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Neighborhood notion in the magnetic-properties study of magnetic materials with a dominant superexchange interaction

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The steplike magnetization observed in a semimagnetic semiconductor in a high magnetic field allows an accurate determination of the exchange interaction of these compounds. Nevertheless, the results obtained from a generalized cluster model or extended nearest-neighbor pair approximation for an interaction longer than nearest neighbor do not agree well with experimental measurements (specific heat, spin-glass study, etc.). From the assumption of a preponderant superexchange, reconsidering the hypothesis of an exchange-constant decrease with the direct distance, we analyze the $Zn_{1-x}Mn_xTe$ magnetization for different Mn compositions, and we obtain good agreement with experimental results. We emphasize that to study the magnetic properties of materials in which this interaction mechanism is preponderant, the neighborhood notion should be reconsidered, taking into consideration the cation-anion-cation distances and angles.

In recent years a great deal of interest has been shown in the high-magnetic-field magnetization of semimagnetic semiconductors (SMSC's) (Ref. 1) with zinc blende or wurtzite structure. The magnetization versus magnetic field relationship presents a steplike behavior which allows a direct determination of the exchange constant between magnetic ions and the study of the distribution of these ions in the host structure.[2-9] For the first time, this behavior was analyzed from a cluster model. The steps are explained by the magnetization of nearest-neighbor (NN) magnetic ions pairs. At low field, due to antiferromagnetic exchange interaction, the pair effective spin $S_{\rm eff}$ is zero. Increasing the field, the effective spin changes and becomes $S_{\rm eff}=1$ for magnetic field B_1, and so on, $S_{\rm eff}=n$ for magnetic field $B_n=nB_1$ with $1<n<2S_0$ ($S_0=\frac{5}{2}$ is the Mn spin). The pair magnetization proceeds by five steps for Mn spins. Nevertheless, the cluster model is not sufficient. It appears there are discrepancies with experimental measurements: (i) the magnetic position of the second step does not correspond to twice that of the first step ($B_2\neq 2B_1$);[3,7-9] (ii) effective temperatures are necessary to account phenomenologically for experimental data at low field (T_0 in Ref. 10) and high field ($T_{\rm eff}$ in Refs. 6, 8, and 9). These temperatures are related to the molecular field applied on the single (T_0) and paired ($T_{\rm eff}$) ions. Two main models were used to explain these discrepancies between theoretical and experimental data: (i) the generalized cluster model (GCM) proposed by Larson *et al.*[11] on the basis of a cluster model, and (ii) the extended nearest-neighbor pair approximation (ENNPA) on the basis of the pair clusters model by Twardowski *et al.*[12] These two analyses give us the possibility to calculate the exchange constant between NN magnetic ions and between magnetic ions more distant than NN. From the GCM, for $Cd_{1-x}Mn_xTe$, the next-nearest-neighbor (NNN) exchange constant J_2 is approximately one-third of the NN exchange constant of J_1 and, from the ENNPA, for $Zn_{1-x}Mn_xSe$, J_2 is approximately half J_1. In all cases, J_2 is important relative to the main exchange interaction. These results do not correspond to previous determinations deduced from spin-glass phase studies. For $Cd_{1-x}Mn_xTe$, Escorne and Mauger[13] have obtained $J_2\simeq J_1/8$. From the same kind of study on several SMSC's, Twardowski *et al.*[12] have determined a radial dependence of exchange interactions between Mn ions. They have established a universal law, $J(R)\cong R^{-6.8}$, which gives $J_2\simeq J_1/10$. These last equalities confirm the small J_2 value with respect to J_1, as expected by Brumage *et al.*[14] for $Zn_{1-x}Mn_xS$ and suggested by Danielian and Stevens[15] for β-MnS (zinc blende structure). Other measurements are in accordance with this result. As an example, the value $J_2/k_B=-0.55$ K, reported for $Cd_{1-x}Mn_xTe$ from specific-heat measurements[16] and assimilated to the NNN exchange interaction as discussed by Shapira *et al.*,[17] may be compared to $J_1/k_B=-6.1\pm0.3$ K for $Cd_{1-x}Mn_xTe$ (Ref. 9) ($J_2\cong J_1/11$). From a study of the exchange mechanism, we believe that the disagreement between the J_2 values should not be related to the approximations or limits of the theoretical model (the GCM or the ENNPA) but may be explained reconsidering the hypothesis of an exchange-constant decrease with the direct distance.

Recent studies on magnetic properties of SMSC's by Larson *et al.*[18] (theory) and Spalek *et al.*[19] (susceptibility measurement) conclude about the predominance of the antiferromagnetic superexchange in comparison with other mechanisms. Superexchange involves filled p shells (valence band) of the anions and the overlap of the d (Mn^{++} ions) and p (anions) shells. As a consequence, the superexchange interaction does not depend on the direct distance but depends on the chemical bonding length between the two magnetic ions interacting and on the cation-anion-cation angle. Assuming a similar dependence on the chemical bonding for more distant neighbors, the neighborhood notion to study the SMSC magnetic properties should be reconsidered. Figure 1 shows, for zinc blende structure, the position of the second, third, and fourth neighbors. One can verify that the ways traveled through the two anions between these neighbor positions are the same for the three cases. Nevertheless, the number of ways is different, and longer ways exist. The exchange interaction is the sum of couplings traveling through the following: two anions and one cation (four couplings for J_2, two for J_3, and one for J_4); three anions and two cations (eight couplings for J_2, ten for J_3, and eight for J_4); four anions and three cations (72 for J_2, 60 for J_3, 58 for J_4), and so on for longer travels. Assuming for the first time that J_2, J_3, and J_4 are mainly due to couplings through two anions and one cation, and neglecting more distant couplings, we may write

$$J_2=2J_3=4J_4\ . \qquad (1)$$

For simplification, we will indistinctly name J_2, J_3, and J_4 the NNN interactions in the sense of superexchange. From a Curie temperature study,[19] a variation of the exchange constant due to lattice distortion has been observed for high Mn concentration. This distortion has been evidenced in SMSC's from extended x-ray absorption fine structure (EXAFS) measurements.[20,21] Nevertheless, the influence of this effect on the NNN exchange constant may be neglected for low Mn concentration. Equality (1) may be introduced as a possible hypothesis for SMSC magnetization analysis from the ENNPA or GCM. The ENNPA (Ref. 12) cannot explain the step shift ($B_2 \neq 2B_1$) and the broadening observed for all SMSC's investigated. Consequently, to account for high-field magnetization, we use for the pairs a self-consistent mixed model (a cluster model and molecular field approximation) similar to the GCM in which the pairs are treated exactly and where the more long-range interactions are analyzed in a molecular field approximation. We call $\bar{\tau}$ the set of paired ions interacting with an exchange intensity of $\tau J_2/4$ $(=\tau J_3/2=\tau J_4)$ with the NNN environment, where τ is the number of couplings with the environment. The Hamiltonian which describes a pair of a set $\bar{\tau}$ can be written as[11]

$$H_{P\tau}=g\mu_B(S_1+S_2)(B-b_\tau)\ ,$$

where S_1 and S_2 are the paired spin vector components along the magnetic field and b_τ is the molecular field applied on this pair. b_τ is given by

$$b_\tau=-(1/g\mu_B)(\tau J_2/4)\langle S_e\rangle\ ,$$

where $\langle S_e\rangle$ represents the thermodynamical as well as the spatial average of a localized spin S_e of the environment in the magnetic field direction. From the Hamiltonian $H_{P\tau}$, with the condition $2J_1 \gg k_BT$, the magnetization of the pair belonging to the set $\bar{\tau}$ is determined as a sum of Boltzmann functions:

$$\frac{M_{P\tau}(T,B)}{M_0}=\frac{P_{2\tau}}{2S_0}\sum_{n=1}^{2S_0}\left[1+\exp\left[\frac{g\mu_B}{k_BT}(B_n-B+b_\tau)\right]\right]^{-1}, \qquad (2)$$

where M_0 is the total saturation, $P_{2\tau}$ is the probability of having a pair submitted to a molecular field b_τ, and B_n is directly related to J_1 by the equality

$$B_n=-(2n/g\mu_B)J_1\ .$$

The total pair magnetization is the summation of the magnetization of all the sets τ:

$$\frac{M_P(T,B)}{M_0}=\left[P_2\Big/\sum_{\tau=0}^{\tau_{\max}}P_{2\tau}\right]\left[\sum_{\tau=0}^{\tau_{\max}}\frac{M_{P\tau}(T,B)}{M_0}\right], \qquad (3)$$

where τ varies from zero, in the case of totally isolated pairs, to $\tau_{\max}$ couplings when all the NNN cation sites are occupied by magnetic ions, and P_2 is the probability of finding one ion in a pair. To determine the magnetization, we assume the following: (i) a random distribution of the magnetic ions which has been confirmed for SMSC's;[4-8] consequently, the probabilities P_1, P_2, and $P_{2\tau}$ may be determined from the Mn concentration; (ii) the proportionality of $\langle S_e\rangle$ with the total magnetization. Under these conditions, Eq. (3) is determined self-consistently. This approximation seems correct owing to the great number of NNN cation sites. In this way, the relative proportion of clusters (single ions, pairs, etc.) in the neighborhood of a chosen pair may be considered identical to those of the whole crystal. This second assumption limits the model to low concentrations due to the possible existence of a high Mn concentration of larger clusters in the NNN pair environment. These clusters have small magnetization per spin and give a small contribution to the molecular field.

In this paper, Eq. (3), where $x=0.054$ and $\tau_{\max}=114$ for a zinc blende structure, is used to account for $Zn_{1-x}Mn_xTe$ magnetization in the high-magnetic-field range ($B>10$ T). The probability of having pairs belonging to sets with $\tau>15$ is negligible ($\sum_{\tau=0}^{15}P_{2\tau}=0.98$ for $x=0.054$). Thus, for convenience of calculation the summation in Eq. (3) will be taken over the sets for $\tau=0-15$. In Fig. 2, we compare the high-field magnetization measurement, given in Ref. 8, with the theoretical magnetization obtained from the sum of $M_P(B,T)$ and the closed triplet contribution $M_{CT}(B,T)$. This last contribution and the value $J_1/k_B=-8.8$ K are determined in Ref. 8. The best fitting of the high-magnetic field magnetization is realized for the only adjustable parameter:

$$J_2/(4k_B)=-0.38\ \mathrm{K}\ .$$

The agreement observed verifies the Mn random distribu-

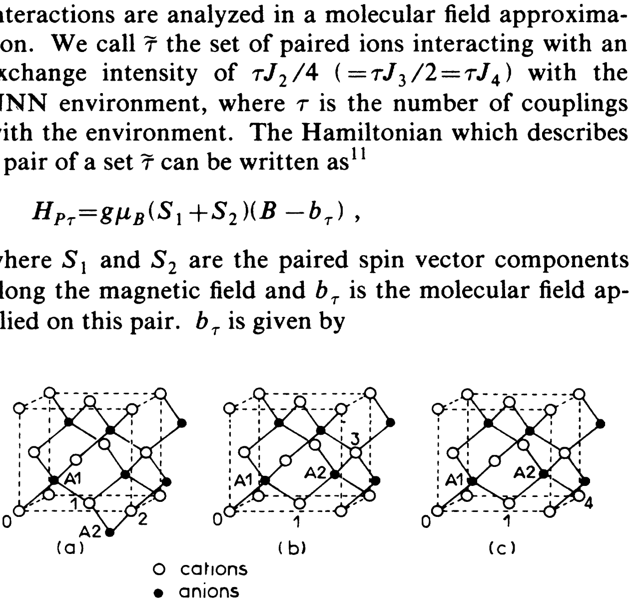

FIG. 1. Interaction of the second (a), third (b), and fourth (c) neighbors of the magnetic ion (open circles) in a zinc blende structure.

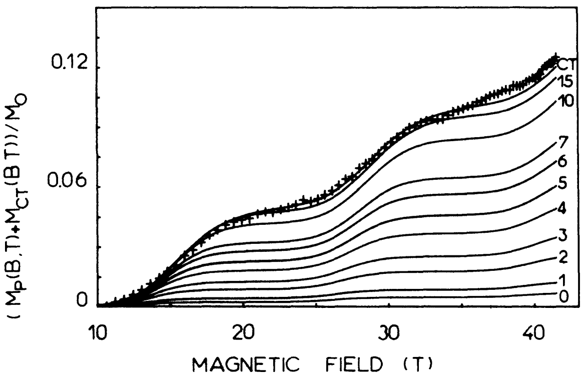

FIG. 2. Pair and closed triplets magnetization of $Zn_{1-x}Mn_xTe$ ($x=0.054$) as a function of magnetic field at 1.6 K. Crosses are pulsed field magnetization data of Ref. 8. The solid curve labeled 0 represents the $\tau=0$ contribution to the magnetization given by Eq. (3). The solid curve labeled 1 is the sum of $\tau=0$ and $\tau=1$ contributions, and so on for the other curves. CT is the sum of the calculated pairs magnetization (curve 15) and the closed triplet magnetization.

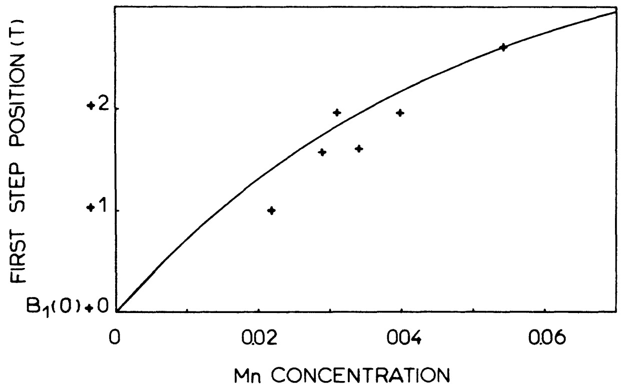

FIG. 3. Crosses represent the first step positions in magnetic field vs Mn concentration of $Zn_{1-x}Mn_xTe$ deduced from Ref. 6 for $x=0.029$ and $x=0.034$; from Ref. 9 for $x=0.031$ and $x=0.040$; from Ref. 8 for $x=0.054$; and from Ref. 22 for $x=0.022$. The solid curve is obtained from Eq. (4).

tion, and also that the use of the NNN interactions is sufficient to account for the observed discrepancy between experiment and a cluster model. Thus it is not necessary to use a temperature parameter T_{eff} as well as a mean molecular field parameter as in Ref. 8.

The results obtained in Refs. 6, 7, and 9 on high-magnetic-field magnetization of $Zn_{1-x}Mn_xTe$ show different first step positions for different concentrations. The model used explains the dependence of this position versus the concentration considering the mean molecular field b which is a mean value of the molecular fields b_τ. The first step position is given by

$$B_1(x)=B_1(0)+b(x)\ , \tag{4}$$

where

$$B_1(0)=-2J_1/g\mu_B$$

and

$$b(x)=-(1/g\mu_B)\tau_{\max}x(J_2/4)\langle S_e\rangle\ .$$

Figure 3 shows the first step position versus Mn concentration. The solid curve represents the shift deduced from Eq. (4) using

$$\langle S_e\rangle=S_0(M_s/M_0+P_2/10)\ ,$$

where M_s is the low-field magnetization saturation which depends, as do P_2 and M_0, on concentration.

In these calculations, we have neglected the more long-range interactions J_i (with $i>4$). Their importance may be estimated using Curie temperature data Θ_c obtained from susceptibility measurements. In the case of a random Mn ion distribution, the ratio Θ_c/x is given by

$$\Theta_c/x=-\tfrac{2}{3}S_0(S_0+1)\sum_i z_iJ_i\ , \tag{5}$$

where z_i is the number of ith neighbors ($z_1=12$, $z_2=6,\ldots$). Using the values $J_1/k_B=-8.8$ K and $J_2/4k_B=-0.38$ K with equalities (1), the value obtained is $\Theta_c/x=-776$ K. This result is close to the one determined by Spalek *et al.*[19] ($\Theta_c/x=-831\pm63$ K) for a large concentration range of $Zn_{1-x}Mn_xTe$, and thus it is reasonable to neglect the other interactions.

Using Eq. (1), we have also neglected the NNN exchange couplings through three anions and two cations and couplings through longer ways. These additional couplings reduce the relative difference between J_2, J_3, and J_4 values. Thus, a more realistic value of J_2 should be between -1.52 and -0.6 [the last value corresponds to the result obtained from the same calculation in which the equality $J_2=J_3=J_4$ replaces Eq. (1)]. We notice the really good agreement with the result obtained from the spin-glass studies ($J_2\cong J_1/10$).

In this paper, we propose an alternative understanding of $Zn_{1-x}Mn_xTe$ magnetic properties considering an exchange neighborhood, in the sense of superexchange, different than the crystallographic one. For a zinc blende structure, this interpretation modifies only the long-range exchange interaction. The main interaction J_1 remains the same. For other crystallographic structures, the modification due to a superexchange environment would be more important, particularly when the main interaction is not necessarily between the NN ions. In the case of $(Cd_{1-x}Mn_x)_3As_2$, for example, the cation-anion-cation distances are the same for the first, second, and third neighbors. Consequently, the determination of J_1, J_2, and J_3 becomes difficult and the hypothesis of a monotonic decrease of exchange constant with direct distance[23] should be reconsidered taking into account a prevailing superexchange.

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