

# Ground state splitting for the $Mn^{2+}$ ion in $PbMnTe$ compounds

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We propose a new mechanism leading to the ground state splitting for the  $Mn^{2+}$  ion in  $PbMnTe$  crystals. The splitting is due to two effects, one of which is the hybridization of  $3d$  electrons with the band states and the other is the internal spin orbit interaction in  $Mn^{1+}$  and  $Mn^{3+}$  states of the manganese ion. We also study the effect of a local crystalline distortion on the character and magnitude of the splitting. The theoretical predictions are compared to experimental results.

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## I. INTRODUCTION

Manganese is the most frequently used magnetic element serving as the substitutional ion in semimagnetic semiconductors (SMSC).<sup>1,2</sup> It is commonly believed that its outermost  $4s^2$  electrons contribute to the crystal bonds while the  $3d^5$  electrons remain localized and, according to Hund's rule, produce the total spin of the  $Mn^{2+}$  ion  $S=5/2$  and its total orbital momentum  $L=0$ . Thus, in the absence of an external magnetic field, the ground state of the Mn ion is sixfold spin degenerate and due to the vanishing angular momentum there is no direct influence of the crystal field on it. Such a picture of the manganese ion in SMSC serves as a starting point in a number of theoretical models describing many experiments like, for example, the magnetization or magnetic susceptibility measurements.

It turns out, however, that the degeneracy of the ground state is lifted. The nature of the splitting depends on the symmetry of the crystal. In the case of IV–VI SMSC as  $PbMnTe$  with the octahedral coordination we obtain two energy levels, which are two- and fourfold degenerate, respectively. If the symmetry is lowered, for example, in the uniaxial strain case, we obtain three doublets. The existence of splitting is confirmed in both II–VI and IV–VI SMSC by electron paramagnetic resonance (EPR) experiments revealing a characteristic five-line fine structure of the resonance spectrum frequently superimposed on a six-line hyperfine structure.<sup>3,4</sup>

During the last more than four decades a great number of models and calculations devoted to the origin of this splitting have been presented in the literature. In most of the papers devoted to the problem the main reason for the splitting is related to a certain admixture of higher-energy spin configurations to the manganese ion ground state  ${}^6S$ .<sup>5–7</sup> The total orbital momentum in these excited states is no longer equal to zero, and we obtain a certain influence of the crystal field on the state of the ion. The ground state  ${}^6S$  wave function is built either from pure atomiclike  $3d$  functions of Mn or contains certain admixture  $p$  or  $s$  type functions originating from the anions surrounding the Mn ion (covalency and overlap effects). Note, however, that in all these theories, the virtual,

excited states taken into account contain the same number of electrons on the  $3d$  orbital as the ground state, it means five. In other words the excited states are limited to the excited states of a single manganese ion and the effect of surrounding is taken into account by point charge type models, covalency and overlaps effects or, more recently, by the use of the so-called extended crystal field model.<sup>8</sup> The only exception found by us in the literature is the Pryce<sup>9</sup> spin-spin mechanism in which the excited configuration  $3d^4s$   ${}^6D$  has been considered.

In the present paper we propose another mechanism leading to the ground state splitting of Mn ion in the crystal field. Namely, we consider (virtual) electronic transitions in which, due to hybridization of  $3d$  orbitals with the surrounding  $s$  or  $p$  orbitals of tellurium, the number of  $3d$  electrons changes by  $\pm 1$  leading to virtual  $Mn^{+1}$  ( $3d^6$ ) or  $Mn^{+3}$  ( $3d^4$ ) electron states of the manganese ion. [Note that in II–VI and IV–VI SMSCs the ground state of the Mn ion is  $Mn^{2+}$  ( $3d^5$ )]. It means that the excited states of our system consist of  $Mn^{1+}$  and the hole in the valence band or  $Mn^{3+}$  and the electron in the conduction band. This type of virtual electron transitions was shown to be of primary importance for  $p$ - $d$  exchange coupling and  $d$ - $d$  magnetic interactions in SMSC.<sup>2,10</sup>

The physical mechanism leading to the splitting will be discussed later, here we only notice that the most important ingredients of our approach are  $sp$ - $d$  hybridization and spin-orbit coupling on a Mn ion. In  $Mn^{+1}$  and  $Mn^{+3}$  configurations the total orbital momentum does not vanish what results in nonzero coupling between orbital and spin degrees of freedom. Hybridization elements in our model depend on the geometry of the manganese surrounding and due to this we may study the influence of the strain on Mn ground state splitting.

In the present paper we concentrate on  $PbMnTe$  SMSC. However, the method we propose may be applied to other semiconductors containing Mn ions as impurities. Our approach enables one also to study the Fermi energy dependence of the splitting. What is particularly important is it automatically takes into account (via the semiconductor host band structure calculations) the spin-orbit interactions on the anions.

In our paper we do not discuss quantitatively all the models known in the literature. Our main aim is to show that for a reasonable set of parameters, the calculated, within the present model, splittings are of the same order of magnitude as observed in experiment and due to this the proposed mechanism should be considered when analyzing EPR spectra.

## II. THEORETICAL MODEL

In this section we construct the Hamiltonian of our model. Let us consider a PbTe crystal at temperature  $T=0$  with one lead atom replaced by the manganese atom. We assume that the band structure and the electron distribution around all the atoms remain the same as in a perfect PbTe crystal, the only difference is the presence of an additional  $d$  orbital with five electrons on one of the cation sites. This model is really simplified because it neglects a number of features related to a large difference between Pb and Mn atoms. However, we believe that its qualitative predictions should remain valid for some more sophisticated models, too. Let us for a moment neglect the hybridization of manganese  $d$  electrons with the band states. The ground state of such a system is sixfold degenerate, the free electrons fill the band states up to the Fermi level, and the factor of six comes from the degeneracy of manganese spin  $5/2$ . We denote this state by  $|\alpha M\rangle$  where  $-5/2 \leq M \leq 5/2$  is the projection of spin on the quantization axis directed along the (001) crystallographic direction. The states  $|\alpha M\rangle$  are the eigenstates of the unperturbed Hamiltonian  $H_0$ .

As was pointed out in the Introduction, we are also interested in the states of the system, for which the number of electrons on the  $d$  orbital is different from five. Let us denote by  $|\beta L^z S^z q_0\rangle$  the state with six electrons on the  $d$  orbital of Mn and one electron less in the Fermi sea. The band state of the electron transferred to the  $d$  shell is characterized by a set of quantum numbers  $q_0$  containing the wave vector from the first Brillouin zone, the number of the band, and one additional quantum number necessary to fully characterize the band state. In the absence of spin-orbit coupling it can be spin of the state, but we should note that in PbTe crystals the spin-orbit interaction is strong and cannot be neglected. From now on we include this quantum number in the band index  $n$ .

According to Hund's rule, for six electrons on the  $d$  shell the total orbital momentum is equal to 2, and the total spin is also equal to 2.  $L^z$  and  $S^z$  ranging between  $-2 \leq L^z \leq 2$  and  $-2 \leq S^z \leq 2$  in the state  $|\beta L^z S^z q_0\rangle$  are the projections on the direction of quantization axis.

Similarly, we denote by  $|\gamma L^z S^z q_0\rangle$  the state with four electrons on the  $d$  shell of manganese and one additional electron  $q_0$  in the band. In the unperturbed Hamiltonian  $H_0$ , we also include the *internal* manganese spin-orbit coupling. Due to the coupling described by  $\lambda_{\beta,\gamma}$  the  $|\beta L^z S^z q_0\rangle$  and  $|\gamma L^z S^z q_0\rangle$  states, as the states with well-defined  $L^z$  and  $S^z$ , are *not* the eigenstates of the unperturbed Hamiltonian. In order to obtain the eigenstates we must build certain their combinations. Introducing the states  $|R_{\beta,\gamma}\rangle$ , which are the eigenstates of the manganese ion in the presence of internal spin-orbit coupling

$$|R_{\beta,\gamma}\rangle = \sum_{L^z S^z} c_{L^z S^z}^{\beta,\gamma} |L^z S^z\rangle, \quad (1)$$

we can write down an unperturbed Hamiltonian of our model in the following form:

$$H_0 = \sum_M E_\alpha |\alpha M\rangle \langle \alpha M| + \sum_{R_{\beta,q_0}} E_{R_{\beta,q_0}} |\beta R_{\beta,q_0}\rangle \langle \beta R_{\beta,q_0}| + \sum_{R_{\gamma,q_0}} E_{R_{\gamma,q_0}} |\gamma R_{\gamma,q_0}\rangle \langle \gamma R_{\gamma,q_0}|. \quad (2)$$

In principle, we can add to  $H_0$  the effects of the crystal field. However, as we verified, the effect of the crystal field on the final results is small. Thus, for simplicity, we neglect it in the following.

Let us turn back to the perturbation part of the Hamiltonian. We consider the perturbation due to the hybridization between the  $3d$  state of manganese and the band states. One can obtain the following expressions:

$$\langle \beta L^z S^z q_0 | H | \alpha M \rangle = \sum_{\sigma} (-1)^{1/2+\sigma} \sqrt{\frac{3-2\sigma S^z}{5}} \times \delta_{S,M+\sigma} \langle \phi_{L^z\sigma} | h | \chi_{q_0} \rangle, \quad (3)$$

$$\langle \gamma L^z S^z q_0 | H | \alpha M \rangle = \sum_{\sigma} (-1)^{L^z} \sqrt{\frac{3+2\sigma S^z}{5}} \delta_{S,M-\sigma} \langle \chi_{q_0} | h | \phi_{-L^z\sigma} \rangle, \quad (4)$$

where  $\sigma = \pm \frac{1}{2}$ ,  $\chi_{q_0}$  is the two-dimensional spinor describing the state  $q_0$ , and  $\phi_{L^z\sigma}$  is the product of the spatial  $3d$  function and the spinor  $|\sigma\rangle$ . Notice that  $h$  in the one-electron hybridization element  $\langle \phi_{L^z\sigma} | h | \chi_{q_0} \rangle$  is spin independent.

Using the hybridization matrix elements we can construct the following effective Hamiltonian for  $\alpha$  states:

$$H_{M,M'} = \sum_{R_{\beta,q_0}} \frac{\langle \alpha M | H | \beta R_{\beta,q_0} \rangle \langle \beta R_{\beta,q_0} | H | \alpha M' \rangle}{E_\alpha - E_{R_{\beta,q_0}}} + \sum_{R_{\gamma,q_0}} \frac{\langle \alpha M | H | \gamma R_{\gamma,q_0} \rangle \langle \gamma R_{\gamma,q_0} | H | \alpha M' \rangle}{E_\alpha - E_{R_{\gamma,q_0}}}, \quad (5)$$

where the sums over  $q_0$  in the first and second terms on the right-hand side run over states, energies of which are below and above Fermi level, respectively. Equation (5) is the standard formula of perturbation theory for degenerate spectra. It enables one to calculate the influence of higher energy states on the states we are mainly interested in.

In order to calculate the matrix elements  $\langle \phi_{L^z\sigma} | h | \chi_{q_0} \rangle$  we have to know the spinor wave functions  $\chi_{q_0}(\mathbf{r})$ . We apply the tight binding model of the electronic structure of PbTe, and we use the parameters presented in Ref. 11. We take into account  $p$  and  $s$  orbitals of cations and anions. For a given momentum  $\mathbf{k}$  belonging to the first Brillouin zone, the tight binding Hamiltonian is diagonalized in the basis of 16 functions of the form

$$\psi_{\mathbf{k}i\sigma}^{c/a}(\mathbf{r}) = \frac{1}{\sqrt{N_c}} \sum_{\mathbf{R}_{c/a}} e^{i\mathbf{k}\mathbf{R}_{c/a}} \varphi_i^{c/a}(\mathbf{r} - \mathbf{R}_{c/a}) |\sigma\rangle, \quad (6)$$

where  $\varphi_i^{c/a}(\mathbf{r} - \mathbf{R}_{c/a})$  with  $i=p_x, p_y, p_z, s$  are the cation or anion atomic orbitals centered on the lattice sites  $\mathbf{R}_c$  or  $\mathbf{R}_a$ , respectively,  $N_c$  is the number of cation sites, and  $|\sigma\rangle$  with  $\sigma = \pm \frac{1}{2}$  is the two-dimensional spinor. After diagonalizing the Hamiltonian matrix, for a given  $\mathbf{k}$  we obtain the band energies  $\varepsilon_{n\mathbf{k}}$  and corresponding eigenfunctions

$$\chi_{n\mathbf{k}}(\mathbf{r}) = \sum_i \sum_{\sigma} \sum_{p=c,a} a_{\mathbf{k}i\sigma}^p \psi_{\mathbf{k}i\sigma}^p(\mathbf{r}), \quad (7)$$

where index  $n=1, \dots, 16$  labels the band number.

The knowledge of the amplitudes  $a_{\mathbf{k}i\sigma}^p$  enables us to calculate the hybridization matrix elements  $\langle \phi_{L\sigma} | h | \chi_{q0} \rangle$ . We assume that there is only an overlap of  $3d$  electrons with six neighboring anions. The necessary values of interatomic matrix elements  $\langle \phi_{L\sigma} | h | \varphi_i^c \rangle$  are calculated according to Ref. 12 and can be expressed using three constants  $V_{sd\sigma}$ ,  $V_{pd\sigma}$ , and  $V_{pd\pi}$ .

Up to now we considered the manganese atom in a perfect octahedral surrounding characteristic for the cation sites in the rocksalt cubic lattice of PbTe. In a real three-dimensional crystal of PbMnTe, this octahedral symmetry may be assumed to be perfect only in the limit of vanishing manganese concentration. Due to the large difference between lead and manganese ionic radii, local deformations of the crystal lattice occur. These deformations are not limited to the nearest neighborhood, but extends over larger distances (a few lattice constants). With the increasing manganese content, the deformations originating from the different atoms start to overlap. Due to a random placement of Mn atoms in the lattice, we expect a random deviation of Mn-Te bond orientations from those in the perfect crystal. It turns out that these deflections have strong influence on the Mn<sup>2+</sup> ground state splitting. Another example of lowering octahedral symmetry around a manganese atom may be found in epitaxial layers which are usually deformed due to thermal strains caused by differences between the layer and substrate.

Let us turn now to the method of calculation of the effective Hamiltonian  $H_{M,M'}$  for the manganese ion in the deformed crystal. Our basic approximation is that the amplitudes  $a_{\mathbf{k}i\sigma}^p$  in Eq. (7) do not change, but the positions of tellurium atoms surrounding manganese and, consequently, the hybridization matrix elements  $\langle \phi_{L\sigma} | h | \chi_{q0} \rangle$  do. The assumption that the amplitudes  $a_{\mathbf{k}i\sigma}^p$  are the same in deformed and undeformed lattices can be justified by the fact that the electron wave function extends over the whole crystal and such local perturbations should not modify it significantly. In the case of epitaxial films we make the additional assumption that the band states of the strained film are the same as in bulk crystal and may be calculated according to the procedure described above. In other words, we are interested in the ground state splitting as a function of changes of Mn-Te bonds (their directions and lengths) with respect to the perfect octahedral environment.

### III. RESULTS AND DISCUSSION

For the perfect octahedral symmetry of the nearest neighborhood the sixfold degenerate ground state of the Mn<sup>2+</sup> ion splits in two levels—doublet and quartet. If the symmetry is lowered the state splits into three doublets. Both results are consistent with general predictions of the group theory and Kramers theorem.<sup>13</sup>

The physical cause of the splitting is due to the combined effect of  $sp-d$  hybridization and the spin-orbit interaction on the  $d$  shell of the Mn ion. In order to clarify this point, it is convenient to consider the spin-orbit interaction in excited states of the Mn ion,  $\lambda \mathbf{L} \cdot \mathbf{S}$ , as a perturbation. (In Sec. II it was included in a nonperturbed Hamiltonian and it was treated in an exact way.) Let us analyze the first order term with respect to  $\lambda$  using a picture of virtual states in the perturbation theory. For simplicity, we assume that spin is a good quantum number in the band. We start with the situation with the Mn<sup>2+</sup> ion in the state  $M$  and the Fermi sea of electrons. In the first step, due to the hybridization, an electron, for example with spin  $+\frac{1}{2}$ , jumps from the band to the manganese  $d$  shell. Since the spin is conserved, the spin of the ion becomes  $M + \frac{1}{2}$ . In the absence of spin-orbit interaction on the Mn<sup>2+</sup> ion, in the second step the electron with spin  $+\frac{1}{2}$  comes back to the band leaving the Mn<sup>2+</sup> ion in the state  $M$ . However, between these two steps, the internal spin-orbit interaction,  $\lambda \mathbf{L} \cdot \mathbf{S}$ , operates and, correspondingly, the Mn ion can be found in states with spin  $M + \frac{3}{2}$ ,  $M + \frac{1}{2}$ , and  $M - \frac{1}{2}$ . That is why after the transfer of electron with spin  $+\frac{1}{2}$  back to the band, the Mn ion may be found in states  $M+1$ ,  $M$ , or  $M-1$ . It results in nonzero off-diagonal matrix elements in the effective Hamiltonian  $H_{M,M'}$ , and the degeneracy of the ground state is removed. The above picture may be also extended for higher order terms in  $\lambda$ .

Which order of perturbation theory in  $\lambda$  is really important depends on the symmetry of the manganese neighborhood and on the spin-orbit interaction in the band (see the Appendix). In the case of perfect octahedral symmetry, the first order terms cancel when all band states from the first Brillouin zone are taken into account. It turns out that the first nonvanishing terms are of the order of  $\lambda^3$ . If the symmetry is lowered the main contribution is due to the first order terms if the spin-orbit interaction in the band is present. If the band states are states with well-defined spin, the lowest order terms are proportional to  $\lambda^2$ .

Because the effective Hamiltonian results from the second order perturbation theory with respect to the  $sp-d$  hybridization, the value of the splitting is quadratic in Slater-Koster hybridization parameters  $V_{sd\sigma}$ ,  $V_{pd\sigma}$ , and  $V_{pd\pi}$ . Thus we conclude that the ground state splitting is proportional to  $V^2 \lambda^n$  where  $V$  is the  $sp-d$  hybridization strength and the exponent  $n \geq 1$  depends on the manganese neighborhood symmetry and the presence of the spin-orbit interaction in the band. The main contribution to the splitting comes from the valence and conduction bands because for these bands the energy cost of transferring an electron from or to the  $3d$  orbital is smallest. Numerical analysis indicates, however, the importance of the integration over the entire first Brillouin zone. One cannot limit the integration to the nearest neigh-

borhoods of the main extrema of the bands. This shows that the model of the semiconductor band structure is an important ingredient of the calculations.

Let us summarize now the main steps leading to the calculation of the effective Hamiltonian  $H_{MM'}$ . First, the eigenproblems of the  $\text{Mn}^{1+}$  and  $\text{Mn}^{3+}$  ions are solved. We obtain eigenenergies  $\epsilon_{R_{\beta/\gamma}}$  and the coefficients  $c_{L^z S^z}^{\beta/\gamma}$  which express the eigenvectors of  $\lambda_{\beta/\gamma} \mathbf{L} \cdot \mathbf{S}$  Hamiltonian in the  $|L^z S^z\rangle$  basis, Eq. (1). For pure spin-orbit interaction these coefficients are easily expressible in terms of Wigner  $3j$  symbols. However, when we add the interaction of  $\text{Mn}^{1+}$  or  $\text{Mn}^{3+}$  ions with the crystal field potential then the analytical formulas do not exist and that is why the diagonalization is performed numerically. The coefficients  $c_{L^z S^z}^{\beta/\gamma}$  are necessary to obtain matrix elements in the nominators in the formula in Eq. (5) from matrix elements from Eqs. (3) and (4).

The next step is the numerical integration over all states in the first Brillouin zone and the summation over all bands. It turns out that if the number of integration points exceeds 5000, the final result practically does not change with further decreasing of integration steps.

For each state  $q \equiv n\mathbf{k}$  from the first Brillouin zone (integration point), by diagonalizing the tight binding Hamiltonian,<sup>11</sup> we calculate the energy  $\epsilon_q$  and the band state wave function  $\chi_{n\mathbf{k}}$ , Eq. (7). For a given strain tensor we calculate the relative positions of six tellurium atoms with respect to the manganese atom. These positions enter Eq. (6) as the points around which the  $p$  and  $s$  orbitals of neighboring Te atoms are centered. The dependence of the Slater-Koster interatomic matrix elements on the relative positions of two atoms is known.<sup>12</sup> Thus having the amplitudes  $a_{ki\sigma}^q$  and the deformation it is possible to calculate matrix elements  $\langle \phi_{L^z \sigma} | h | \chi_q \rangle$ . Using the coefficients  $c_{L^z S^z}^{\beta/\gamma}$  we obtain matrix elements  $\langle \alpha M | \beta R_{\beta q} \rangle$  and  $\langle \alpha M | \gamma R_{\gamma q} \rangle$  which appear in nominators in Eq. (5). The energies of the  $|R_{\beta/\gamma q}\rangle$  states in the denominators equal  $E_{R_{\beta q}} = \epsilon_0 + \epsilon_{R_{\beta}} - \epsilon_q$  and  $E_{R_{\gamma q}} = \epsilon_0 + \epsilon_{R_{\gamma}} + \epsilon_q$ , respectively, with  $\epsilon_0$  being the energy necessary to transfer an electron from the top of the valence band to the  $3d$  shell or from the  $3d$  shell to the top of the valence band. After performing the sum in Eq. (5) we obtain the matrix elements  $H_{MM'}$  of the effective Hamiltonian.

Depending on the deformation (see below), the obtained  $6 \times 6$  numerical matrix has the form as in Eq. (10) or Eq. (11) and we may calculate the coefficients  $B_4, B_{20}, B_{40}$  or  $C_4, C_{20}, C_{40}$  which describe the influence of the octahedral crystal field and the distortion on the splitting. In particular, the coefficients  $B_{20}$  or  $C_{20}$  are proportional to the anisotropy constant  $D$  ( $D=3B_{20}$  or  $D=3C_{20}$ , respectively), a quantity which we compare to the experimental results.

In the literature we have found two reports of EPR measurements for PbTe:Mn epitaxial layers. In the first one the layer was grown on  $\text{BaF}_2$  substrate,<sup>14</sup> whereas in the second one it was on KCl substrate.<sup>15</sup> That is why in the following analysis we consider lattice distortions corresponding to these two cases.

The direction of growth of PbTe on  $\text{BaF}_2$  is along the  $[111]$  PbTe crystallographic direction. It is usually assumed that the strain is homogeneous in the plane perpendicular to the  $[111]$  direction and can be characterized by a single pa-

rameter  $\epsilon_{\parallel}^{[111]}$  (in-plane strain). The components of strain tensor  $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$  and  $\epsilon_{xy} = \epsilon_{yz} = \epsilon_{zx}$  can be expressed by  $\epsilon_{\parallel}^{[111]}$  in the form

$$\epsilon_{xx} = \frac{4c_{44}}{c_{11} + 2c_{12} + 4c_{44}} \epsilon_{\parallel}^{[111]}, \quad (8)$$

$$\epsilon_{xy} = -\frac{c_{11} + \frac{4}{3}c_{12}}{c_{11} + 2c_{12} + 4c_{44}} \epsilon_{\parallel}^{[111]}, \quad (9)$$

where the values of elastic moduli for PbTe are<sup>16</sup>  $c_{11} = 10.53 \times 10^{10} \text{ N/m}^2$ ,  $c_{12} = 0.70 \times 10^{10} \text{ N/m}^2$ , and  $c_{44} = 1.32 \times 10^{10} \text{ N/m}^2$ . Assuming that the above relations are valid for the nearest neighborhood of the Mn ion, it is possible to calculate the positions of six nearest tellurium atoms and, consequently, the effective Hamiltonian  $H_{M,M'}$ .

After transforming to the coordinate system with the  $z$  axis along the  $[111]$  crystallographic direction, the Hamiltonian takes the following form:

$$H_{M,M'}^{[111]} = -\frac{2}{3} B_4 (O_{40} + 20\sqrt{2} O_{43}) + B_{20} O_{20} + B_{40} O_{40}, \quad (10)$$

where the operators  $O$  are defined in Ref. 13.

In the case of KCl substrate, the PbTe:Mn layer grows along the  $[001]$  crystallographic direction. The nonvanishing components of the strain tensor are equal to  $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{\parallel}^{[001]}$  and  $\epsilon_{zz} = -(2c_{12}/c_{11}) \epsilon_{\parallel}^{[001]}$ . In this case the Mn—Te bonds are oriented along crystallographic directions. However, the Mn—Te distances in the  $x$ - $y$  plane are different from those along the  $[001]$  direction. This results in the dependence of the parameters  $V_{sd\sigma}$ ,  $V_{pd\sigma}$ , and  $V_{pd\pi}$  on the crystallographic direction. The effective Hamiltonian in the system of coordinates with the axis parallel to crystallographic directions takes the form

$$H_{M,M'}^{[001]} = C_4 (O_{40} + 5O_{44}) + C_{20} O_{20} + C_{40} O_{40}. \quad (11)$$

For the values of deformations which are interesting from an experimental point of view the main contribution to the splitting comes from terms proportional to  $O_{20}$ . In both cases the effective Hamiltonian may be approximated by  $H \approx D(S_z^2 - 35/12)$  where the constant  $D$  for small deformations is proportional to  $\epsilon_{\parallel}$  and  $S_z$  is the  $z$ 'th component of the spin  $\frac{5}{2}$  operator.

There are four groups of parameters entering the present theory. The first is related to the band structure of PbTe, the second to the properties of the Mn ion—the intra-atomic spin-orbit couplings  $\lambda_{\beta} = -\lambda_{\gamma} = -90 \text{ cm}^{-1}$  (Ref. 13) and the energy  $\epsilon_0$  necessary to transfer one additional electron from the top of the valence band to the  $d$  shell of Mn or to transfer one electron from the  $d$  shell to the top of the valence band. The value of  $\epsilon_0$  is not known for PbTe:Mn, we expect, however, that it should be of the same order as in other semimagnetic semiconductor compounds—of the order of a few electron volts.

TABLE I. Comparison of experimental values of anisotropy constant  $D$  with theoretical predictions for three values of  $\epsilon_0$ . The values of  $D$  are expressed in terms of corresponding magnetic fields ( $H=D/2\mu_B$ ) in Gauss.

	PbTe:Mn/BaF <sub>2</sub>	PbTe:Mn/KCl
Strain $\epsilon_{  }^a$	0.0003	-0.0048
$D_{exp}$	$\pm 7^b$	-107 <sup>c</sup>
$D_{th}(\epsilon_0=1.6 \text{ eV})$	-2.9	-109.1
$D_{th}(\epsilon_0=2.5 \text{ eV})$	-1.0	-39.3
$D_{th}(\epsilon_0=3.5 \text{ eV})$	-0.36	-13.7

<sup>a</sup>Reference 20.

<sup>b</sup>References 14 and 21.

<sup>c</sup>Reference 15.

The Slater-Koster parameters  $V_{sd\sigma}$ ,  $V_{pd\sigma}$ , and  $V_{pd\pi}$  are responsible for the  $sp-d$  hybridization. Their values for PbTe:Mn are not known also. In order to estimate the Mn<sup>2+</sup> ground state splitting we assume  $V_{sd\sigma}=0.523 \text{ eV}$ ,  $V_{pd\sigma}=-0.518 \text{ eV}$ , and  $V_{pd\pi}=0.323 \text{ eV}$ . These values were used in Ref. 17 in calculations of the band structure of MnTe and the functional dependence of  $V$ 's on Mn—Te distance was taken from Refs. 18 and 19.

Finally, we must know deformation of the nearest neighborhood of the Mn atom. In calculations we assume that the relations for different components of the strain tensor are the same as for the macroscopic layer. Such an approach may serve as the first approximation only. Due to smaller ionic radius, the manganese atom introduced into the PbTe matrix produces some kind of a “hole” causing the difference between the deformation near the Mn atom and the one far from the impurity.

In Table I we present results of calculations for three values of  $\epsilon_0$ . We see that for physically acceptable values of parameters the calculated splittings are comparable with experimental results. For PbTe:Mn grown on KCl substrate the sign of  $D$  agrees with that reported in Ref. 15. (In Ref. 14 only the absolute value of  $D$  was measured.<sup>21</sup>)

#### IV. CONCLUSIONS

In the present paper we have investigated a mechanism of the Mn<sup>2+</sup> ground state splitting. It is caused by the combined effect of  $sp-d$  hybridization and the spin-orbit coupling in the manganese states Mn<sup>1+</sup> and Mn<sup>3+</sup>. The main difference between the present approach and the mechanisms considered earlier in the literature (Refs. 5–7) is that we include into consideration the excited states of the Mn ion, in which the number of electrons on the  $d$  shell differs from five. Our method takes into account spin-orbit effects not only on the Mn ion, but also in the band states. We have shown that the results of calculations are rather close to experimentally observed values of the ground state splitting, which means that the presented mechanism can be responsible for the observed effect. The method can be also applied to other semiconductor compounds containing manganese as the magnetic element.

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#### APPENDIX

In order to clarify the connection between the symmetry and the lowest order of  $\lambda$  in which the ground state splitting occurs, let us take an arbitrary state  $q_0$  from the first Brillouin zone and consider the following expression:

$$\begin{aligned}
 Q_{M_1 M_2}^{(n)} = & \sum_{L_1^z S_1^z \sigma_1} \sum_{L_2^z S_2^z \sigma_2} (-1)^{L_1^z + L_2^z} \sqrt{\frac{5}{2} + 2\sigma_1 M_1} \\
 & \times \sqrt{\frac{5}{2} + 2\sigma_2 M_2} \delta_{S_1^z, M_1 - \sigma_1} \delta_{S_2^z, M_2 - \sigma_2} \\
 & \times \langle L_1^z S_1^z | (\lambda \mathbf{L} \cdot \mathbf{S})^n | L_2^z S_2^z \rangle \\
 & \times \sum_{q \in \{q_0\}} \langle \phi_{-L_1^z \sigma_1} | h | \chi_q \rangle \langle \chi_q | h | \phi_{-L_2^z \sigma_2} \rangle, \quad (A1)
 \end{aligned}$$

where the sum over  $q$  runs over all states from the first Brillouin zone, which may be obtained from  $q_0$  by symmetry transformations. The sums of this kind are contained in Eq. (5) and the difference is that in Eq. (A1) only the  $n$ th order terms with respect to internal manganese spin-orbit coupling  $\lambda$  are extracted. Let us consider  $O_h$  symmetry first. For this symmetry the matrix  $Z_{L_1^z \sigma_1, L_2^z \sigma_2} = \sum_{q \in \{q_0\}} \langle \phi_{-L_1^z \sigma_1} | h | \chi_q \rangle \langle \chi_q | h | \phi_{-L_2^z \sigma_2} \rangle$  is built from four invariants and has the following form:

$$\begin{aligned}
 Z_{L_1^z \sigma_1, L_2^z \sigma_2} = & A_1 I + A_2 (L_x^4 + L_y^4 + L_z^4) + A_3 \mathbf{L} \cdot \boldsymbol{\sigma} \\
 & + A_4 (L_x^3 \sigma_x + L_y^3 \sigma_y + L_z^3 \sigma_z), \quad (A2)
 \end{aligned}$$

where  $A_1, A_2, A_3, A_4$  are the constants depending on  $q_0$ , and  $I$  is the identity matrix. If we consider a situation where the spin of the band states is a good quantum number then  $A_3 = A_4 = 0$ . This is easily seen from the definition of  $Z$  because in this case the band wave functions may be chosen proportional to  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$  or to  $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ , and the matrix  $Z$  is diagonal in  $\sigma_1, \sigma_2$ . Performing direct calculations we find that  $Q_{M_1 M_2}^{(n)}$  are diagonal for  $n=1, 2, 3$ , and, consequently, the ground state splitting is proportional to  $\lambda^4$ . If the band spin-orbit interaction cannot be neglected (this is the case of PbTe), the splitting is proportional to  $\lambda^3$ .

In a similar manner we can analyze the cases of lower order symmetry. For the tetragonal deformation, the matrix

$Z_{L_1^z \sigma_1, L_2^z \sigma_2}$  contains the term proportional to  $A_5 L_z^2 + A_6 L_z \sigma_z$ . Again, performing direct calculations we get the result that for nonzero and zero band spin-orbit couplings, the splitting is proportional to  $\lambda$  and to  $\lambda^2$ , respectively.

The above considerations have been performed for the case when the excited configuration of manganese is  $\text{Mn}^{3+}$ . In an analogous manner, with slight modifications of formula (A1), they may be applied to the  $\text{Mn}^{1+}$  case.

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