Indirect exchange interaction in lead salts

L. Liu* and G. Bastard
Groupe de Physique des Solides de l'Ecole Normale Supérieure,†
24 rue Lhomond, 75231 Paris Cedex 05, France
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The indirect exchange interaction between magnetic ions embedded in a lead salt host lattice, mediated by the spin-dependent polarization effects, is theoretically studied. It is found that the interaction is ferromagnetic in sign and greatly enhanced in strength because of the multivalley band structure of the host material. The interaction decays exponentially with the interspin distance, and the decay constant is determined by the energy gap and the effective masses of the electron and the hole. A recent experiment in $Pb_{1-x}Mn_xTe$ is also briefly discussed.

Recently there has been some interest in the interaction between magnetic ions dilutely embedded in a nonmagnetic semiconductor host. In such a system, the magnetic interaction mediated by the spin-dependent polarization of the valence-band electrons may become important with a proper set of band parameters. This so called indirect exchange interaction has been theoretically studied by several authors.[1–5] For a finite-gap semiconductor with isotropic energy bands, the interaction was found to decay exponentially with the interspin distance like $e^{-\lambda R}$. The decay constant λ is determined by the energy gap and the effective masses of the electron and the hole. For narrow-gap semiconductors with small electron and hole masses, the interaction range can be relatively long, extending over several lattice spacings. For zero-gap semiconductors[3,5] like $Hg_{1-x}Mn_xTe$, the interaction drops off like $R^{-\nu}$ with $5 \geq \nu \geq 4$. Since the spin-dependent polarization process in a semiconductor involves interband electron-hole excitations, one may expect that the indirect exchange interaction should be greatly enhanced in a semiconductor host with a multivalley band structure which provides for more electron-hole excitation channels. The family of lead salts like PbTe, in addition to having a narrow energy gap and small electron and hole effective masses, has precisely such a multielectron valley and multi-hole-valley structure, and hence should show strong polarization effects. We thus decided to make a model calculation of the indirect exchange interaction in lead salts with a band structure similar to that of PbTe in this paper. Apart from the complications arising from the anisotropy of the energy bands, the calculation is very similar to that of Ref. 5. The interaction is shown to be ferromagnetic and decay exponentially with the interspin distance. We shall also give a brief discussion on the recent susceptibility data in $Pb_{1-x}Mn_xTe$ obtained by Andrianov *et al.*[6]

The semiconductor PbTe crystallizes in the NaCl structure. Both the conduction- and the valence-band edges occur at the L point of the Brillouin zone. In the immediate vicinity of the L points, the energy bands are described by

$$E_c^{\mu} = E_g + \tfrac{1}{2}\hbar^2\left(\frac{(k_x^{\mu})^2+(k_y^{\mu})^2}{m_{et}} + \frac{(k_z^{\mu})^2}{m_{el}}\right),$$
$$E_v^{\mu} = -\tfrac{1}{2}\hbar^2\left(\frac{(k_x^{\mu})^2+(k_y^{\mu})^2}{m_{ht}} + \frac{(k_z^{\mu})^2}{m_{hl}}\right), \tag{1}$$

where the energy is measured from the top of the valence band, and the wave vector from the μth L point (L_μ, $\mu = 1,2,3,4$). The z direction is chosen to be along the Γ-L_μ axis.

If we neglect the spin-orbit coupling, the indirect exchange interaction between two spins $\vec{S}_i$ and $\vec{S}_j$ localized at the magnetic ion sites is of the Heisenberg type[3,5]:

$$H = -H_{ij}\vec{S}_i\cdot\vec{S}_j\,, \tag{2}$$

and

$$H_{ij} = \tfrac{1}{2}\sum_{nn'\vec{k}\vec{k}'}(f_{n\vec{k}} - f_{n'\vec{k}'}) \times \frac{|J(n\vec{k},n'\vec{k}')|^2\exp[i(\vec{k}-\vec{k}')\cdot\vec{R}]}{E_{n'}(\vec{k}') - E_n(\vec{k})}\,, \tag{3}$$

where $f_{n\vec{k}}$ is the Fermi distribution function for the $\vec{k}$ state in the nth band, and $\vec{R}$ is the lattice vector joining $\vec{S}_i$ and $\vec{S}_j$. The exchange integral J, as usual, involves the localized magnetic orbitals and the Bloch orbitals.[5] In this calculation J is taken to be a constant. The summation over $\vec{k}$ and $\vec{k}'$ is confined within the first Brillouin zone.

To calculate H_{ij} in Eq. (3), we assume two bands, a conduction band which is completely empty and a valence band which is fully occupied at $T=0$. We break the $\vec{k}$ summation over the Brillouin zone into that over different electron and hole valleys. As we shall neglect the band nonparabolicity, we simply use

Eq. (1) for the energy denominator. We further extend the integration limit for each valley to infinity. Due to the nature of the integrand, the dominating contribution comes only from a small region centered at the band-edge point.[7] The final result is given by

$$H_{ij}=\sum_{\mu,\nu} H_{ij}^{\mu\nu}\cos(\vec{k}_0^{\mu}-\vec{k}_0^{\nu})\cdot\vec{R}\ , \tag{4}$$

with

$$H_{ij}^{\mu\nu}=\frac{\Omega^2 J_{\mu\nu}^2 (m_{et}^2 m_{ht}^2 m_{el} m_{hl})^{1/2} E_g^2}{\pi^3\hbar^6\lambda^2 r_{\mu\nu}^2} K_2(\lambda r_{\mu\nu}) \tag{5}$$

and

$$\lambda^2 r_{\mu\nu}^2 \equiv \frac{2E_g}{\hbar^2}[m_{hl}(R_z^{\mu})^2+m_{el}(R_z^{\nu})^2 + m_{ht}(R_\rho^{\mu})^2+m_{et}(R_\rho^{\nu})^2]\ . \tag{6}$$

In Eq. (4) the summation μ runs over the four hole valleys and the summation ν over the four electron valleys. The wave vectors $\vec{k}_0^{\mu}$ and $\vec{k}_0^{\nu}$ specify the position of the valence- and the conduction-band edges, respectively. The crystal volume Ω appears in Eq. (5) as $J_{\mu\nu}$, the exchange integral between the μth and the νth valley, is to be evaluated with the Bloch wave functions normalized to unity over the whole crystal. The function K_2 is the modified Bessel function of the second order.[8] In Eq. (6), where $\lambda^2 r_{\mu\nu}^2$ is defined, R_z^{μ} denotes the projection of $\vec{R}$ onto the $\Gamma-L_{\mu}$ axis, and R_ρ^{μ} its projection on the plane perpendicular to this axis.

For PbTe, $\vec{k}_0^{\mu}-\vec{k}_0^{\nu}$, the vector connecting two L points, is always a reciprocal-lattice vector. Therefore contributions from electron-hole excitations involving different pairs of valleys always add to each other and the resulting positive sign of H_{ij} in Eq. (4) corresponds to a ferromagnetic interaction. This would not be the case if the band extrema were occurring, say, inside the Brillouin zone. Then H_{ij} would contain an oscillating factor and thus undergo sign reversals.

Using the asymptotic expansion for $K_2(z)$,[8] we obtain the following behavior for $H_{ij}^{\mu\nu}$ at large and at small interspin separations:

$$H_{ij}^{\mu\nu}\simeq\frac{\Omega^2 J_{\mu\nu}^2 E_g^2}{\pi^3\hbar^6}\left(\frac{\pi m_{et}^2 m_{ht}^2 m_{el} m_{hl}}{2\lambda r_{\mu\nu}}\right)^{1/2}\frac{e^{-\lambda r_{\mu\nu}}}{\lambda^2 r_{\mu\nu}^2}\ , \quad \lambda r_{\mu\nu}\gg 1$$

$$H_{ij}^{\mu\nu}\simeq\frac{2\Omega^2 J_{\mu\nu}^2 E_g^2 (m_{et}^2 m_{ht}^2 m_{el} m_{hl})^{1/2}}{\pi^3\hbar^6\lambda^4 r_{\mu\nu}^4}\ , \quad \lambda r_{\mu\nu}\ll 1\ . \tag{7}$$

We see that for small interspin distances, the magnetic interaction drops off like R^{-4}. For large distance, it decreases exponentially with a decay constant λ determined by Eq. (6). For small energy gap and effective masses, the range of the interaction, i.e., λ^{-1}, can be relatively long. The qualitative behavior corresponds exactly to what has been found for semiconductor hosts with isotropic bands.[3,5]

Our calculation was performed for an idealized case where the conduction band is completely empty. But usually PbTe is a degenerate n-type semiconductor with a Fermi wave vector $k_F \lesssim 3\times 10^6$ cm^{-1}. Due to this sharp cutoff in wave vectors, an extra oscillating factor will occur in $H_{ij}^{\mu\nu}$. However, this oscillation is not important with a wavelength of around 30 Å or more. We may also remark that at this carrier concentration, the intraband indirect exchange interaction, i.e., the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, is negligible as compared with the interband term discussed here.

Andrianov *et al.*[6] measured the magnetic susceptibility in $Pb_{1-x}Mn_xTe$ ($x\lesssim 6\%$) and found from the sign of the Curie-Weiss temperature θ that the interaction between Mn ions is antiferromagnetic. It seems then that although the magnetic ion concentration is low, the superexchange mechanism still dominates the ferromagnetic indirect exchange interaction. This is perhaps partly due to some clustering of magnetic ions in their samples. They also observed a nonmonotonic dependence of θ on the manganese concentration x such that its magnitude first increases, reaching a maximum of about 100 K at $x\simeq 0.6\%$ and then decreases to almost zero at $x\simeq 6\%$. This anomalous behavior may be a result of the competition between the superexchange and the indirect exchange, which, as mentioned, carry different signs. There are 12 secondary valence-band maxima along the Σ axis (i.e., [110]) in PbTe which are separated from the principal maxima by 0.3 eV in energy.[9] In addition, secondary conduction-band minima also exist along the Σ axis according to the calculated band structure.[9] It is then conceivable that the gap between the L and the Σ extrema will be narrowed with the addition of Mn ions. Then, a tremendous increase in the strength of the indirect exchange interaction is expected as many new channels are opening up for electron-hole excitations. The strong ferromagnetic indirect exchange will cancel the antiferromagnetic superexchange and gives rise to a nearly vanishing θ at $x\simeq 6\%$. Unfortunately, a quantitative confirmation of this interpretation cannot be made at this stage when there is a complete lack of knowledge as to how the band structure of PbTe is modified by the addition of Mn ions.

*Permanent address: Department of Physics and Astronomy, Northwestern University, Evanston, Ill. 60201.
†Laboratoire associé au Centre National de la Recherche Scientifique.

[1]N. Bloembergen and T. J. Rowland, Phys. Rev. 97, 1969 (1955).
[2]J. Ginter, J. Kossut, and L. Swierkowski, Phys. Status Solidi (b) 96, 735 (1979).
[3]G. Bastard and C. Lewiner, Phys. Rev. B 20, 4256 (1979); C. Lewiner and G. Bastard, J. Phys. C 13, 2347 (1980).
[4]A. A. Abrikosov, J. Low Temp. Phys. 39, 217 (1980).
[5]L. Liu, Solid State Commun. 35, 187 (1980); Phys. Rev. B (in press).
[6]D. G. Andrianov, N. M. Pavlov, A. S. Savelev, V. I. Fistul, and G. P. Tsiskarishvili, Fiz. Tekh. Poluprovodn. 14, 1202 (1980) [Sov. Phys. Semicond. 14, 711 (1980)].
[7]We may estimate the linear dimension of the region giving dominating contribution as equal to λ defined in Eq. (6).
[8]E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, Cambridge, 1952), p. 373.
[9]Y. W. Tung and M. L. Cohen, Phys. Rev. 180, 823 (1969).