probably involve changes in sign as well as changes in magnitude for the real case, similar to the results in Fig. 1 where the bands were separated by 4.2 eV or less. On the other hand, the analytical results in Fig. 3 may give an antiferromagnetic result because the assumption of an infinite Brillouin zone overemphasizes the contribution from large $\mathbf{k}$ values, compensating for the error due to the model band structure. In view of these comments, we have made no attempt to estimate a Curie-Weiss temperature from our results for the model band structure. There is an obvious need for calculations based on real bands and wave functions. The advantage of the numerical scheme is that these extensions can be readily incorporated, and it is expected that future work will include a detailed investigation of semiconductors using realistic bands for the first time.

From the above results, the indirect-exchange interaction in semiconductors may well alternate in sign as the distance between the localized moments is increased, as in the case of localized moments in metals. Therefore the spin-glass phase observed in dilute magnetic semiconductors[14] may not be a result of the frustration mechanism[15] in the fcc lattice alone, but may also involve an alternation in sign of the exchange interaction which is the basis for the spin-glass phase in metals.

ACKNOWLEDGMENTS

This work was supported by the Australian Research Grants Scheme.

[1]C. Kittel, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968) Vol. 22, p. 1.

[2]N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

[3]S. Lara, R. Moreira Xavier, and C. A. Taft, J. Phys. Chem. Solids **39**, 247 (1978).

[4]J. K. Furdyna, J. Appl. Phys. **53**, 7637 (1982).

[5]R. R. Galazka, in *Proceedings of the 14th International Conference on the Physics of Semiconductors,* edited by B. L. H. Wil-

son (IOP, London, 1973), p. 133.
[6]R. Sokel and W. A. Harrison, Phys. Rev. Lett. **36**, 61 (1976).
[7]J. Ginter, J. Kossut, and L. Swierkowski, Phys. Status Solidi B **96**, 735 (1979).
[8]V. Lee and L. Liu, Phys. Rev. B **29**, 2125 (1984).
[9]G. Bastard and C. Lewiner, Phys. Rev. B **20**, 4256 (1979).
[10]C. Lewiner and G. Bastard, J. Phys. C **13**, 2347 (1980).
[11]G. Lehmann and M. Taut, Phys. Status Solidi B **54**, 469 (1972).
[12]O. Jepson and O. K. Anderson, Solid State Commun. **9**, 1763 (1971).
[13]J. Rath and A. J. Freeman, Phys. Rev. B **11**, 2109 (1975).
[14]S. Nagata, R. R. Galazka, D. P. Mullin, H. Akbarzadeh, G. D. Khattak, J. K. Furdyna, and P. H. Keesom, Phys. Rev. B **22**, 3331 (1980).
[15]L. de Seze, J. Phys. C **10**, L353 (1977).