Indirect exchange interaction between Mn$^{2+}$ ions in Pb$_{1-x}$Mn$_x$Te

Ven-Chung Lee

Department of Physics, National Taiwan University, Taipei, Taiwan 107, Republic of China

(Received 17 March 1986)

A phenomenological model is presented to provide an explanation of the nonmonotonic behavior of the paramagnetic Curie temperature of Pb$_{1-x}$Mn$_x$Te with concentration $x$. The band structure of PbTe is first calculated by the linear-combination-of-atomic-orbitals method and then used in a perturbative calculation of the indirect exchange interaction between manganese ions. For the case with interspin distance larger than the lattice constant, the indirect exchange is antiferromagnetic. We assume that in the case of small Mn$^{2+}$ concentration, the formation of clusters represents a preliminary state of precipitation in the matrix and clusters consisting of three or four Mn$^{2+}$ ions predominate. The nonmonotonic behavior of the Curie temperature may be explained with the assumption of a ferromagnetic interaction between nearest-neighbor Mn$^{2+}$ ions in the clusters.

I. INTRODUCTION

Recently there has been some interest in the interaction between magnetic ions dilutely embedded in a nonmagnetic semiconductor host. Magnetic susceptibility measurements of Pb$_{1-x}$Mn$_x$Te single crystal have shown that the Mn$^{2+}$ ions are coupled by an antiferromagnetic interaction.\(^1\) Experimental investigations of Hg$_{1-x}$Mn$_x$Te have evidenced a similar antiferromagnetic interaction between the Mn$^{2+}$ localized moments.\(^2\) At high temperature the magnetic susceptibility $\chi(T)$ of these two alloys were found to follow a Curie-Weiss law $[\chi^{-1}=a/(T+\Theta)]$ with the paramagnetic Curie-Weiss temperature $\Theta>0$. For Hg$_{1-x}$Mn$_x$Te the Curie-Weiss temperature $\Theta$ varies almost linearly with the Mn$^{2+}$ composition $x$. However, the dependence of $\Theta$ on $x$ for Pb$_{1-x}$Mn$_x$Te is a curve with a minimum such that its magnitude first increases almost linearly within $x \sim 0.4\%$, reaching a maximum of about 100 K at $x \sim 0.6\%$, and then decreases to almost zero at $x \sim 6\%$. These experimental results have shown the existence of a long-range antiferromagnetic exchange interaction in these crystals.

A magnetic ion embedded in a semiconductor matrix will spin polarize the Bloch electrons of the host lattice through the direct exchange interaction between them. The polarized Bloch electrons, in turn, mediate a spin interaction between two magnetic ions, the so-called indirect exchange interaction. This is, in fact, the semiconductor analogy of the well-known Ruderman-Kittel-Kasuya-Yosida\(^3\) (RKKY) interaction in metals. But while intraband processes are involved in polarizing conduction electrons in the RKKY interaction, the polarization process in a semiconductor involves interband electron-hole excitations which depend on the band structure of the host materials. The properties of the indirect exchange interaction have been studied in several model calculations.\(^4\)–\(^9\) However, most authors have assumed parabolic bands and a constant interband-exchange matrix element. These assumptions are valid only in the immediate vicinity of the band edges. The indirect exchange interaction so obtained depends on band-edge parameters such as the energy gap and electron and hole mass. When these parameters are small, the interaction range becomes long. The sign of the interaction depends on whether the energy gap is direct or indirect; in the former case the interaction is ferromagnetic; and in the latter the interaction becomes oscillatory in interspin distance.

In determining the interband contribution to the indirect exchange, two band features are of importance: the energy separation between the initial and the final state, and the symmetry of their wave functions. The importance of the energy gap is obvious because it gives the electron-hole excitation energy. The second point needs some elaboration. A Bloch wave function has two kinds of symmetry: a translational symmetry characterized by its wave vector $\mathbf{k}$ and a local symmetry usually referred to as atomic $s$- or $p$-like. As the valence-band electrons are polarized by a very localized interaction (i.e., their direct exchange with the local-moment Mn$^{2+}$ $d$-electrons), the local symmetry of the initial and final states determines whether there is an interband-exchange coupling between them. Owing to the translational symmetry, the Bloch electron changes its phase from one lattice point to the other. Because of this phase change, different interband transitions interfere with each other. Hence it is the combined translational and local symmetry which determined the net contribution from a given valence conduction-band pair. Our previous work\(^10\),\(^11\) shows that if two bands have local symmetry mixing with each other (e.g., $s$-$p$ mixing), their net contribution to the indirect exchange is ferromagnetic (with the exception of the cross term), while a pair of noninteracting bands contributes an antiferromagnetic interaction at large interspin distances.

From the discussions above, it becomes obvious that one needs to know the band structure before determining the nature of the indirect exchange. We have decided to use the semiempirical linear combination of atomic orbital (LCAO) method to calculate the band structure of PbTe. This method is chosen because not only the local symmetry of a state is well represented by an atomic basis set, but also the crystal symmetry is reflected in the LCAO band energy and wave function. By adopting a sem-
iemperical procedure, we further ensure that the energy gap and the orbital mixing coefficients obtained are reliable. We only carry out the calculation for nonmagnetic bands along one particular direction in the zone, i.e., the cubic axis. To obtain the band structure for all other \textbf{k} states, we make an isotropic band approximation. Under this approximation, the band energy and the mixing coefficients in the wave function only depend on the magnitude of the \textbf{k} vector but not its direction. The wave function of any \textbf{k} state is obtained from that of a corresponding state (i.e., state with the same magnitude \textbf{k}) along a cubic axis by simply rotating the quantization axis for the basis atomic orbitals from cubic to the \textbf{k} direction in question. As it will be discussed, this is not a bad approximation for PbTe crystallizing in the rock-salt structure.

With the band structure known, we treat the polarization of the valence-band electrons due to the Mn\textsuperscript{2+} local spin by the perturbation theory. We assume that in the case of small Mn\textsuperscript{2+} concentration, the formation of clusters represents a preliminary state of precipitation in the matrix and clusters consisting of three or four Mn\textsuperscript{2+} ions predominate. Numerical calculation indicates that there are long-range antiferromagnetic exchange interactions between the Mn\textsuperscript{2+} ions separated by distance larger than the lattice constant. The nonmonotonic behavior of the Curie temperature with concentration \textit{x} can be explained with the assumption of a ferromagnetic interaction between nearest-neighbor Mn\textsuperscript{2+} ions in the clusters. Our previous work\textsuperscript{11} has shown that similar variation of the exchange interaction with the interspin distance provides a possible explanation for the observed magnetic interaction in europium chalcogenides.\textsuperscript{12}

This paper is organized as follows: Section II describes the band structure, and Sec. III the indirect exchange calculation. The comparison with experimental results is presented in Sec. IV. Finally, Sec. V is devoted to a discussion of our results.

II. ENERGY BAND

In this section we calculate the nonmagnetic band structure of PbTe along the cubic axis (i.e., \(\Gamma - \Delta - X\)) by the LCAO method. We consider three valence bands generated from the Te 5\textit{p} orbitals and three conduction bands from Pb 6\textit{p} states. The LCAO wave function of a \textbf{k} state in the \textit{n}th band may be expressed as follows:

\[
\Psi_{nk} = \sum C_{\mu}^{n}(\textbf{k}) |\mu \textbf{k}\rangle ,
\]

where the basis function \(|\mu \textbf{k}\rangle\) is a Bloch sum of one of the six atomic orbitals centered either at the Pb or the Te site, and the \(\mu\) summation runs over all orbitals which are mixed into a given band. The energy of a band state and the mixing coefficients \(C_{\mu}^{n}\) are obtained by solving a secular equation consisting of the crystal Hamiltonian matrix elements between Bloch sums \(|\mu \textbf{k}\rangle\) in (2.1). The detailed forms of the LCAO Hamiltonian for various crystal structures have been worked out by Slater and Koster.\textsuperscript{13} Neglecting the energy intervals beyond the next-nearest-neighbor (NNN) interaction (Pb-Pb or Te-Te), we give in Table I the Hamiltonian matrix elements for the rock-salt structure and a \textbf{k}-state along the \(\Delta\) direction.

The energy band structure of PbTe has been studied by many authors.\textsuperscript{14,15} The various band structures calculated by different methods are all quite similar in their general features. A feature common to all of the calculations is the existence of an additional well-defined valence-band maximum and conduction-band minimum along the \(\Gamma - \Delta - X\) direction, while the fundamental direct energy gap occurs at the \(L\) point of the Brillouin zone (BZ). Among the mentioned calculations, Conklin et al.\textsuperscript{16} have calculated the band structure for the spin-independent relativistic Hamiltonian by the APW method. We choose the values for the energy integrals semiempirically such that the overall features of their band structure are reproduced. This approach is quite similar to that of Mattheiss\textsuperscript{17} who used LCAO as an interpolation scheme to obtain the band structure for transition-metal oxides over the entire zone when the states at a few symmetry points were determined by a more accurate method. We give the values of the eight parameters used in Table II. The calculated band structure is shown in Fig. 1.

Among the band features, the orbital symmetry mixing of the bands referred to at the beginning of this section is

| TABLE I. LCAO Hamiltonian matrix elements for the rock-salt structure with wave vector \textbf{k} along the (001) direction. The notation \((\mu \textbf{k})\equiv \langle \mu \textbf{k} | H | \nu \textbf{k} \rangle\) is used to denote the Hamiltonian matrix element. The energy integrals are denoted by \((\mu \nu \pi\tau)\) and \((\mu \nu \sigma\tau)\). The orbital energies are denoted by \(P_{M}\) and \(P_{\alpha}\). The subscripts \(M\) and \(x\) label the Pb and Te, respectively. The dimensionless \(\alpha\) stands for \((\frac{2}{3})|kR_{0}|, R_{0}\) being the lattice constant. For more detailed definition of various parameters, see, for example, Ref. 17. |
|---|
| Pb-Pb interactions |
| \((x/x) = (y/y) = P_{M} + 2(p\sigma \pi)_{M}(1 + \cos \alpha) + 2(p\pi \pi)_{M}(1 + 3 \cos \alpha)\) |
| \((z/z) = P_{M} + 4(pp \pi)_{M} \cos \alpha + 4(pp \pi)_{M}(1 + \cos \alpha)\) |
| Te-Te interactions |
| \((x/x) = (y/y) = P_{x} + 2(p\sigma \pi)_{x}(1 + \cos \alpha) + 2(p\pi \pi)_{x}(1 + 3 \cos \alpha)\) |
| \((z/z) = P_{x} + 4(pp \pi)_{x} \cos \alpha + 4(pp \pi)_{x}(1 + \cos \alpha)\) |
| Pb-Te interactions |
| \((x/x) = (y/y) = 2(p\sigma \pi)_{M} + 2(p\pi \pi)_{M}(1 + \cos \alpha)\) |
| \((z/z) = 2(pp \pi)_{M} \cos \alpha + 4(pp \pi)_{M}\) |
TABLE II. Values for the energy integrals used in the LCAO band calculation. The energy integrals are in units of eV.

<table>
<thead>
<tr>
<th></th>
<th>( \langle pp\sigma \rangle_M )</th>
<th>( \langle pp\pi \rangle_M )</th>
<th>( P_x )</th>
<th>( \langle pp\sigma \rangle_x )</th>
<th>( \langle pp\pi \rangle_x )</th>
<th>( \langle pp\sigma \rangle_{\Delta x} )</th>
<th>( \langle pp\pi \rangle_{\Delta x} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>0.208</td>
<td>-0.042</td>
<td>-1.40</td>
<td>0.206</td>
<td>-0.041</td>
<td>-1.93</td>
<td>-0.387</td>
</tr>
</tbody>
</table>

important because the symmetry contents of a given pair of interband states decide whether they are coupled by the local exchange interaction (which they have with the localized d electrons). In Fig. 1, it shows a nearly mirroring band structure. States with the same local symmetry are interacted to form bands with bonding and antibonding mixtures of \( p_x \) orbitals (\( \Gamma_{15} = \Delta_1 - X' \)) or \( p_x \), \( p_y \) orbitals (\( \Gamma_{15} = \Delta_5 - X' \)) from the Pb and Te ions, respectively. The strongest mixing occurs at the \( X \) point for all kinds of bands. The mixing of the \( \Gamma_{15} = \Delta_5 - X' \) bands is nearly uniform along the \( \Gamma - X \) axis, while there is no mixing for the \( \Gamma_{15} = \Delta_1 - X' \) bands near the valley region (i.e., band edges near the \( \Delta \) point).

The band mixing as described above is indeed a built-in feature of the LCAO Hamiltonian matrix given in Table I. Since the various parameters contained in the secular equation are determined semiempirically, we expect that our calculated values of the mixing coefficients \( C^p_\mu \) in (2.1) and the calculated energy dispersion curves are reliable. The calculated values of the mixing coefficients \( C^p_\mu \) are in good agreement with that of Conklin \textit{et al.} at the symmetry points \( \Gamma \) and \( X \), respectively. It is noted that for a pair of interacting bands, the energy dispersion and the symmetry mixing are actually related; the two bands go apart from each other in energy because of their mutual interaction. We recall that in our semiempirical procedure, the well-defined valence-band maximum and the conduction-band minimum near the \( \Delta \) point have been used as one of the input pieces of information. This should help us in making a rather accurate determination of the mixing coefficients for the \( \Gamma_{15} = \Delta_1 - X' \) bands. Other important energy gap values are also taken from a more precise band calculation. This should further ensure that the crystal-field effect and the NNN (Pb-Pb, Te-Te) interactions are also correctly estimated and hence the energy dispersion curves obtained are reliable.

Although, in principle, using the LCAO method, we could calculate the band structure throughout the entire zone, we have decided to make an isotropic band approximation for evaluating bands at an arbitrary \( k \) point. Under this assumption, both the band energies and the mixing coefficients \( C^p_\mu \) in (2.1) are assumed to be isotropic. In other words, they are functions of the magnitude \( k \) only. At the same time, the atomic orbitals which form the basis functions \( |\psi(k)\rangle \) should be taken as quantized along the \( k \) axis. This is to say that in setting up the LCAO Hamiltonian matrix for an arbitrary \( k \) state, we take that particular \( k \) direction as the quantization axis for the atomic orbitals. Of course, choosing a different quantization axis should not change the final results, so that this procedure by itself is not an approximation. The approximation comes when we assume that the Hamiltonian so obtained for an arbitrary \( k \) point is identical to the one given in Table I which is appropriate for a state along the \( \Gamma - \Delta - X \) axis with the same magnitude \( k \). This is not a bad approximation for the rock-salt structure where a cation is surrounded by six anion neighbors along the cubic axis. For a region near the \( \Gamma \) point, this approximation is certainly valid. For a region adjacent to the six cubic axis, this approximation is again very good. For a region in between, we have estimated the percentage deviation of the approximation from the exact LCAO results to be less than a few times \( 10^{-1} \). In addition, as one goes from one cubic axis to the other (where the errors vanish), one expects the errors to fluctuate. Therefore, for the indirect exchange which is the collective effect of all \( k \) states in the zone, the errors caused by the isotropic band

FIG. 1. Calculated energy bands for PbTe along a cubic axis (\( \Gamma - X \)). The numerical number label the symmetry of the band. The zero of energy has been adjusted to coincide with the \( \Gamma_{15} \) state.
approximation may cancel each other out to some extent. Of course, certain features of the bands, like the fundamental direct energy gap at the \( L \) point and the splitting of the \( \Delta_k \) bands at a general \( k \) point, are not accounted for in this approximation.

### III. INDIRECT EXCHANGE INTERACTION

In \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \), the \( d \) electrons of \( \text{Mn}^{2+} \) are well localized at the \( \text{Pb} \) site to form a local moment. Owing to the direct exchange interaction between the \( d \) electrons and the valence-band Bloch electrons, the latter are magnetically polarized. Through these polarized electrons, the local spins interact with each other. If the spin-orbit coupling is neglected, the indirect exchange interaction between two \( \text{Mn} \) spins \( S_1 \) and \( S_j \) separated by a distance \( R_{ij} \) is of the Heisenberg form according to second-order perturbation theory:

\[
\Delta E = -2J_1(R_{ij})S_i \cdot S_j. \tag{3.1}
\]

The coupling constant \( I(R_{ij}) \) is determined by exchange-induced interband excitations.

\[
I(R_{ij}) = \frac{1}{4} \sum_{(n,k),(n',k')} |M(n',k';n,k)|^2 e^{i(k'-k) \cdot R_{ij}} \frac{E_n(k') - E_n(k)}{E_n(k') - E_n(k)} + \text{c.c.}, \tag{3.2}
\]

where \( E_n(k') \) and \( E_n(k) \) are the conduction- and the valence-band energies, respectively. The summation of wave vector \( k \) is over the entire valence band, and that of \( k' \) over the entire conduction band. The oscillating factor \( e^{i(k'-k) \cdot R_{ij}} \) arising from the change of phase of Bloch electrons over two \( \text{Mn} \) sites is displayed explicitly in (3.2) and the interband-exchange matrix element \( M \) is independent of the site of either of the two spins. Owing to this oscillating factor, different interband excitations interfere with each other, and the net indirect exchange may then carry different sign at different interspin distance \( R_{ij} \). The site independent matrix element \( M \) evaluated with any \( \text{Mn}^{2+} \) lattice point as the origin is explicitly expressed as

\[
M(n',k';n,k) = \int d^3r_1 \int d^3r_2 \psi_{n,k}(r_1) \phi_d^*(r_2) \times \frac{e^2}{\epsilon_{12}} \phi_d(r_1) \psi_{n,k}(r_2), \tag{3.3}
\]

where \( \phi_d \) is the orbital wave function for the localized \( d \) electrons and \( \psi_{n,k} \) as in Sec. II, denotes the nonmagnetic Bloch wave function. The exchange matrix element is assumed to be independent of the magnetic quantum number of the \( d \) orbital, or equivalently, it may be regarded as an average over all occupied \( d \) orbitals. Owing to this simplification, the exchange interaction in (3.1) can be expressed in terms of the total spin of the \( \text{Mn}^{2+} \) ion. As the ground state of the \( \text{Mn}^{2+} \) ion is a spherical symmetric \( ^3S \) state, the integral \( M \) in (3.3) may be viewed qualitatively as a matrix element of a spherical symmetrical local exchange operator connecting two interband Bloch states.

Using LCAO wave function in (2.1) to evaluate the interband matrix element \( M \), one may simply replace each Bloch sum \( |\mu k\rangle \) by one atomic orbital, either centered at the \( \text{Pb} \) site or its six neighboring \( \text{Te} \) sites. As the exchange operator may be regarded as isotropic, only atomic orbitals having the same angular momentum and the same magnetic quantum number are connected by the local exchange. In addition, since the \( \text{Pb} \) \( 6p \) and \( \text{Te} \) \( 5p \) orbitals are centered at different sites, we assume that among these orbitals only the diagonal exchange integrals \( J_{\mu\mu} \) exist. By reason of symmetry all \( J_{\mu\mu} \) connecting the \( \text{Pb} \) \( 6p \) orbitals are equal to each other and so are those connecting the \( \text{Te} \) \( 5p \) orbitals. Thus we only have to consider two atomic exchange integrals \( J_{6p} = J_{6p,6p} \) and \( J_{5p} = J_{5p,5p} \), denoting \( 6p-d \) and \( 5p-d \) exchange, respectively, and we treat them as known parameters in this paper. In calculating \( M \), we also recall that under our isotropic band approximation, the quantization axis of the atomic orbital varies with the \( k \) state. Then one notes that two atomic orbitals having different magnetic quantum number but space quantized along two different directions may still be connected by the local exchange interaction because they are not necessarily orthogonal to each other. Conversely, it is also possible for two orbitals with the same magnetic quantum number to be orthogonal to each other when they are not oriented along the same axis. Considering all these points, we may write down a general form of the matrix element as follows:

\[
M(n',k';n,k) = \sum_{\mu\nu} C^\mu_{\nu}(k')C^\nu_{\mu}(k)\theta_{\mu\nu}(\Omega)J_{\mu\nu}, \tag{3.4}
\]

where the function \( \theta_{\mu\nu} \) denotes the overlap between the angular part of the atomic orbital \( \phi_{\mu} \) quantized along the conduction band \( k' \) axis with that of \( \phi_{\nu} \) which is oriented along the valence band \( k \) axis. For \( 6p \) and \( 5p \) orbitals which have directional dependence, the overlap \( \theta \) is a function of the angle \( \Omega \) between the two wave vectors \( k \) and \( k' \). The mixing coefficients \( C^\mu_{\nu} \) on the other hand, depend only on the magnitude of the wave vector \( k \) under the isotropic band approximation. The form of \( \theta \) for various pairs of bands can be determined by using the well-known transformation property of spherical harmonics under rotations.\(^{18}\)

We give in Table III the explicit forms of \( \theta \) associated with various interband transitions. We see that there are two distinct types of angular dependence. Between interacting bands belonging to the same irreducible representation (e.g., \( \Delta_1 - \Delta_1, \Delta_1 - \Delta_2 \)) the interband-exchange coupling is the strongest when the wave vectors of the initial and final states are parallel to each other. On the other band, for noninteracting bands (e.g., \( \Delta_1 - \Delta_3 \)) there is no interband coupling when the wave vectors of the two states are parallel to each other. As it has been found previously,\(^{10,11}\) the contribution to the exchange interaction from these two types of interband coupling are qualitatively different.

We can rewrite (3.2) in the form:

\[
I(R_{ij}) = \sum_q I(q)e^{iqr_{ij}}, \tag{3.5}
\]

where \( q = k' - k \) is the momentum transfer in the electron-hole excitation process, and \( I(q) \) can be written
TABLE III. Directional dependence of the exchange matrix element.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Angular dependence $\theta_{\mu\nu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_1 - \Delta_1$</td>
<td>$6p_\xi - 6p_\xi$</td>
</tr>
<tr>
<td>$\Delta_5 - \Delta_5$</td>
<td>$6p_\xi - 6p_\xi$</td>
</tr>
<tr>
<td></td>
<td>$5p_\xi - 5p_\xi$</td>
</tr>
<tr>
<td></td>
<td>$5p_\xi - 5p_\xi$</td>
</tr>
<tr>
<td></td>
<td>$6p_\xi - 6p_\xi$</td>
</tr>
<tr>
<td></td>
<td>$5p_\xi - 5p_\xi$</td>
</tr>
<tr>
<td>Nonparallel coupling</td>
<td>$6p_\xi - 6p_\xi$</td>
</tr>
<tr>
<td></td>
<td>$5p_\xi - 5p_\xi$</td>
</tr>
</tbody>
</table>

as the total sum of all the interband transitions listed in Table III with the two exchange integrals $J_M$ and $J_x$ as parameters:

$$I(q) = \sum_{n',n,k} J_{\xi \eta} J_{\mu \nu} (q) - \sum_{\xi,\eta} J_{\xi \eta} J_{\mu \nu} (q) ,$$

$$I_{\mu \nu} (q) = \sum_{\xi,\mu',\eta} F_{\mu \nu, \mu', \eta} (q) ,$$

and

$$I_{\eta \nu} (q) = \sum_{\xi, \mu' \nu} F_{\eta \mu' \nu} (q) .$$

The first term in (3.6), i.e., $I_{\mu \nu} (q)$, comes from an interband transition in which both the excitation (valence to conduction band) and the de-excitation (from conduction back to valence band) are via atomic orbitals having the same angular momentum and being centered at the same kind of lattice sites. The second term $I_{\eta \nu} (q)$ accounts for a case in which the two processes involve different types of atomic basis. As the angular factor $\theta_{\mu \nu}$ in the interband matrix element depends on the magnetic quantum number of the atomic orbitals involved, we display the $\mu, \nu$ indices explicitly and write

$$I_{\mu \nu} (q) = \sum_{\xi,\eta} F_{\xi \eta} (q) \xi, \eta = 6p_\xi, 5p_\eta .$$

The function $I(q)$, for parallel and nonparallel coupling (e.g., $\theta = \cos\Omega$), the contribution of the $F$ function to the indirect exchange is ferromagnetic. On the other hand, the contribution from the nonparallel interband coupling (e.g., $\theta = \sin\Omega$) is antiferromagnetic. In Fig. 2, we show some typical examples of our calculated $F$ functions based on the LCAO bands of Sec. II. One can clearly distinguish the two types of coupling, the parallel and the nonparallel, from the figure. As the exchange integrals $J_M$ and $J_x$ are treated as parameters here, we present our calculated results in the following form:

$$I(R_{ij}) = A(R_{ij}) J_M^2 + B(R_{ij}) J_M J_x + C(R_{ij}) J_x^2 ,$$

where each term denotes the total contribution from all interband transitions given in Table III. The calculated values of the constants in (3.11) for $R_{ij}$ from $R_{ij} = 0$ to $5$ are given in Table IV.

<table>
<thead>
<tr>
<th>$R_{ij}$</th>
<th>$A$ (eV$^{-1}$)</th>
<th>$B$ (eV$^{-1}$)</th>
<th>$C$ (eV$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.6 \times 10^{-1}$</td>
<td>$-1.3 \times 10^{-1}$</td>
<td>$3.3 \times 10^{-1}$</td>
</tr>
<tr>
<td>$R_0$</td>
<td>$-2.7 \times 10^{-3}$</td>
<td>$-7.9 \times 10^{-3}$</td>
<td>$-8.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>2$R_0$</td>
<td>$-5.8 \times 10^{-4}$</td>
<td>$5.7 \times 10^{-4}$</td>
<td>$-6.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>3$R_0$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$-2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>4$R_0$</td>
<td>$-5.4 \times 10^{-5}$</td>
<td>$2.2 \times 10^{-5}$</td>
<td>$-8.4 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
\( R_{ij} = 4R_0 \) are given in Table IV. For the case with \( R_{ij} > R_0 \), the indirect exchange is antiferromagnetic. If we assume that \( J_M \) and \( J_x \) are approximately equal to each other, then the indirect exchange interaction \( I(R_{ij}) \) is a long-range antiferromagnetic interaction, in agreement with experiments.⁵ Beyond \( R_{ij} = 4R_0 \), \( I(R_{ij}) \) varies with interspin distance \( R_{ij} \) according to a power law approximately as follows:

\[
I(R_{ij}) \sim R_{ij}^{-\alpha},
\]

(3.12)

where \( \alpha \) is approximately equal to 4–5 and varies slowly with the interspin distance \( R_{ij} \). The above approximate relationship is valid from \( R_0 \) to \( 4R_0 \). As for the nearest-neighbor (NN) magnetic interaction, we cannot calculate its value precisely. This difficulty is due to the presence of an oscillating factor in (3.2). When the cutoff imposed by the upper limit in the integration of either the valence band \( k \) or the conduction band \( k' \) does not coincide with whole periods of oscillation, spurious results may be obtained. This is the case here as the NN distance \( (R_0/\sqrt{2}) \) is not equal to an integer multiple of the lattice constant. Therefore, under the present scheme, at best we can only give a reasonable estimate for the NN interaction using the values of \( I(R_{ij}) \) calculated for \( R_{ij} = 0 \) and \( R_{ij} = R_0 \). It is noted that at \( R_{ij} = 0 \), the net value for \( I(R_{ij}) \) is positive while, as stated, the net interaction is negative at \( R_{ij} = R_0 \). Hence there is a change of interaction sign somewhere in between \( 0 < R_{ij} < R_0 \). We assume that the value of \( I(R_0/\sqrt{2}) \) is positive, i.e., the NN interaction is ferromagnetic, and can be estimated by interpolation between \( I(0) \) and \( I(R_0) \).

IV. COMPARISON WITH EXPERIMENTAL RESULTS

A complete analysis of the magnetic properties of \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \) requires the detailed information about the way how the \( \text{Mn}^{2+} \) ions are distributed in the crystal lattice. The assumption of a random distribution of impurities seems to be a reasonable choice only for the case that the Curie-Weiss temperature \( \Theta \) varies almost linearly with the impurity concentration. An example which satisfies this assumption is the semimagnetic zero-gap semiconductor \( \text{Hg}_{1-x}\text{Mn}_x\text{Te} \) alloys.¹⁹ The experimental investigation showed an almost linear dependence of \( \Theta \) on the manganese concentration \( x \) over a wide range of concentration (0.1% \(< x < 30\% \)). However, the assumption of a random distribution of impurities is not suitable for \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \). Experimental investigations of the magnetic properties of \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \) indicated that the formation of magnetic clusters in which the clusters consisting of three \( \text{Mn}^{2+} \) ions predominate in the composition range \( x < 1\% \) seems to be a better assumption.¹ By analogy with nonconducting europium chalcogenides,¹² which, like \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \), crystallize in the NaCl lattice, it seems that the magnetic interaction between the \( \text{Mn}^{2+} \) ions in \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \) may include a ferromagnetic NN interaction and long-range antiferromagnetic interactions. The magnetic properties are determined by the competition between the contributions from these two opposite kinds of interaction. As the numbers of the ion-pair coupled with ferromagnetic or antiferromagnetic interaction are determined by the probabilities of occurrence of clusters with different number of \( \text{Mn}^{2+} \) ions, the anomalous behavior of \( \Theta \) as a function of \( \text{Mn}^{2+} \) concentration is the result of a particular variation of cluster probabilities with the \( \text{Mn}^{2+} \) concentration.

In order to compare our theory with experiments, we need to calculate the magnetic susceptibility of \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \). In the molecular field approximation (high temperature), the magnetic susceptibility \( \chi \) obeyed the Curie-Weiss law

\[
\chi^{-1} = a(T - \Theta),
\]

(4.1)

with a negative Curie-Weiss temperature \( \Theta \) which can be expressed in terms of the exchange coupling constant \( I(R_{ij}) \) as

\[
k_B \Theta = \frac{S(S+1)}{3N} \sum_{i,j} I(R_{ij}),
\]

(4.2)

where \( N \) is the total number of \( \text{Mn}^{2+} \) ions, and the summations of \( i \) and \( j \) run over the actual positions of \( \text{Mn}^{2+} \) ions, i.e., \( R_i \) and \( R_j \), respectively. From experimental works,¹,²,¹⁰ it was observed that the manganese ions in \( \text{Pb}_{1-x}\text{Mn}_x\text{Te} \) crystals were in the \( S = \frac{1}{2} \) state and were substitutional impurities. By assuming a cluster distribution for the \( \text{Mn}^{2+} \) ions, we can express \( k_B \Theta \) as
\[ k_B \Theta = [S(S+1) x / 3] \times \left[ I(R_0 / \sqrt{2}) \sum_{i \geq 2} Z_i P_i(x) + \sum_{R_j \geq R_0} I(R_j) \right]. \tag{4.3} \]

The first term in (4.3) denotes the contributions from the Zi NN ion pairs within the clusters of various equivalent multplet, i.e., \( P_2, P_3, \) and \( P_4 \) denote the cluster probabilities of the clusters of pair, equivalent triplet, equivalent quadruplet, respectively. The second term represents the contribution from ion-pairs with interspin distance \( R_j > R_0 \) which are assumed to be distributed randomly in the crystal lattice. All other nonequivalent clusters are not explicitly considered, and their contributions to the exchange interaction are included in the long-range term, i.e., the second term in (4.3). With the assumption of random distribution for the long-range term, the summation can be calculated from the known table,\(^{21}\) if there is a functional dependence form of \( R_{ij}^{-\alpha} \) for \( I(R_{ij}) \) with \( R_{ij} \geq R_0 \). If we assume that \( \alpha = 5 \) is valid for the long-range interaction, the lattice sum of the second term in (4.3) is equal to 28.11.

In the case of completely random distribution, the cluster probabilities of the clusters with pairs, triplets, and other higher multplets, as a function of the total impurity concentration in the crystal, can be determined statistically.\(^{22,23}\) However, experimental result\(^1\) showed that clusters consisting of three Mn\(^{2+} \) ions will predominate in the composition range \( x < 1\% \).

So, we assume that the triplet cluster \( P_3(x) \) will predominate and then the quadruplet \( P_4(x) \) will gradually dominate with the further increasing of the Mn\(^{2+} \) concentration. Owing to the lack of information about the detailed clusters distribution of Mn\(^{2+} \) in Pb\(_{1-x}\)Mn\(_x\)Te and its variation of the Mn\(^{2+} \) concentration, we cannot make a precise quantitative comparison between our theory and the experiments. Restricting our model with the higher multplet clusters neglected, the Curie-Weiss temperature \( k_B \Theta \) can be expressed as

\[ k_B \Theta = S(S+1) x [I(R_0 / \sqrt{2}) [2P_2(x) + 3[3P_3(x)] + 6[4P_4(x)]] + 28.11 I(R_0)] / 3. \tag{4.4} \]

Obviously, there are many functional forms of \( P_2(x), P_3(x), \) and \( P_4(x) \) which satisfy Eq. (4.4) and give a nonmonotonic variation of the Curie-Weiss temperature \( \Theta \) with Mn\(^{2+} \) concentration \( x \) similar to that of experimental result.\(^1\) When we use the atomic exchange integral value\(^{24}\) of about 1 eV for \( J_M=J_s \) and assume that the value of \( I(R_0 / \sqrt{2}) \) is positive and can be estimated by interpolation, the experimental Curie-Weiss temperatures can be explained with suitable choice of cluster probabilities. We show the simulated Curie-Weiss temperature \( \Theta(x) \) in Fig. 3. One set of the possible forms of the corresponding cluster probabilities \( P_2(x), P_3(x), \) and \( P_4(x) \) is shown in Fig. 4.

The curve in Fig. 3 which represents the variation of the Curie-Weiss temperature \( \Theta \) with the Mn\(^{2+} \) concentration is a complete simulation of that determined experimentally by Andrianov et al.\(^1\) In Fig. 4 it shows that clusters consisting of three Mn\(^{2+} \) ions predominate in the case of the least doped Pb\(_{1-x}\)Mn\(_x\)Te.

**V. DISCUSSION**

As we have seen, the nonmonotonic behavior of the Curie-Weiss temperature with the manganese concentra-

![Graph showing the Curie-Weiss temperature with Mn\(^{2+} \) concentration](image)

**FIG. 3.** The variation of the Curie-Weiss temperature \( \Theta \) with the Mn\(^{2+} \) concentration \( x \). This curve is a complete simulation of that in Ref. 1.

![Typical forms of the calculated cluster probabilities](image)

**FIG. 4.** Typical forms of the calculated cluster probabilities with which the magnetic property of Pb\(_{1-x}\)Mn\(_x\)Te follows that shown in Fig. 3. Calculated values are based on the assumption that \( J_M=J_s=1 \) eV, and we set \( I(R_0 / \sqrt{2})=1.24 \times 10^{-11} \) eV by interpolation between \( I(0) \) and \( I(R_0) \). The cluster probabilities are labeled in the following way: (1) \( 2P_2(x) \); (2) \( 3P_3(x) \); (3) \( 4P_4(x) \).
tion within the range $x < 6\%$ can be explained by present model whose main features included the ferromagnetic NN interaction, long-range antiferromagnetic interactions, and the cluster distribution of the Mn$^{2+}$ ions. As to the assumed ferromagnetic NN interaction, there is a similar mechanism observed in experimental investigation of Pb$_{1-x}$Fe$_x$Te crystal$^{25}$ in which there is formation of magnetic clusters and atoms in these clusters are bound by a ferromagnetic interaction. Since these two crystals have the same host lattice our assumption for the ferromagnetic NN interaction in Pb$_{1-x}$Mn$_x$Te seems to be reasonable.

As to the quantitative result obtained in this paper, their accuracy, of course, is limited by the approximations adopted. We have made an isotropic approximation including the assumption that the orbitals are always quantized along the $k$ axis. For crystals like PbTe which possess high degree of symmetry (cubic), this is not a bad approximation.

Let us now consider the variation of the cluster probabilities, especially, the equivalent triplet and quadruplet $P_3(x)$ and $P_4(x)$ with the impurity concentration $x$. Since only the clusters of these two kinds are adopted, their magnitudes are likely to be overestimated in the high concentration case. If clusters consisting of more than four atoms and other nonequivalent clusters are taken into account, the cluster probabilities $P_3(x)$ and $P_4(x)$ will then show a reasonable decaying feature and reduce their magnitudes since the clusters of higher multiplet will contribute to part of the NN interaction and, accordingly, share part of the cluster probability of the lower multiplet clusters, i.e., $P_3(x)$ and $P_4(4)$. Unfortunately, a quantitative confirmation of this interpretation cannot be made at this stage when detailed knowledge as to how the clusters are formed and their variation with the impurity concentration are not available.

ACKNOWLEDGMENTS

The author would like to express his gratitude to Professor L. Liu for illuminating discussions. This work was supported partially by the National Science Council of the Republic of China.

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12For a general review, see, for example, S. Methfessel and D. C. Mattis, Encyclopedia of Physics (Springer, Berlin, 1968), Vol. XVIII/1, p. 389.


