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MAGNETIC PROPERTIES OF SEMIMAGNETIC SEMICONDUCTOR MATERIALS $A^{II}B^{VI}$ AND $A^{IV}B^{VI}$ TYPE

ZAHARI ZLATANOV

Department of General Physics

Захари Златанов. МАГНИТНИ СВОЙСТВА НА ПОЛУМАГНИТНИ ПОЛУПРОВОДНИКОВИ МАТЕРИАЛИ ОТ СИСТЕМИТЕ $A^{II}B^{VI}$ И $A^{IV}B^{VI}$

В статията са представени някои от магнитните свойства на II–VI и IV–VI полумагнитни полупроводници (ПмПп), легирани с преходни метали и йоните на редкоземни елементи. Дадени са различни методи за определяне на обменните взаимодействия. Първоначално се използва температурата на Кюри-Вайс θ, получена от измерване на магнитната възприемчивост при високи температури. Второ, определя се структурата на енергетичните нива на малки кластери от спинове, главно такива от двойки йони. Обменното взаимодействие е по-слабо в ПмПп, съдържащи редкоземни йони, отколкото в тези материали с преходни метали, доколкото магнитните свойства на редкоземните йони зависят главно от техните f-електрони, които са свързани по-силно с ядрата, отколкото електроните от d-обвивките, примерно при елемента Mn. Магнитната възприемчивост на II–VI полумагнитните полупроводници е изследвана на образци с концентрации на примесния елемент в областта от стойности $0,01 < x < 0,1$. Представените резултати, като данните за магнитната възприемчивост, са анализирани, използвайки модела на NN-кластерите (модел J_1). Резултатите от анализа дават стойности на обменната константа между близките съседни йони от $-6,9$ за $Cd_{1-x}Mn_xTe$ до $-11,9$ за $Zn_{1-x}Mn_xTe$. Определяща за стойността на J_1 е температурата на Кюри-Вайс θ. В II–VI ПмПп (такива като $Cd_{1-x}Mn_xTe$) обменното взаимодействие намалява монотонно с разстоянието. При някои IV–VI сплави NN-обменното взаимодействие е по-слабо в сравнение с NNN-взаимодействието (примерно при $Pb_{1-x}Gd_xTe$). Данните за IV–VI материалите се обясняват чрез отчитане на взаимодействието между изолираните редкоземни йони и двойки от йони, както и отчитане на приноса от по-големи кластери, който е незначителен за малки стойности на x ($x < 0,01$). При $Pb_{1-x}Gd_xTe$ материалите се предполага обменно взаимодействие между следващите след най-близките съседни (NNN) магнитни йони като следствие от кристалната структура тип NaCl.

Zahari Zlatanov. MAGNETIC PROPERTIES OF SEMIMAGNETIC SEMICONDUCTOR MATERIALS $A^{II}IB^{VI}$ AND $A^{IV}B^{VI}$ TYPE

Magnetic properties of II–VI and IV–VI semimagnetic semiconductors doped with transition-metals and rare-earth ions are presented. Different types of methods of determining the exchange interactions were reviewed. The first one uses the Curie-Weiss temperature θ, obtained from susceptibility measurements at high temperatures. The second consists of several methods of probing the energy-level structure of small clusters of spins, mostly pairs. The exchange interaction is smaller in SmSs containing rare-earth ions than in those containing transition metals, since the magnetic properties of rare-earth ions depend mostly on their f-shell electrons, which are shielded and bound more closely to the nucleus than the d-shell electrons in Mn. Susceptibility measurements on the II–VI semimagnetic semiconductors have been performed on samples with $0.01 < x < 0.1$. The results given in the present study, as the susceptibility data were analyzed with good agreement using NN clustertmodel (J_1 model). The results give an exchange constant between nearest neighbors -6.9 for $Cd_{1-x}Mn_xTe$ to -11.9 for $Zn_{1-x}Mn_xTe$. Values of J_1 deduced from the Curie-Weiss temperature θ. In II–VI SmSs (such as $Cd_{1-x}Mn_xTe$) the exchange interaction decreases monotonically with the distance. In several IV–VI compounds, the NN interaction is smaller in comparison with the NNN interaction (for example $Pb_{1-x}Gd_xTe$). The data for IV–VI materials also have been explained by taking into account isolated raretearth ions and pairs with contributions from larger clusters being nearly negligible for the small values of x ($x < 0.01$) that were investigated. As consequence of the rock salt structure of these compounds is proposed also an exchange interaction between next-nearest neighbor ions.

Keywords: semimagnetic semiconductors, magnetic susceptibility, impurities, microstructure

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1. INTRODUCTION

Semimagnetic Semiconductors (SmSs) (or Dilute-magnetic semiconductors) are compound semiconductors in which a fraction of the cations are magnetic. For many purposes one may regard a SmSs as being composed of two subsystems: 1) the magnetic subsystem consisting of the 3d magnetic ions, and 2) the electronic subsystem consisting of the stlike electrons and p-like holes near the conduction and valence band edges. The most striking phenomena observed in SmSs are those which arise from the sp-d interaction between the magnetic and electronic subsystems. Because of this interaction, a perturbation of the magnetic subsystem, e.g., by applying a magnetic field $\boldsymbol{H}$ or changing the temperature T, affects the electronic subsystem. This leads to a host of interesting magneto-optical and magneto-transport phenomena, such as a giant Faraday rotation, bound magnetic polarons, and giant magnetoresistance anomalies [1–3].

Control of both spins and charges of doped carriers has attracted much interest in Semimagnetic Semiconductors (SmSs) because the combination of the two degrees of freedom is expected to open up new functionalities in optoelectronic and magnetoelectric devices [4,6,7,8]. In the case of 3d transition metals doped III–V materials (for example $Ga_{1-x}Mn_xAs$) adding Mn into GaAs provides both carriers and a local spins [5]. The electronic structure of Mn-doped II–VI based SmSs has been extensively studied by photoemission spectroscopy [9,10]. For investigation of electronic structure parameters of some materials, as $Zn_{1-x}Mn_xY$ (Y = Te, Se and S) cluster model analyses have been used [11].

In this study shall be focusing on the 3d magnetic subsystem (and 4f for IV–VI SmSs). Specifically, shall review the experimental methods which have been used to study the d-d exchange interactions between the 3d magnetic cations. Very little of what shall say has to do with the sp-d interaction. For the purposes of this study SmSs are merely examples of dilute magnetic systems with antiferromagnetic interactions.

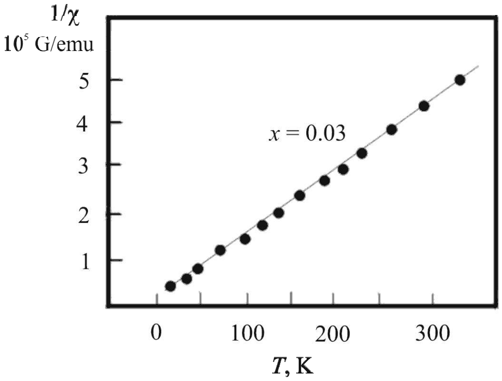


Fig. 1. Susceptibility data for $Zn_{1-x}Mn_xTe$ material. These data are used to extract θ and value of J_1 estimated from θ: $J_1/k_B = -12$

Two types of methods of determining the d-d exchange interactions will be reviewed. The first uses the Curie-Weiss temperature θ, obtained from susceptibility measurements at high temperatures. The second consists of several techniques of probing the energy-level structure of small clusters of spins, mostly pairs. Because the information obtained from studies of pairs is more accurate, and also because of our own interest, the emphasis will be on "pair spectroscopy". The discussion will be limited to II–VI SmSs containing either manganese or (cobalt) Fe, (and IV–VI containing rare-earth elements, as gadolinium).

2. THEORETICAL MODELS, EXPERIMENTAL DATA AND DISCUSSION

2.1. CRYSTAL STRUCTURE AND MAGNETIC ION

The best known examples of SmSs are II–VI compounds, e.g., $Cd_{1-x}Mn_xTe$. (Here, and throughout, x is the fraction of cations which are magnetic.) The crystal structure of these compounds is either zinc-blende or wurtzite. In both structures, each cation is at the center of a tetrahedron whose corners are occupied by the surrounding four anions. There is strong evidence that the magnetic ions in SmSs are at the cation sites. Thus, a magnetic ion in either the zinc-blende or wurtzite structures finds itself in a tetrahedral crystal field. In the case of the wurtzite structure there is, in addition, a small unaxial crystal field.

Looking at the cations alone, the cation sublattice of the zinc-blende structure is fcc, while that of the wurtzite is hcp. For either structure, each cation has 12 nearest-neighbor (NN) cations, and 6 next-nearest-neighbor (NNN) cations. The NNN distance r_{NNN} is larger than the NN distance r_{NN} by a factor of $2^{1/2}$. The number of NN cations (both magnetic and non-magnetic) is usually designated by z_1, while the number of NNN cation sites is designated by z_2. Thus, $z_1 = 12$, and $\mathrm{z}_2 = 6$. Next-nearest-neighbors are also called second neighbors. The numbers and distances of neighbors which are farther away than r_{NNN} (e.g., 3rd, 4th and 5th neighbors) are different for the zinc-blende and wurtzite structures.

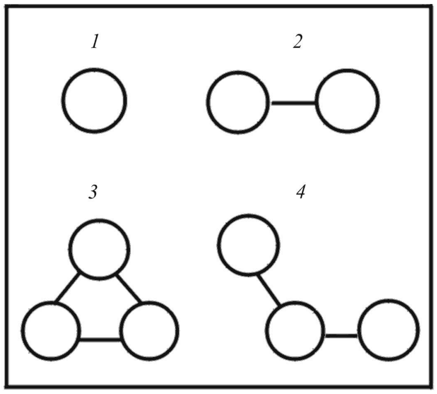


Fig. 2. Small-size clusters (not larger than triplets): *1*—single (consisting of a magnetic ion, which has no NN magnetic neighbors), *2*—NN pair (or J_1 pair) (consisting of two NN magnetic ions which have no other magnetic NN's), *3*—closed J_1 triplet (CT), *4*—open J_1 triplet (OT). These clusters are formed only when the fraction x of magnetic ions is small, $x < 0.1$

In nearly all the works to date the magnetic ions in the II–VI SmSs were either Mn^{++} or Co^{++} or Fe^{++}. Among these, SmSs with Mn^{++} were studied much more extensively. For a free Mn^{++} ion the $3\mathrm{d}^5$ electronic configuration leads, via Hund's rules, to an ${}^6S_{5/2}$ ground state with a zero orbital angular momentum, a spin $S = 5/2$, and a $\boldsymbol{g}$ factor of 2.00. If the Mn^{++} ion is placed in a crystal then the crystal field should not split the ${}^6S$ ground level because this level is orbitally non-degenerate. No spin-orbit splitting of the ground level is expected either, because $L = 0$. Experimentally, EPR studies [12] show some splittings of the ground state, but these splittings are very small, much less than 0.1 K. The $\boldsymbol{g}$ factors of Mn^{++}

in II–VI SmSs differ from 2.00 by less than 1%. Thus, for most purposes the Mn^{++} ion may be regarded as an ideal spin with $S = 5/2$ and $\boldsymbol{g} = 2$.

For Fe^{++}, the $3\mathrm{d}^6$ electronic configuration leads to a ${}^5D_4$ ground state for the free ion. The splittings of the ${}^5D$ level in a crystal with the zinc-blende or the wurtzite structures was discussed theoretically in [13,14,15]. The crucial result is that the ground state in the crystal is a singlet.

Such a ground state is magnetically inactive because it does not split when a magnetic field is applied. At low temperatures, where only the ground state is occupied, the susceptibility is due to the admixture of the ground state with excited states. This is the well known Van Vleck paramagnetism, which is temperature independent at low T. Because the first excited state of Fe^{++} in these materials is only $\sim$ 20K above the ground state, such a temperature independence is achieved only in the liquidthelium range.

The singlet ground state of Fe^{++} makes the physics of the magnetism of this ion quite different from that of Mn^{++}. Here we shall be concerned only with the latter two ions. A review of the magnetism of Fe^{++} in SmSs was recently given by Twardowski [16].

3. MAGNETIC INTERACTIONS OF THE 3d IONS

Our starting point is the individual 3d ions. As discussed above, a Mn^{++} ion may be regarded as an ideal spin $S = 5/2$, and a Co^{++} ion may be regarded as an effective spin $S = 3/2$. The latter is subjected to a weak singletion anisotropy, DS_z^2, if the ion is in the wurtzite structure.

From general experience with 3d ions one expects that the dominant magnetic coupling between these ions is the isotropic exchange interaction

$$\boldsymbol{H}_{\mathrm{exch}} = -2 \sum_{<ij>} J_{ij} S_i S_j, \tag{1}$$

where J_{ij} is exchange constant between spins S_i and S_j, and the sum is on all pairs <ij> of magnetic ions. Usually the exchange constants J_{ij} decrease rapidly with distance. Therefore one expects that the exchange constant $J_1 \cong J_{\mathrm{NN}}$, between NN magnetic ions, will be the largest.

Theoretical calculations of the exchange constants for Mn^{++} ions in II–VI SmSs were carried out by Larson et al. [17]. They showed that superexchange is the dominant exchange mechanism, and that J_1 is the largest exchange constant. This J_1 is antiferromagnetic (negative, in our notation), with a typical value of -10 K. The second-neighbor exchange constant $J_2 \cong J_{\mathrm{NNN}}$ is also antiferromagnetic, and is an order of magnitude smaller than J_1.

Two other types of exchange interactions, besides the isotropic exchange, may be present [18]. The usual (symmetric) anisotropic exchange is that part of the exchange interaction which depends on the directions of the spins relative to the lattice, and which is symmetric with respect to the interchange of the two interacting spins.

One typical term, sometimes called the pseudodipolar exchange, has the form

$$D'(3S_{iz}S_{jz} - S_iS_j).$$

In the present materials one expects this anisotropic exchange to be very small compared to the isotropic exchange [19]. We shall ignore the symmetric anisotropic exchange entirely.

A second type of anisotropic exchange is the Dzyaloshinski-Moriya (DM) interaction, which is antisymmetric with respect to the interchange of the two interacting spins. For a pair of spins, i and j, it has the form

$$\boldsymbol{H}_{\mathrm{DM}} = -2D_{ij} \cdot (S_i \times S_j). \tag{2}$$

The largest D_{ij} is expected to be for nearest neighbors. Its magnitude D_1 for NN Mn^{++} ions was calculated by Larson and Ehrenreich [20]. The somewhat surprising result is that D_1 depends mainly on the spin-orbit coupling in the anion. As a result, D_1 increases with the atomic number of the anion, i.e., largest for tellurides and smallest in sulfides. Even for the tellurides the DM term is small, i.e., $|D_1/J_1| = 0.05$. For this reason we shall ignore the DM term in much of our discussion. Its effects will be considered separately, as a perturbation.

In the presence of a magnetic field $\boldsymbol{H}$, there is a Zeeman interaction

$$\boldsymbol{H}_{\mathrm{Zeeman}} = \sum_i g\mu_B S_i \cdot \boldsymbol{H}, \tag{3}$$

where μ_B is the Bohr magneton. Here, the tiny anisotropy of the g tensor was ignored, and this tensor was replaced by a scalar $\boldsymbol{g}$ factor. This term arises from the admixture of the ground state with higher orbital states [13, 21]. The effects of this term are usually unimportant except at high temperatures. This term will be included only when needed.

4. EXCHANGE CONSTANTS FROM THE CURIE-WEISS TEMPERATURE

The magnetic susceptibility of SmSs was discussed by Spalek et al. [22]. At high temperatures the susceptibility per unit volume χ obeys the Curie–Weiss law

$$\chi = \frac{C}{T - \theta}\,. \tag{4}$$

The Curie constant C is given by

$$C = \frac{xNg^2\mu_B^2 S(S+1)}{3k_B}, \tag{5}$$

where N is the total number of cations (magnetic and nonmagnetic) per unit volume, and k_B is the Boltzmann constant. The Curie-Weiss temperature θ is given by

$$\theta = \frac{2xS(S+1)}{3k_B} \sum_i z_i J_i, \tag{6}$$

where J_i is the exchange constant between a central magnetic ion and a magnetic ion which is on the i-th coordination sphere (sphere of i-th distant neighbors), and z_i is the number of cation sites on that sphere. Assuming that J_1 is much larger than all other exchange constants, Eq. (6) gives

$$\theta \cong \frac{2z_1xS(S+1)J_1}{3k_B}, \tag{7}$$

where $z_1 = 12$ for the present materials.

Equations (6) and (7) are similar to the standard expressions for θ in an ordinary undiluted paramagnet ($x = 1$), except that in a SmSs z_i is replaced by z_ix. The crucial assumption behind this replacement is that the magnetic ions are randomly distributed over the cation sites. For such a random distribution the average number of magnetic ions on the i-th coordination sphere is z_ix.

Experimental data for θ are used to obtain information about the J_i's, via Eqs.(6) or (7). The most common practice has been to use Eq.(7) to estimate J_1. Another use of θ is to check that the magnetic ions are, in fact, randomly distributed. If this is the case then, from Eq.(6), θ should be proportional to x. Here, it is assumed that the J's are independent of x, which is expected to be true if the range of x is not too wide.

Table 1. Values of J_1 deduced from the Curie-Weiss temperature θ

Material	J_1/k_B, K	Ref.
$Cd_{1-x}Mn_xTe$	- 6.9	22
$Cd_{1-x}Mn_xSe$	-10.6	22
$Zn_{1-x}Mn_xTe$	-11.9	22
$Zn_{1-x}Mn_xSe$	-13.7	23

In extracting θ from the experimental data, several precautions must be exercised. The measured susceptibility must be corrected, to account for the (negative) diamagnetic susceptibility of the lattice, χ_d. (In the case of Co^{++}, one must also subtract a small temperature independent term which arises from the admixture of higher orbital states). In all cases, it is necessary to ascertain that the temperature is sufficiently high for Eq.(4) to hold. A good way to do this is to estimate the error in θ by performing calculations using high-temperature series expansions.

Fig.1 shows an example of susceptibility data used to extract θ.

In Table 1 are listed some values of J_1 estimated from θ using Eq.(7).

5. NEAREST–NEIGHBOR CLUSTER MODEL (J_1 MODEL)

The most accurate methods of determining J_1 are based on studies of pairs, each consisting of two magnetic ions which are NN of each other. The NN cluster model (J_1 model) is a simple model which brings out the physics behind these methods. The main assumption of the model is that all exchange interactions except those between NN's can be ignored. This is a reasonable assumption in view of the fact that J_1 is the dominant exchange constant. Of course the NN cluster model will fail in some situations. For example, the magnetization calculated from this model may be seriously in error when J_2 is larger than both $k_B T$ and the Zeeman energy per spin. For now consider a Hamiltonian which includes only NN isotropic exchange interactions [Eq.(1)] and the Zeeman energy [Eq.(3)]. Distant-neighbor exchange interactions and anisotropies of all kinds are ignored.

The NN exchange interactions can be regarded as "bonds" connecting NN spins. The magnetic ions (or spins) in a SmSs are then viewed as belonging to clusters of different sizes. The smallest cluster is a single, consisting of a magnetic ion which has no NN magnetic neighbors. The next type of cluster is the NN pair (J_1 pair), consisting of two NN magnetic ions which have no other magnetic NN's. Following the pairs there are two types of triplets: closed and open. A closed J_1 triplet (CT) consists of three magnetic ions any two of which are coupled by J_1. In an open J_1 triplet (OT) there are J_1 bonds only between the first and second, and between the second and third spins (but not between the first and third spins). These clusters are sketched in Fig.2. Besides these smalltsize clusters there are larger clusters, such as various types of quartets and quintets.

The NN cluster model has been employed in magnetism for many years. The model is useful only when the great majority of spins are in small-size clusters, usually not larger than triplets. This is the case only when the fraction x of magnetic ions is small, say $x < 0.05$ or, at most, $x > 0.1$.

For each small cluster it is possible to obtain an exact solution for the behavior as a function of T and $\boldsymbol{H}$. This can be done because (in the J_1 model) the individual clusters are independent of each other. Having obtained these solutions, one can predict several effects. First, there is resonance or Raman-like excitations between energy levels of clusters of various types. Second, by summing the contributions of all the clusters one can calculate macroscopic quantities such as the susceptibility, the magnetization, or the specific heat.

The solution for a single isolated spin is trivial. The energy levels resulting from the Zeeman splittings can be probed by EPR, but this only yields the $\boldsymbol{g}$ factor (in this simple model). The magnetization of the singles follows the Brillouin function, and their susceptibility obeys the Curie law.

The Hamiltonian for a J_1 pair is

$$\mathrm{H} = -2J_1 S_1 \cdot S_2 + g\mu_\mathrm{B} H(S_{1z} + S_{2z}). \tag{8}$$

This Hamiltonian is diagonal in the magnitude S_T of total spin of the pair, and in the projection m of the total spin S_T along $\boldsymbol{H}$. The energy levels can be obtained by noting that:

$$S_\mathrm{T} = S_1 + S_2,$$

obeys the relation

$$S_\mathrm{T} \cdot S_\mathrm{T} = S_1 \cdot S_1 + S_2 \cdot S_2 + 2S_1 \cdot S_2. \tag{9}$$

With $S_1 = S_2 = S$ this leads to the energies

$$E = \langle S_\mathrm{T} m | H | S_\mathrm{T} m \rangle = -\frac{J_1}{S_\mathrm{T}(S_\mathrm{T}+1)} - 2S(S+1) + \mu_\mathrm{B} m H. \tag{10}$$

The energy-level diagram for a pair at $\boldsymbol{H} = 0$ is shown in Fig. 3. (This figure is for Mn^{++}.)

For the ground level, the total spin is zero, corresponding to an antiferromagnetic alignment of S_1 and S_2. For each successive level the total spin S_T increases by one unit, and the energy increases by an integer multiple of $2\,|J_1|$.

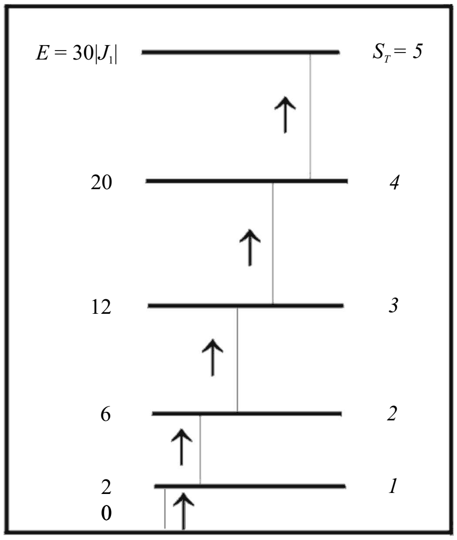


Fig. 3. The energy-level diagram for pair at $\boldsymbol{H} = 0$ (these levels are for Mn^{++})

The energy levels of open and closed J_1 triplets are known [24], but will not be discussed here in detail. For either type of triplet the total spin S_T and its projection m along H are good quantum numbers. For a CT of either Mn^{++} , the ground level at $\boldsymbol{H} = 0$ has $S_\mathrm{T} = S$, i.e., 5/2 for Mn^{++}. The first excited level is several $|J_1|$ higher.

The number of clusters of a given type depends on the probability P_i that a magnetic ion is in this type of cluster. These probabilities were first calculated by Behringer for various crystal structures [25]. A random distribution of the magnetic ions was assumed. Let P_1, P_2, P_3, P_4 be the probabilities that a magnetic ion will find itself in a cluster which is a single, a J_1 pair, an open J_1 triplet (OT), or a closed J_1 triplet (CT), respectively. Then for the zinc–blende and wurtzite structures, $P_1 > P_2 > P_3 > P_4$ when $x < 0.1$.

The probability P_2 for being in a pair reaches a maximum of 24% at $x = 0.05$. The maximum probabilities of being in an OT or in a CT are 11% and 2.5%, respectively. Usually the calculations based on the NN cluster model consider only clusters with three spins or less. The probability $P{>}3$ that a magnetic ion is in a cluster larger than a triplet increases with x. At $x = 0.03$, 0.05, and 0.10 the values of $P > 3$ are 3%, 11%, and 41%, respectively.

For any cluster the magnitude S_T of the total spin is a good quantum number. The value of S_T in the zero–field ground level of the cluster will be called S_T (ground). At the other extreme, at very high magnetic fields where all the spins in the cluster are parallel, the cluster is in a state with $S_\mathrm{T} = S_\mathrm{T}$ (ferro). The designation “ferro” emphasizes the ferromagnetic (parallel) alignment of the spins. For all clusters except singles,

$$S_\mathrm{T}(\text{ground}) < S_\mathrm{T}(\text{ferro}).$$

This is a consequence of the antiferromagnetic interaction.

For a single, $S_\mathrm{T}(\text{ground}) = S_\mathrm{T}(\text{ferro}) = S$, i.e., 5/2 for a single of Mn^{++}. For a pair, $S_\mathrm{T}(\text{ground}) = 0$, and $S_\mathrm{T}(\text{ferro}) = 2S$. For an OT, $S_\mathrm{T}(\text{ground}) = S$, which is only a third of the value of $S_\mathrm{T}(\text{ferro})$. A CT of Mn^{++} has $S_\mathrm{T}(\text{ground}) = 1/2$. For a CT of Mn^{++} this corresponds to 1/15 of the value of $S_\mathrm{T}(\text{ferro})$. For larger clusters, such as the various types of quartets, $S_\mathrm{T}(\text{ground})$ is expected to be only a fraction of $S_\mathrm{T}(\text{ferro})$. This is a consequence of the antiferromagnetic interaction. At a temperature $\boldsymbol{k}_\mathrm{B} T \ll 2|J_1|$, and when $\boldsymbol{H} = 0$, all clusters are in their zero-field ground levels.

6. EFFECT OF DISTANT-NEIGHBOR INTERACTIONS

The exchange interactions between distant neighbors are weak compared to the NN exchange interaction. These effects were treated by Larson et al. using an effective-field method [26].

The J_1–J_2 model for low x

Consider a SmSs with $x = 0.01$. To find out how the NNN interaction affects to J_1 pairs the $J_1 - J_2$ model was introduce. In this model, both J_1 and J_2 are non-zero, but all other J's vanish. We also assume that both J_1 and J_2 are antiferromagnetic, and that $|J_2| \ll |J_1|$. Because x is low, it is useful to consider a cluster model. There are now three categories of clusters: 1) pure J_1 clusters, with J_1 bonds only; 2) pure J_2 clusters and 3) mixed clusters, with both J_1 and J_2 bonds. Each of these three categories contains clusters of different types. The various types of clusters which occur in the J_1–J_2 model (up to triplets), as well as their probabilities, were discussed by Kreitman and Barnett [27].

In the NN cluster model (J_1 only), 100% of the spins in the present example (with $x = 0.01$) are in J_1 pairs. When J_2 is included, 92.3% of these original pairs still remain as pure J_1 pairs, but 6.6% of the original pairs are now in mixed open triplets (each with a J_1 and a J_2 bonds). The remaining 1.1% of the original J_1 pairs are in larger mixed clusters. These larger clusters were ignored and in the model focus on the two main groups: pure J_1 pairs, and mixed open triplets

Larson et al. [26] used an effective field method to treat the influence of distant-neighbor interactions (J_2, J_3, etc.) on the J_1 pairs. Each J_1 pair sees an effective field $\boldsymbol{h}_c$ due to the distant neighbors. This $\boldsymbol{h}_c$ is usually different for different J_1 pairs, because the positions of the distant neighbors relative to a pair are different. For example, some J_1 pairs have no NNNs, some have one NNN, and others have two or more NNNs. Thus, in any given crystal there is a distribution of $\boldsymbol{h}_c$'s.

Investigation of IV–VI SmSs

Magnetic properties of IV–VI solid solutions containing rare-earth ions have been investigated , though not as widely as those of transition-metal-doped II–VI and IV–VI SmSs [28]. In some materials, as $Sn_{1-x}Gd_xTe$ and $Pb_{1-x}Gd_xTe$ the magnetic susceptibility was measured and a small antiferromagnetic exchange interaction found [29,30,31]. The data have been explained by taking into account isolated rare-earth ions (that is the case of cluster–single magnetic ion–or spin) and pairs with contributions from larger clusters being nearly negligible for the small values of x that were investigated (Fig.4). The nearest-neighbor exchange interactions that were obtained were quite small, similar to those in other IV–VI SmSs with the NaCl structure.

Table 2. Exchange parameter of IV-VI SmSs as a function of concentration x

Material	x	J/k_B, K
$Sn_{1-x}Gd_xTe$	0.09	-0.56
	0.05	-0.69

A summary of the exchange parameter values for three rare-earth-doped IV–VI SmSs is given in Table II. It is estimated, that the errors in parameters are no more than 30%. The nearest-neighbor exchange interaction in $\mathrm{Sn}_{1-x}\mathrm{Gd}_x\mathrm{Te}$ is antiferromagnetic, with the value of J/k_B –0.70

In the Gd chalcogenides, nearest-neighbor exchange and next-nearest-neighbor exchange are antiferromagnetic. Exchange parameter in $\mathrm{Pb}_{1-x}\mathrm{Gd}_x\mathrm{Te}$ is J/k_B [K] = –0.36.

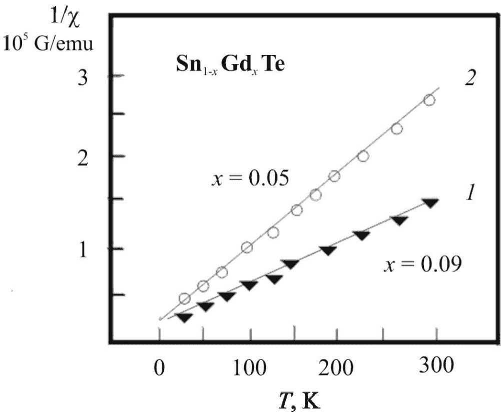


Fig. 4. Inverse susceptibility of $\mathrm{Sn}_{1-x}\mathrm{Gd}_x\mathrm{Te}$ (the measurements were carried out up to 300 K): *1*—for sample with $x = 0.09$, *2*—for $x = 0.05$. The samples are cutting from single crystals grown by the Bridgman technique

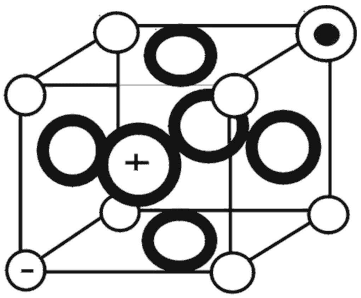


Fig. 5. Unit cell of PbTe monocrystalline material with structure type rock salt

Therefore, for our magnetically disordered, rare-earth-doped IV–VI SmSs the same superexchange model is used the same superexchange model as for Mn-doped IV–VI and II–VI SmSs [32], assuming that the magnetic properties of SmSs are determined mainly by the nearest-neighbor superexchange interaction via an anion. The exchange parameters J/k_B in rare-earth-doped SmSs are smaller in magnitude than in $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ and other Mn-doped IV–VI SmSs. The exchange interaction is expected to be smaller in SmSs containing rare-earth ions than in those containing Mn, since the magnetic properties of rare-earth ions depend mostly on their f-shell electrons, which are shielded and bound more closely to the nucleus than the d-shell electrons in Mn.

Lead telluride is a IV–VI semiconductor compound with rock salt structure. Gadolinium, which is a $4f^7$ rare-earth magnetic ion, was introduced in the lattice host PbTe to obtain $Pb_{1-x}Gd_xTe$ semimagnetic semiconductor alloys. The aim of investigation of the magnetic properties of these materials is to study the exchange effect between Gd ions in this structure.

Several works were devoted to the determination of the exchange constant between nearest-neighbors (NN) from susceptibility measurements [33,34]. In II–VI semimagnetic semiconductors (such as $Cd_{1-x}Mn_x$ Te), the exchange interaction decreases monotonically with the distance [35]. Because the crystallographic structure of $Pb_{1-x}Gd_xTe$ is different from those of the II–VI semimagnetic semiconductors (zinc blende or wurtzite), its exchange interactions could be analyzed as for the rare-earth magnetic semiconductor (non semimagnetic), GdTe, which has the same rock salt structure. In several of these compounds, the NN interaction is negligible in comparison with the next-nearest-neighbor (NNN) interaction.

When the NN ions interaction was the main exchange interaction [36] (the case of II–VI SmSs) a NN cluster model was usually used to account for the magnetic properties, because in wurtzite or zink-blende structures the exchange between magnetic ions is due to the superexchange interaction [37] and decreases monotonically with the ion-ion distance.

From the formula

$$\frac{2J}{k_{\mathrm{B}}} = \frac{3}{zS(S+1)}\frac{\theta}{x} \tag{11}$$

with J representing the NN interaction and z the number of NN ions ($z_1 = 12$) a J value in the range -0.25 to -0.5 K was found [34]. Obviously, if J is the NNN exchange constant (J_2 or J_{NNN}) their value becomes twice as high because there are six NNN ions ($z_2 = 6$) (which is in better agreement with the value in [34]). When the J_2 value is deduced directly from the Curie temperature, this value depends on the sample homogeneity (homogeneity about $x\%$ and single-phases).

In the case of monocrystalline $Pb_{1-x}Gd_xTe$, using the data from EPR experiments and data from structural investigations, as X-ray, microhardness—a model can be proposed of positions of magnetic ions in the crystal lattice PbTe (Fig. 5, Fig. 6). If the magnetic properties susceptibility and J_1 were measured (at lower concentrations $x < 0.1$), according J_1 model, it is possible confirme the model of ordering of magnetic ions in the host lattice (presented on Fig. 5). Such model of superlattice is shown, for example, on Fig. 7*a*) and Fig. 7*b*), for Gd ions at lower concentrations x ($x < 0.1$). Also the probability could be estimated for that crystal structure (using experimental data from magnetic measurements of other SmSs with the same crystal structure and similar magnetic properties). For the case of $x < 0.05$, from this model of the magnetic-ion superlattice $z_1 = 12$ and $z_2 = 6$ were obtained for NN and NNN, respectively.

The position of magnetic ions, into host lattice, as substitutional ions at lower concentrations x (not interstitial ions or large clusters), and coordination number

z are in agreement with the data from above mentioned studies. In this case, also can be proposed model of superlattice, formed from magnetic ions Gd.

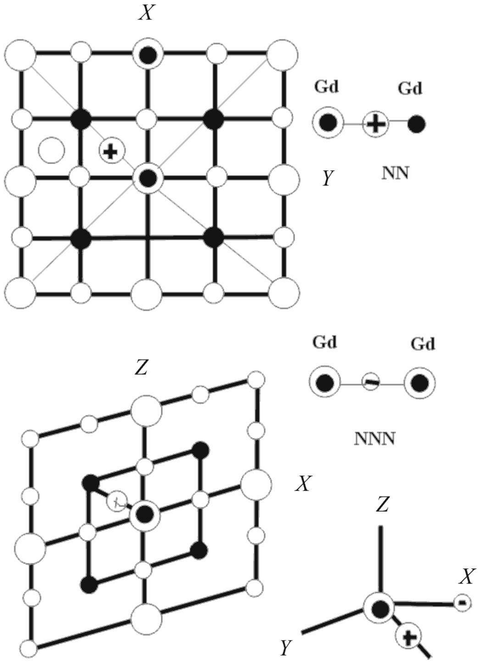


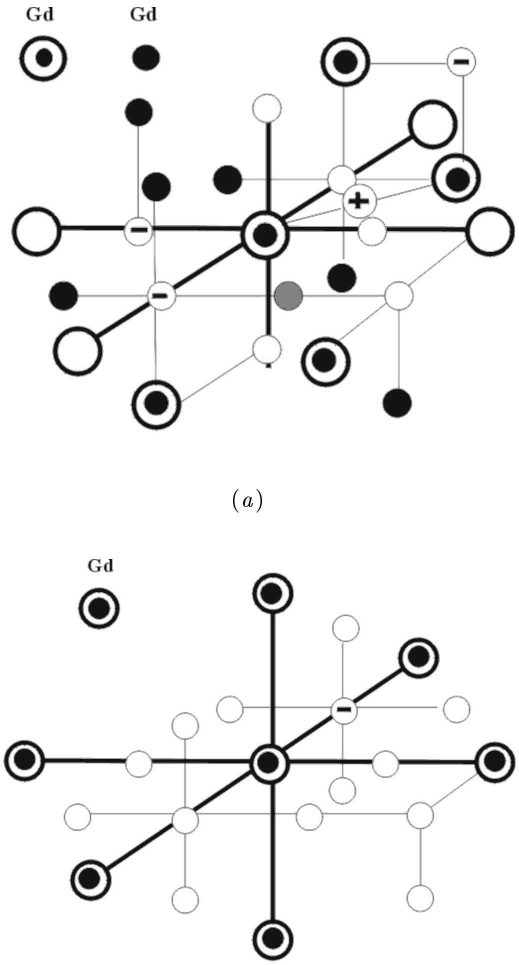
Fig.6. Impurity atoms ordering into host lattice PbTe in the case of NN and NNN exchange interactions at low concentrations of magnetic ions. For Pb $_{1-x}$Gd$_x$Te antiferromagnetic materials $x < 0.1$. (This example of magnetic ion ordering is for clusters type–1, see Fig.2, when have been superexchange interaction via anion into the host lattice

7. CONCLUSION

Theoretical calculations of the exchange constants J for Mn^{++} ions in II–VI SmSs showed that superexchange is the dominant exchange mechanism, and that J_1 is the largest exchange constant. This J_1 is antiferromagnetic (negative, in our notation), with a typical value of -10 K . The second–neighbor exchange constant $J_2 \cong J_{\mathrm{NNN}}$ is also antiferromagnetic, and is an order of magnitude smaller than J_1.

The NN cluster model is useful only when the great majority of spins are in small-size clusters, usually not larger than triplets. This is the case only when the fraction x of magnetic ions is small, say $x < 0.05$ or, at most, 0.1.

Looking at the cations alone, the cation sublattice of the zinc-blende structure is fcc, while that of the wurtzite is hcp. For either structure, each cation has 12 nearest-neighbor (NN) cations, and 6 next-nearest-neighbor (NNN) cations. (The NNN distance r_{NNN} is larger than the NN distance r_{NN} by a factor of $2^{1/2}$. The number of NN cations (both magnetic and non-magnetic) is usually designated by z_1, while the number of NNN cation sites is designated by z_2. Thus, $z_1 = 12$, and $z_2 = 6$. Next-nearest-neighbors are also called second neighbors. The numbers and distances of neighbors which are farther away than r_{NNN} (e.g., 3rd, 4th and 5th neighbors) are different for the zinc-blende and wurtzite structures.



(a)

(b)

Fig. 7. Position of magnetic ions gadolinium into $\mathrm{Pb}_{1-x}\mathrm{Gd}_x\mathrm{Te}$ SmSc with fcc structure at (a) J_{NN}, and (b) J_{NNN} with coordination numbers $z_1 = 12$, $z_2 = 6$, respectively

The magnetic properties of IV–VI SmSs $Sn_{1-x}Gd_xTe$ and $Pb_{1-x}G_xTe$ are similar. The average exchange interaction between the rare-earth ions is antiferromagnetic and the values of J/k_B lie below 1 K and are smaller than in manganese-doped, PbTe-based SmSs. This is probably due to the fact that the magnetic properties of rare-earth ions depend mostly on their f-shell electrons, which are shielded and bound more closely to the nucleus than the d-shell electrons in manganese.

In all rare-earth-doped IV–VI chalcogenides, the low-field susceptibility data indicates that there is the main antiferomagnetic exchange, possibly from nearest-neighbors or more distant next-nearest-neighbors.

The exchange interaction parameter J/k_B is larger in $Sn_{1-x}Gd_xTe$ than in $Pb_{1-x}Gd_xTe$. This result is consistent with the expectations of the model of superexchange interaction via anions in these materials, since the cation-anion spacing in SnTe is smaller than in PbTe.

The host lattice PbTe is IV–VI crystal with fcc structure. The model of ordering of magnetic ions Gd, also their place sites, as substitutional ions (not interstitial atoms or large clusters), and coordination number z were conformed by structural X-ray and EPR investigations. The model of superlattice, formed from magnetic ions gadolinium, is proposed for $Pb_{1-x}Gd_xTe$ semimagnetic semiconductor at low impurity concentrations $x < 0.1$.

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Zahari Zlatanov
St. Kliment Ohridski University of Sofia
Faculty of Physics
Department of General Physics
5, James Bourchier Blvd.
1164 Sofia, Bulgaria
E-mail: zlatanov@phys.uni-sofia.bg