PHYSICAL REVIEW B **72**, 094429 (2005)

Ground state splitting of ^8S rare earth ions in semiconductors

A. Łusakowski
Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, 02-668 Warsaw, Poland

(Received 22 March 2005; revised manuscript received 6 May 2005; published 23 September 2005)

We propose a mechanism leading to ground state splitting for rare earth ^8S ions in semiconductor crystals. The resulting splitting is due to three effects; the first is the intra-atomic $4f$-$5d$ spin-spin interaction, the second one is the spin-orbit interaction for $5d$ electrons, and the third one is their hybridization with the valence band states of the semiconductor host. The resulting splitting depends significantly on the position of the $5d$ level with respect to the semiconductor host band structure. We also discuss a different model, already known in the literature, which is also based on the ion–band state hybridization. For both models, as an example, we present results of numerical calculations for rare earth ions in the IV-VI semiconductor PbTe.

DOI: 10.1103/PhysRevB.72.094429 PACS number(s): 71.70.Ch, 71.70.Ej

I. INTRODUCTION

The present paper is devoted to the theoretical analysis of the ground state splitting of rare earth (RE) ^8S ions in semiconductor crystals. Very well known and studied examples of such ions are Eu^{2+} and Gd^{3+}. It is believed that the magnetic properties of these ions are determined by the half-filled $4f$ shell. According to Hund's rule, for this electron configuration, the ground state should be characterized by the total angular momentum $L=0$ and the total spin $S=7/2$. In other words the ground state should be $^8S_{7/2}$ which is eightfold degenerate, independently of the crystal environment. Such a model explains quite well magnetic susceptibility or magnetization measurements where the spin of the ion interacts with an external magnetic field or with the spin of another ion and the energies of Zeeman or ion-ion exchange interactions are of the order of 1 K.

However, electron paramagnetic resonance (EPR) experiments, which probe the system on a much finer energy scale, clearly demonstrate that the above picture is an approximate one only. It turns out that in crystals the degeneracy of the ion's ground state is lifted, and the nature of the splitting depends on the symmetry of the environment. For example, for O_h symmetry, the case with which we deal in the present paper, the ground state is split into three levels: doublet, quartet, and doublet. In accordance with group theory, the effective spin Hamiltonian describing the splitting caused by the ion's crystal environment is of the form

$$H=\frac{b_4}{60}(O_4^0+5O_4^4)+\frac{b_6}{1260}(O_6^0-21O_6^4), \qquad (1)$$

where the operator equivalents O_k^m for spin $S=7/2$ are 8×8 matrices defined, for example, in Ref. 1. The energy levels of the Hamiltonian (1) are $(-18b_4-12b_6)^{(2)}$, $(2b_4+16b_6)^{(4)}$, $(14b_4-20b_6)^{(2)}$, where the superscripts (2) and (4) denote the degeneracy of the levels.

From EPR experiments, if the quality of the samples is high, it is possible to obtain not only the absolute values of coefficients b_4 and b_6, but also their signs. This may be achieved by performing measurements on the same sample at different temperatures. The splittings, together with the level degeneracies, are shown schematically in Fig. 1 for $b_4>0$ and $b_4<0$. The energy diagrams in Fig. 1 correspond to the splittings of Eu^{2+} and Gd^{3+} ions in PbTe. Here we will often refer to this compound as an example, but the calculation methods and the general predictions of the theory may be applied to any semiconductor containing RE S state ions. From the literature we know that for the Eu ion $b_4=129$ MHz,[2–4] while for the Gd ion $b_4=-110.16$ MHz.[5] The coefficient b_6 is usually about two orders of magnitude smaller and because its influence on the ground state splitting is very small it will not be analyzed in the following. Notice that the signs of b_4 for Eu^{2+} and Gd^{3+} ions are opposite. This is rather strange, because at first sight, except for the small relative difference in nuclear charge, these two ions are very similar and their crystal neighborhoods are the same (six tellurium atoms placed in the vertices of a regular octahedron).

The problem of the ground state splitting of rare earth $^8S_{7/2}$ ions is very old. A very comprehensive discussion of the possible physical mechanisms leading to the splitting has been presented by Wybourne.[6] In Ref. 6, using perturbation theory and results of numerical calculations, he analyzed the case of Gd^{3+} ion in the crystal environment of D_{3h} symmetry. The main idea is that due to the strong spin-orbit coupling interaction for $4f$ electrons the higher-energy $4f^7$ states $^{2S+1}L_{7/2}$ with different L and S are mixed into the ion's ground state,

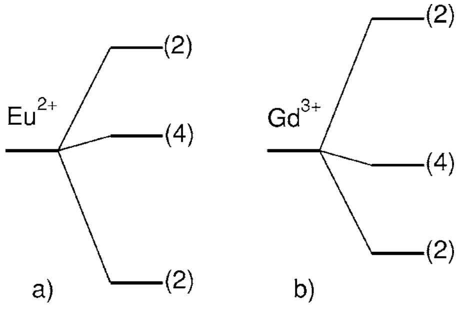

FIG. 1. Differences in the splittings of the ground state levels for (a) Eu^{2+} and (b) Gd^{3+} ions in PbTe crystal. The numbers show the degeneracies of the levels.

1098-0121/2005/72(9)/094429(8)/$23.00

$$|{}^8S_{7/2}\rangle \to s|{}^8S_{7/2}\rangle + p|{}^6P_{7/2}\rangle + d|{}^6D_{7/2}\rangle \ldots, \tag{2}$$

where s, p, and d,… are numerical coefficients.[6,7] Due to the nonzero p, d, … the ion is no longer in a pure ${}^8S_{7/2}$ state; it may interact with the crystal field and this interaction leads to the ground state splitting.

The results obtained by Wybourne have been improved recently by Smentek *et al.*[8] On the basis of extensive numerical relativistic calculations for Gd^{3+} ion they derived the effective spin Hamiltonian for this ion in a crystal neighborhood of arbitrary symmetry (relativistic crystal field theory). In particular, for O_h symmetry the effective spin Hamiltonian may be written in the form of Eq. (1) where the coefficient b_4 reads

$$b_4 = \frac{A_0^4 U^{(4)}}{6\sqrt{154}}\left(\frac{1}{\sqrt{2}} b_4(04) + b_4(13)X^{(13)4} + b_4(15)X^{(15)4}\right). \tag{3}$$

The definitions and numerical values of $U^{(4)}$, $b_4(\kappa t)$, and $X^{(\kappa t)4}$ may be found in Ref. 8. A_0^4 is the crystal field coefficient, which, in the simplest six-point charge model is equal to $A_0^4 = 7e^2 a_0^4/2d^5$ where $a_0 \approx 0.5$ Å is the atomic length unit, d is the distance between cation and anion, and e is the electron's charge.[9] Taking Eu and Gd in PbTe as an example, we see that the relativistic crystal field theory alone cannot explain simultaneously ground state splitting for both ions because the experimentally determined signs of b_4 are opposite. It is very improbable that replacing the Eu ion by a Gd ion will change the sign of A_0^4 because the neighborhoods of two ions are the same. Comparing the values of coefficients s, p, and d, for gadolinium and europium, presented in Table 5.1 in Ref. 7, we see that they are nearly identical. Although the $4f$ wave function for Eu is slightly more extended in space than for Gd,[10] it is very difficult to show the way in which such small differences between two ions can lead to opposite signs of b_4.

In the literature several other mechanisms leading to ground state splitting have been considered. They are listed for example in Ref. 11 where also the appropriate formulas for b_4 are collected. Analyzing these formulas, one may conclude that for the same reason, i.e., similarity of coefficients in Eq. (2) for Eu and Gd, these mechanisms, in the same crystal environments, should lead to similar results for both ions.

The inadequacy of a model in which the RE ion interacts with the environment by the electrostatic crystal field potential only has been already noticed in the literature.[7,12,13] In 1978 Barnes *et al.*,[13] analyzing the ground state splitting for Gd^{3+} ion in different crystals, noticed that in insulators there is proportionality between the crystal field coefficient A_0^4 and the coefficient b_4, while in metals such proportionality does not exist. They proposed a model in which $4f$ electrons interact with the band states via a hybridization processes. Using second order perturbation theory with respect to the hybridization, they constructed an effective spin Hamiltonian for the ground state of the Gd^{3+} ion. As the excited states of the system they took into account configurations in which the number of electrons on the $4f$ shell changes by ±1, i.e., the $4f^8$ configuration plus one hole in the Fermi sea or the $4f^6$ configuration plus one additional electron in the band. According to Hund's rule, in the excited states $4f^8$ and $4f^6$ the angular momentum is nonzero. Taking into account internal spin-orbit coupling, the authors of Ref. 13 obtained an effective spin-lattice interaction leading to the ground state splitting.

In Sec. IV we will reconsider this model because we think that in its derivation and solution presented in Ref. 13 some important points have been missed.

The main idea of Barnes *et al.* is very interesting; however, the final results strongly depend on the constants describing the hybridization between $4f$ electrons and the band states. Due to strong localization of the $4f$ shell, it is very often assumed in the literature that this hybridization is very small. For example in calculations of the exchange integral between $4f$ spin and band carriers in PbEuTe, Dietl *et al.*[14] found that the contribution to the final result due to hybridization between $4f$ and band states is negligible.

Contrary to $4f$ electrons, $5d$ states of RE ions are very extended in space and their hybridization with band states is certainly much stronger. In the literature we have found examples of successful explanations of magnetic properties of RE ions in semiconductors which are based on the assumption that the interaction between $4f$ electrons and band states goes via internal $4f$-$5d$ exchange interaction and hybridization between $5d$ and band states. For instance, using such a model, in 1970 Kasuya[15] explained the Eu—Eu exchange constant in EuO. The Kasuya mechanism was used also, as a starting point, by Story *et al.*[16] in the theory explaining the Fermi energy dependence of the Gd—Gd exchange constant in SnGdTe mixed crystals. The $4f$-$5d$ interaction was also invoked by Dietl *et al.*[14] in calculation of the *sp*-*f* exchange integral between the localized Eu spin and the band carriers in PbEuTe.

In the present paper we generalize this mechanism by including spin-orbit coupling and the crystal field potential for $5d$ states and apply it to the calculation of the coefficient b_4. In the model, which will be explained and discussed in detail in the next sections, the ground state splitting occurs due to the combined effect of intra-atomic, Heisenberg type, $4f$-$5d$ exchange interaction, spin-orbit interaction on $5d$ orbitals, and the hybridization of RE $5d$ levels with the valence band states. Our model includes the spin-orbit interaction in the semiconductor host band states. It turns out that the functional dependence of b_4 on the $5d$ spin-orbit constant is different for semiconductors with strong band spin-orbit interaction than for those for which this interaction may be neglected. For semiconductors with strong band spin-orbit effects one may expect that the proposed mechanism is more effective. One of the important parameters of the model is ϵ_0, the energy necessary to transfer an electron from the valence band to the $5d$ shell. The magnitude of the resulting $4f$ ground state splitting decreases very quickly with increasing ϵ_0. That is why the position of the $5d$ level with respect to the Fermi energy determines whether the mechanism is important or not. For example, as will be discussed in Sec. III, for Gd in PbTe this energy is small, of the order of 0.5 eV,[17] and the resulting b_4 is of the order of the one observed in experiment. For Eu ϵ_0 is several times larger and the calculated splitting is much smaller.

In the next section we describe the model and derive an approximate, analytical result for b_4. This formula enables us to discuss the salient features of the model, in particular the dependence of b_4 on the parameters of the theory. In Sec. III we present details of numerical calculations and Sec. IV is devoted to discussion of the model by Barnes *et al.*[13] Some additional remarks are presented in the last section.

II. THE EFFECTIVE SPIN HAMILTONIAN

Let us consider a semiconductor crystal with one cation replaced by a RE atom. The unperturbed part of our model Hamiltonian describes ground and excited states of the system. These two groups of states are connected by $5d$ band state hybridization, which we treat here as a perturbation. Below, we describe these two parts of the Hamiltonian.

In the ground state of the system the electrons fill the band levels up to the Fermi energy. We assume that the band structure is not changed significantly by the presence of the RE atom. In our model the RE atom is treated as the host cation atom with additional $4f$ and $5d$ orbitals. There are seven electrons on $4f$ orbitals and the $5d$ shell is empty. Based on Hund's rule, the spin of the ion $S=7/2$ and its angular momentum $L=0$; thus the ground state of the system is eightfold degenerate and is described by M, the projection of the spin on a quantization axis.

As the excited states we take configurations with one additional electron on the $5d$ level and one electron less in the band. The Hamiltonian describing $4f^7 5d^1$ configuration of the ion reads

$$H_{4f^7 5d^1} = -J\mathbf{S}\cdot\mathbf{s} + \lambda_t \mathbf{L}_t\cdot\mathbf{s} + \lambda_e \mathbf{L}_e\cdot\mathbf{s} + V_{cr}. \tag{4}$$

The first term describes the exchange interaction between the $4f$ spin $\mathbf{S}$ and the spin $\mathbf{s}=\frac{1}{2}\boldsymbol{\sigma}$ of the $5d$ electron. The second and the third term describe the spin-orbit interaction on the $5d$ shell. The operators L_{ti} $(i=x,y,z)$ are the angular momentum operators between the $5d$ states of t_{2g} symmetry and L_{ei} between the t_{2g} and e_{2g} states, respectively. If $t_{2g}(d_{yz},d_{xz},d_{xy})$ and $e_g(d_{z^2},d_{x^2-y^2})$ states are defined according to Ref. 9 then the operators L_{ti} and L_{ei} have the following matrix form:

$$L_{tx}=\begin{bmatrix}0&0&0&0&0\\0&0&i&0&0\\0&-i&0&0&0\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix},\quad L_{ty}=\begin{bmatrix}0&0&-i&0&0\\0&0&0&0&0\\i&0&0&0&0\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix},L_{tz}=\begin{bmatrix}0&i&0&0&0\\-i&0&0&0&0\\0&0&0&0&0\\0&0&0&0&0\\0&0&0&0&0\end{bmatrix}, \tag{5}$$

$$L_{ex}=\begin{bmatrix}0&0&0&-i\sqrt{3}&-i\\0&0&0&0&0\\0&0&0&0&0\\i\sqrt{3}&0&0&0&0\\i&0&0&0&0\end{bmatrix},L_{ey}=\begin{bmatrix}0&0&0&0&0\\0&0&0&i\sqrt{3}&-i\\0&0&0&0&0\\0&-i\sqrt{3}&0&0&0\\0&i&0&0&0\end{bmatrix},L_{ez}=\begin{bmatrix}0&0&0&0&0\\0&0&0&0&0\\0&0&0&0&2i\\0&0&0&0&0\\0&0&-2i&0&0\end{bmatrix}. \tag{6}$$

In the case of a free ion the two spin-orbit constants λ_t and λ_e are equal; however, if the ion is placed into the crystal they are, in general, different.[9] Finally, the last term in Eq. (4) describes the influence of the crystal field on the $5d$ energy levels and it has the form

$$V_{cr}=Dq\begin{bmatrix}-4&0&0&0&0\\0&-4&0&0&0\\0&0&-4&0&0\\0&0&0&6&0\\0&0&0&0&6\end{bmatrix}. \tag{7}$$

After diagonalizing the 80×80 matrix $H_{4f^7 5d^1}$ we obtain eigenvectors $|R\rangle$ and the corresponding eigenvalues ϵ_R. The eigenvectors $|R\rangle$ may be expressed in the basis $|Md_i\sigma\rangle$:

$$|R\rangle = \sum_{Md_i\sigma} |Md_i\sigma\rangle\langle Md_i\sigma|R\rangle \tag{8}$$

where $-7/2\leq M\leq 7/2$ and $\sigma=\pm\frac{1}{2}$ are the projections of the $4f$ and $5d$ spins on the quantization axis, respectively, and d_i are t_{2g} for $i=1,2,3$ and e_g for $i=4,5$ $5d$ orbitals.

In our model we assume that the $5d$ levels of RE hybridize with the band states. (The hybridization of the $4f$ shell in the present section is neglected.) The hybridization matrix elements $\langle R,q|h|M\rangle$ describe the probability amplitude of a transition from a ground state $|M\rangle$ to excited state $|R,q\rangle$ with h being the one-electron hybridization Hamiltonian, and the quantum number $q\equiv n\mathbf{k}$ describes the band state of an electron with the corresponding energy ϵ_q transferred to the $5d$ shell. The wave vector $\mathbf{k}$ belongs to the first Brillouin zone and n is an additional index necessary to fully characterize the band state. For bands with negligible spin-orbit coupling, where the electron spin is a good quantum number, n corresponds to the band's number and the projection of the electron's spin.

In the second-order perturbation theory with respect to the hybridization between $5d$ levels of the RE ion and the band states, which often is called the Schrieffer-Wolff transformation, we obtain the effective spin Hamiltonian for the RE ion in the crystal:

$$H_{MM'} = -\sum_{R,q} \frac{\langle M|h|R,q\rangle\langle R,q|h|M'\rangle}{\epsilon_0 + \epsilon_R - \epsilon_q}. \tag{9}$$

In Eq. (9) the sum over q runs over all occupied band states. The sum in the denominator is the energy of the excited state of the system where ϵ_0 denotes the energy necessary to transfer an electron from the Fermi level, which we assume to be the zero of the energy scale, to the lowest-energy state of $4f^7 5d^1$ configuration.

Using Eq. (8) and the fact that

$$\langle M d_i \sigma q|h|M'\rangle = \delta_{MM'}\langle d_i\sigma|h|q\rangle, \tag{10}$$

we may rewrite Eq. (9) in the form

$$H_{MM'} = -\sum_{R,q}\sum_{d_{i1}\sigma_1, d_{i2}\sigma_2} \frac{\langle d_{i2}\sigma_2|h|q\rangle\langle q|h|d_{i1}\sigma_1\rangle\langle M d_{i1}\sigma_1|R\rangle\langle R|M' d_{i2}\sigma_2\rangle}{\epsilon_0 + \epsilon_R - \epsilon_q}. \tag{11}$$

Equation (11) is the main result of the present paper. If we know the values of matrix elements $H_{MM'}$ then, comparing them to Eq. (1), we obtain the coefficient b_4. In the next section we present details and results of numerical calculations for the example case of PbTe semiconductor, here we derive an approximate, analytical formula for b_4 valid to the fourth order with respect to the intra-atomic spin-orbit coupling. This analytical formula will enable us to discuss and understand the general properties and dependencies of b_4 on different parameters of the model.

Let us take an arbitrary state characterized by the wave vector $\mathbf{k}_0$ from the first Brillouin zone and let us denote by $\{\mathbf{k}_0\}$ the set of states which may be obtained from $\mathbf{k}_0$ by symmetry transformations of O_h, including Kramers conjugation. More precisely, we take an arbitrary wave vector $\mathbf{k}_0$ from the first Brillouin zone, we find all the wave vectors which may be obtained from $\mathbf{k}_0$ by symmetry operations and the set $\{\mathbf{k}_0\}$ contains the Kramers conjugate pairs corresponding to these vectors. On symmetry grounds, the matrix $Z_{d_{i1}\sigma_1,d_{i2}\sigma_2} \equiv \sum_{q\in\{\mathbf{k}_0\}}\langle d_{i1}\sigma_1|h|q\rangle\langle q|h|d_{i2}\sigma_2\rangle$, appearing in Eq. (11), must have the following form:

$$Z_{d_{i1}\sigma_1,d_{i2}\sigma_2} = p_t I_t + p_e I_e + q_t \mathbf{L}_t\cdot\boldsymbol{\sigma} + q_e \mathbf{L}_e\cdot\boldsymbol{\sigma} \tag{12}$$

where the matrices I_t and I_e are unit operators in the t_{2g} and e_g subspaces, respectively, i.e.,

$$I_t = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \quad I_e = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}. \tag{13}$$

The coefficients p_t, p_e, q_t, q_e depend on the band structure and on the quantum number $\mathbf{k}_0$. If we neglect the band spin-orbit interaction then q_t and q_e disappear. However, in many cases, for example for PbTe, such an assumption is unjustified and, as we will see below, q_t and q_e, in some sense, play the role of the ion's spin-orbit constants.

Let us notice that $\epsilon_q = \epsilon_{\mathbf{k}_0} = \text{const}$ for all $q\in\{\mathbf{k}_0\}$. Then the effective Hamiltonian $H_{MM'}$, Eq. (11), may be rewritten as the trace over d_i and σ degrees of freedom of the product of two matrices:

$$H_{MM'} = \frac{1}{48}\sum_{\mathrm{k}_0} \mathrm{Tr}_{d_i\sigma} Z Q(M,M'), \tag{14}$$

where the matrix $Q(M,M')$ is defined as

$$Q_{d_{i1}\sigma_1,d_{i2}\sigma_2}(M,M') = -\sum_R \frac{\langle M d_{i1}\sigma_1|R\rangle\langle R|M' d_{i2}\sigma_2\rangle}{\epsilon_0 + \epsilon_R - \epsilon_{\mathbf{k}_0}}, \tag{15}$$

and the factor $1/48$ is necessary to take into account multiple counting of states (the O_h group has 48 elements).

Equation (15) may be expanded in the series of λ_t and λ_e. Denoting $H_\lambda = \lambda_t \mathbf{L}_t\cdot\mathbf{s} + \lambda_e \mathbf{L}_e\cdot\mathbf{s}$ the expansion is

$$\frac{1}{E - \frac{1}{2}J\mathbf{S}\cdot\boldsymbol{\sigma} + V_{cr} + H_\lambda} = G_0\sum_{n=0}^{\infty}(-H_\lambda G_0)^n, \tag{16}$$

where $E = \epsilon_0 - \epsilon_q + 7/4J + 4Dq$. Notice that the lowest eigenvalue of the operator $-\frac{1}{2}J\mathbf{S}\cdot\boldsymbol{\sigma} + V_{cr}$ equals $-(7/4J + 4Dq)$ and the subtraction of this term is in accordance with the definition of ϵ_0. The operator $G_0 \equiv 1/\left(E + \frac{1}{2}J\mathbf{S}\cdot\boldsymbol{\sigma} + V_{cr}\right)$ is

$$G_0 = (A_t + B_t\mathbf{S}\cdot\boldsymbol{\sigma})I_t + (A_e + B_e\mathbf{S}\cdot\boldsymbol{\sigma})I_e, \tag{17}$$

with

$$A_t = \frac{\epsilon_0 - \epsilon_q + \frac{9}{4}J}{(\epsilon_0 - \epsilon_q)(\epsilon_0 - \epsilon_q + 4J)},$$

$$B_t = \frac{J}{2(\epsilon_0 - \epsilon_q)(\epsilon_0 - \epsilon_q + 4J)}, \tag{18}$$

$$A_e = \frac{\epsilon_0 - \epsilon_q + 10Dq + \frac{9}{4}J}{(\epsilon_0 - \epsilon_q + 10Dq)(\epsilon_0 - \epsilon_q + 10Dq + 4J)},$$

$$B_e = \frac{J}{2(\epsilon_0 - \epsilon_q + 10Dq)(\epsilon_0 - \epsilon_q + 10Dq + 4J)}. \tag{19}$$

Calculation of traces in Eq. (14) is a simple but very tedious task, which may be simplified by use of a computer program. We collect terms proportional to

$$S_x^4 + S_y^4 + S_z^4 = \frac{1}{20}(O_4^0 + 5O_4^4) + \frac{2331}{16} \tag{20}$$

and we obtain the coefficient b_4, up to the fourth power in the ion's spin-orbit coupling:

$$\begin{aligned} b_4 = -\frac{3}{2}\sum_{\mathbf{k}_0} B_t^2 B_e \lambda_e \Bigg\{ & q_t B_t \lambda_t \lambda_e + q_e (B_t \lambda_t^2 - 2B_e \lambda_e^2) \\ & - \frac{1}{2}\lambda_e [2q_t (A_t - A_e) B_t \lambda_e^2 + 8 q_e (A_e B_t - A_t B_e) \lambda_t \lambda_e \\ & + p_t A_t (3B_t \lambda_t^2 - 2B_e \lambda_e^2) + p_e A_e (B_t \lambda_t^2 - 2B_e \lambda_e^2)] \Bigg\}. \end{aligned} \tag{21}$$

Let us discuss the main features of the obtained formula.

First, let us notice that $b_4 = 0$ for $\lambda_e = 0$. This is the general result valid for all orders of perturbation theory. It is related to the fact that if $\lambda_e = 0$ there is no spin-orbit coupling between t_{2g} and e_g orbitals and this coupling is the only one which mixes these two groups of states in Hamiltonian H_λ. The operator G_0, Eq. (17), also does not mix t_{2g} and e_g states and, consequently, the same holds for the operator $Q_{d_{i1}\sigma_1, d_{i2}\sigma_2}(M, M')$ [see Eqs. (15) and (16)]. Notice, that for $\lambda_e = 0$, in Eq. (16), in the subspace of e_g states, only the zeroth-order term survives and this term will certainly not lead to terms in the effective spin Hamiltonian which have O_h symmetry. Moreover, due to this decoupling, the trace in Eq. (14) does not depend on q_e. Thus, concerning the orbital degrees of freedom, we may limit the considerations to the t_{2g} subspace. But in this subspace the problem is completely symmetrical with respect to the operations of full rotational group because L_{tx}, L_{ty}, L_{tz} satisfy the angular momentum commutation relations for $L = 1$ and in the effective Hamiltonian there will be no O_h terms. We conclude that the nonzero spin-orbit coupling λ_e connecting the t_{2g} and e_g states is the most important parameter of the model.

Second, notice that the order of the ion's spin-orbit coupling, λ, in which we obtain nonzero b_4, depends on the band spin-orbit coupling. If the spin-orbit coupling is absent in the band then $q_t = q_e = 0$ and the lowest-order terms are proportional to λ^4. For nonzero band spin-orbit coupling they are proportional to λ^3. In this sense the band spin-orbit coupling plays the role of ion's spin-orbit coupling.

The formulas for A_t, B_t, A_e, and B_e show that the coefficient b_4 very quickly decays with the excitation energy ϵ_0. On the other hand, these formulas suggest also that the most important contribution to the final results comes from the hybridization of $5d$ level with the states close to the Fermi level.

Finally let us notice that the crystal field potential for $Dq > 0$ reduces the parameter b_4. This may be understood on the basis of the preceding discussion devoted to the role of λ_e. Enlarging the energy distance between t_{2g} and e_g states leads to the effective decrease of the coupling between these two groups of states.

III. RESULTS

In this section we show an example of numerical calculations for a RE ion in PbTe semiconductor.

The electron band wave functions and band energies ϵ_q are calculated according to the tight binding model developed in Ref. 18. In this model the band states are build from p and s orbitals of Pb and Te. 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

$$\psi_{\mathbf{k}i\sigma}^{c/a}(\mathbf{r}) = \frac{1}{\sqrt{N_c}}\sum_{\mathbf{R}_{c/a}} e^{i\mathbf{k}\cdot\mathbf{R}_{c/a}} \varphi_i^{c/a}(\mathbf{r} - \mathbf{R}_{c/a})|\sigma\rangle, \tag{22}$$

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

$$|q\rangle \equiv |n\mathbf{k}\rangle = \sum_i \sum_\sigma \sum_{p=c,a} a_{\mathbf{k}i\sigma}^p \psi_{\mathbf{k}i\sigma}^p(\mathbf{r}), \tag{23}$$

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

The knowledge of the amplitudes $a_{\mathbf{k}i\sigma}^p$ enables us to calculate the hybridization matrix elements $\langle d_i\sigma|h|q\rangle$. We assume that there is only an overlap of $5d$ RE orbitals with six neighboring anions. The necessary values of inter atomic matrix elements $\langle d_i|h|\varphi_j^a\rangle$ are calculated according to the Table 20-1 of Ref. 19 and can be expressed using three constants $V_{sd\sigma}$, $V_{pd\sigma}$, and $V_{pd\pi}$ defined as in Ref. 19:

$$V_{ldm} = \eta_{ldm}\frac{\hbar^2 r_d^{3/2}}{m_0 d^{7/2}}, \tag{24}$$

where $\eta_{sd\sigma} = -3.13$, $\eta_{pd\sigma} = -2.95$ and $\eta_{pd\pi} = 1.36$, m_0 is the bare electron's mass, $d = 3.2$ Å is the cation-anion distance in PbTe, and r_d is a fitting parameter related to the radius of the $5d$ RE orbital and is of the order of 1 Å. In calculations we put $r_d = 2.5$ Å and we obtain $V_{sd\sigma} = -1.62$ eV, $V_{pd\sigma} = -1.51$ eV, and $V_{pd\pi} = 0.70$ eV. These values are close to the ones used in Ref. 20 in calculations of the EuTe band structure.[21]

The summation over $\mathbf{k}_0$ in Eq. (11) is replaced by the integration over the Brillouin zone according to the formula:

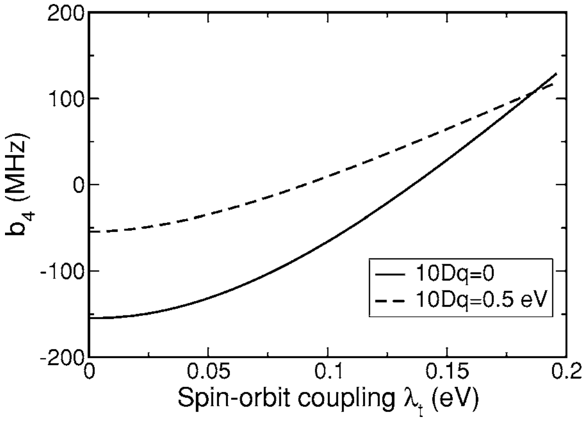

FIG. 2. Dependence of b_4 on the spin-orbit constant λ_t for $\lambda_e=0.1$ eV, $J=0.25$ eV, $\epsilon_0=0.35$ eV and for two different values of the crystal field parameter $10Dq$.

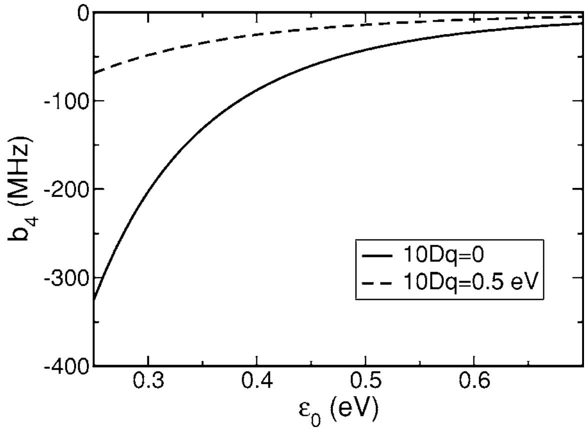

FIG. 3. Dependence of b_4 on the transfer energy ϵ_0 for $\lambda_e=0.1$ eV, $\lambda_t=0.05$ eV, $J=0.25$ eV, and for two different values of crystal field parameter $10Dq$.

$$\sum_{\mathbf{k}_0} \to V\int_{BZ} \frac{d^3\mathbf{k}}{(2\pi)^3}, \tag{25}$$

where V is the volume of the crystal.

The value of ϵ_0, i.e., the energy necessary to transfer an electron from the top of the valence band to the $5d$ level of the RE ion is one of the most important parameters of the theory. According to Ref. 17 the $5d$ level of Gd in PbTe lies about 0.2 eV above the bottom of the conduction band. Adding the value of the energy gap in PbTe, which is equal to 0.2 eV we obtain $\epsilon_0=0.4$ eV for Gd in PbTe. From the resonant photoemission spectroscopy experiments we know that the $4f$ level of Eu in PbTe lies approximately 1.6 eV below the top of the valence band[22,23] while for Gd it is placed about 10 eV below the top of the valence band.[22] That is why we expect that ϵ_0 for Eu is larger than for Gd. This expectation is confirmed by optical measurements by Krenn *et al.*[24] According to Ref. 24 the position of the $4f$ level of Eu is very close to the top of the valence band and the energy of the internal Eu transition $4f^7(^8S_{7/2})\to 4f^6(^7F_J)5dt_{2g}$ is about 2.25 eV, thus ϵ_0 is of the order of 2 eV. The precise value is not important because as we will see the value of the coefficient b_4 decays very quickly with increasing ϵ_0 and if ϵ_0 is bigger than 1 eV the contribution to b_4 from the present mechanism becomes negligible.

In the literature we have not found values for the spin-orbit constants λ_t and λ_e for RE ions in PbTe. One may find only a value of the single spin-orbit constant λ. The existing data are not very consistent, however. In Ref. 25 we find $\lambda=0.08$ eV for Eu and $\lambda=0.13$ eV for Gd. According to more recent theoretical relativistic calculations,[26] the $5d$ spin-orbit constant for free lanthanide ions is of the order of 0.06 eV. In our calculations we take $\lambda_e=0.1$ eV and in Fig. 2 we present the results for b_4 as a function of λ_t for $\epsilon_0=0.35$ eV, $J=0.25$ eV (Ref. 25) and for two different values of $10Dq=0$ and 0.5 eV. We clearly see that the nonzero crystal field splitting of $5d$ strongly decreases b_4. Taking into account the theoretical calculations[27] of λ_t and λ_e performed for $3d$ ions in crystals of NaCl crystal structure, we expect that also in the present case the real λ_t should be less than λ_e.

In Fig. 3 we show the decay of b_4 with increasing ϵ_0 for $\lambda_e=0.1$ eV, $\lambda_t=0.05$ eV, and for two values of the crystal field parameter Dq.

As is clear from the above discussion, the main problem in calculations is the lack of knowledge of precise values of the number of necessary parameters of the model. However, it seems that the estimations made above suggest that the proposed mechanism gives a ground state splitting of the right order of magnitude and, moreover, in the case of Gd in PbTe it gives the proper sign of the coefficient b_4. Also, from Fig. 3 we see that it is enough to increase ϵ_0 by about 1 eV to significantly decrease b_4, which although negative, becomes very small and may be neglected. It means that for such cases, for example for Eu in PbTe, the main contributions to the splitting are due to other mechanisms, like relativistic crystal field theory which generates a positive sign of b_4.

The above considerations indicate that the proposed model should be taken into account in theoretical analysis of EPR spectra.

IV. BARNES, BABERSCHKE, AND HARDIMAN MODEL

As has been discussed in the Introduction the main idea of the model proposed by Barnes *et al.*[13] is to consider the excited states of the system in which the number of electrons on the ion's $4f$ shell changes by ±1. Let us concentrate in this section on processes that lead to $4f^7\leftrightarrow 4f^6$ transitions. The ground state of the system is the same as that considered in Sec. II, namely, the RE ion in the $4f^7$ configuration plus the Fermi sea of electrons. This eightfold-degenerate state of the system is characterized by $-7/2\leqslant M\leqslant 7/2$—the projection of the $4f^7$ spin 7/2 on a quantization axis which we take along the (001) crystallographic direction.

In the excited states we have the ion in the $4f^6$ configuration plus one additional electron above the Fermi level characterized, as in Sec. II, by the quantum number q. Assuming the validity of Hund's rule for $4f^6$ configuration, $L=3$ and $S=3$, the Hamiltonian for the ion in the excited state reads

$$H = (\lambda_4 \mathbf{L}_4 + \lambda_5 \mathbf{L}_5 + \lambda_{25} \mathbf{L}_{25} + \lambda_{45} \mathbf{L}_{45}) \cdot \mathbf{S} + V_{cr}. \qquad (26)$$

In the above equation the indices 2, 4, 5 correspond to the decomposition of the D^3 representation into irreducible representation Γ_2, Γ_4 and Γ_5 of the cubic group.[1] For example $\mathbf{L}_4$ is the angular momentum operator between base functions of the Γ_4 representation and $\mathbf{L}_{45}$ between the Γ_4 and Γ_5 base functions. $\mathbf{S}$ is the spin operator of the length $S=3$ and V_{cr} is a diagonal matrix describing the crystal field potential.

Let us stress that from the physical point of view it is rather unreasonable to describe the spin-orbit interaction using four different constants λ_4, λ_5, λ_{25}, and λ_{45}. The $4f$ shell is strongly localized and contrary to $5d$ orbitals, the influence of the neighborhood should be negligible. The only reason for introducing four constants instead of a single one is that it is easier to understand the influence of the crystal field on the coefficient b_4.

The important difference between our formulation of the model and that of Barnes *et al.*[13] is in the form of hybridization elements. We propose that

$$\langle L_z S_z q | H | M \rangle = (-1)^{L_z+1} \sum_{\sigma=\pm 1/2} \sqrt{\frac{7/2 + 2\sigma M}{7}} \times \delta_{S_z, M-\sigma} \langle q | h | \phi_{-L_z \sigma} \rangle. \qquad (27)$$

The state $|L_z S_z q\rangle$ is the excited state of the system in which the projection on the quantization axis of the total angular momentum and spin of the ion are L_z and S_z, respectively, and there is one additional electron characterized by q above the Fermi energy. The element $\langle q|h|\phi_{-L_z\sigma}\rangle$ describes hybridization between the band state q and the $4f$ spin orbital $\phi_{-L_z\sigma}$. The coefficient $(-1)^{L_z+1}\sqrt{(7/2+2\sigma M)/7}$, omitted in Ref. 13, may be derived using explicit forms of antisymmetric many electron functions for ion's states $|L_z S_z\rangle$ and $|M\rangle$.[28]

The further steps of calculation of the effective spin Hamiltonian are, with minor modifications, very similar to those described in the previous sections. Because of much higher complexity of the angular momentum algebra for $L=S=3$ it is not easy to derive formulas analogous to those from Sec. II. That is why the conclusions are based on numerical calculations only, performed for a PbTe crystal, the semiconductor we use as an example in the present paper.

In general, the results are similar to those for the model described in Sec. II. First, we observe a decrease of modulus of b_4 with the increase of ϵ_0 (see Fig. 4). Notice that in this section ϵ_0 denotes the energy necessary to transfer an electron from the $4f$ shell to the Fermi energy level. Second, for ϵ_0 and other parameters of the model kept constant, b_4 changes with the crystal field potential parameter Δ_{cr}; however, as we see in the inset in Fig. 4 these changes are not very fast. Δ_{cr} is defined here as the total splitting of $4f^6$ manifold in the crystal field, i.e., $\Delta_{cr}=E_{\Gamma_4}-E_{\Gamma_2}$. The mechanism of changes of b_4 with Δ_{cr} is similar to the one analyzed in Sec. II. From the performed numerical analysis it turns out that $b_4 \equiv 0$ for $\lambda_{45}=0$. The relative energy positions of Γ_2, Γ_4, and Γ_5 states, which change with Δ_{cr}, are important, because they decide the effectiveness of the transitions caused by spin-orbit interaction. However, compared to $5d$, in the case of the $4f$ shell this influence is rather small. This is due to a completely different ratio of the spin-orbit to the crystal field strength. For the $4f$ orbitals the effects caused by the crystal field are much smaller than those due to spin-orbit interaction.

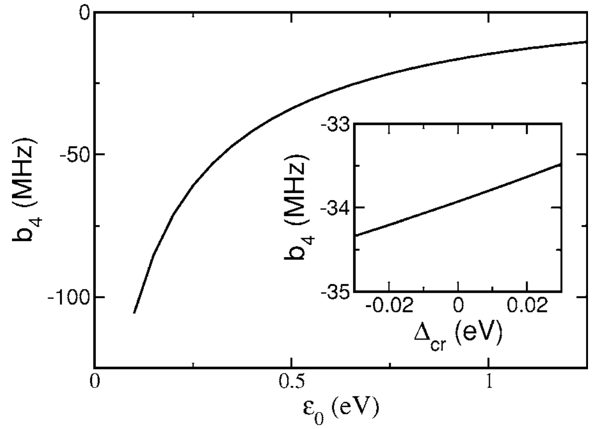

FIG. 4. Dependence of b_4 on the transfer energy ϵ_0 for $\lambda_{4f}=0.0276$ eV, $V_{sd\sigma}=-0.2$ eV, $V_{pd\sigma}=-0.2$ eV, and $V_{pd\pi}=0.1$ eV and the crystal field splitting $\Delta_{cr}=0$. The inset shows the dependence of b_4 on Δ_{cr} for $\epsilon_0=0.5$ eV.

This main difference between our results and those by Barnes *et al.* is that the authors of Ref. 13 overlooked the fact that even for zero crystal field potential we obtain nonzero ground state splitting of the RE ion. This splitting, however, may be achieved only if the symmetry of the band wave functions and, consequently, the proper symmetry of hybridization matrix elements is taken into account. If these symmetries are neglected and the $4f$ band hybridization is described by a single constant V_{fk} (see Ref. 13) then, apart from the crystal field potential, the rest of the system's Hamiltonian is invariant with respect to operations of the rotation group and the ground state remains degenerate. Then, indeed, in the first approximation, the splitting will be proportional to the crystal field and this is the only contribution calculated in Ref. 13.

On the basis of our analysis, it is clear that in the case of $4f$ band state hybridization, the most important parameter of the model is not Δ_{cr} but ϵ_0, the energy necessary to transfer an electron from $4f$ shell to the conduction band (see Fig. 4).

V. CONCLUSIONS

In this paper we have proposed a model leading to the splitting of the ground state of ^8S rare earth ions in crystals. The main ingredients of the model are $4f$-$5d$ exchange interaction, spin-orbit coupling for $5d$ electrons, and the hybridization of $5d$ electrons with the band states. The numerical calculations have been performed for PbTe, a semiconductor from the IV-VI group of compounds. We have also limited our considerations to the O_h symmetry of the ion's neighborhood. Of course, the model may be applied to any semiconductor and, with slight modifications in hybridization matrix elements, to lower symmetry cases.

In Sec. IV we discussed the model proposed by Barnes *et al.* In particular, we have shown the importance of the careful treatment of the symmetry of the hybridization matrix. If the symmetry of a problem of this kind is lost due to too big simplifications in the model formulation we may also lose an important, from the physical point of view, class of solutions, as has happened in Ref. 13.

The general conclusion resulting from the analysis of both models is in accordance with the point of view presented in Ref. 13, namely, that the ground state splitting of ^8S ions in crystals is not governed by their internal properties only, but the position of the ion's $4f$ and $5d$ levels relative to the host crystal band structure is at least of equal importance.

ACKNOWLEDGMENTS

The author would like to thank Professor R. R. Gałazka and Professor T. Story for helpful discussions and for the critical reading of the manuscript. This work was partly supported by KBN Grant No. PBZ-044/P03/2001.

---

[1] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).

[2] G. B. Bacskay, P. J. Fensham, I. M. Ritchie, and R. N. Ruff, J. Phys. Chem. Solids **30**, 713 (1969).

[3] T. Nakamura, A. Ishida, and H. Fujiyasu, Thin Solid Films **161**, 149 (1988).

[4] Y. S. Gromovoj, S. V. Plyatsko, F. F. Sizov, and S. D. Darchuck, J. Phys.: Condens. Matter **1**, 6625 (1989).

[5] M. Bartkowski, D. J. Northcott, J. M. Park, A. H. Reddoch, and F. T. Hedgcock, Solid State Commun. **56**, 659 (1985).

[6] B. G. Wybourne, Phys. Rev. **148**, 317 (1966).

[7] D. J. Newman and W. Urban, Adv. Phys. **24**, 793 (1975).

[8] L. Smentek, B. G. Wybourne, and J. Kobus, J. Phys. B **34**, 1513 (2001).

[9] S. Sugano, Y. Tanabe, and H. Kanimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic Press, New York, 1970).

[10] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[11] G. G. Siu and D. J. Newman, J. Phys. C **15**, 6753 (1982).

[12] H. A. Buckmaster and Y. H. Shing, Phys. Status Solidi A **12**, 325 (1972).

[13] S. E. Barnes, K. Baberschke, and M. Hardiman, Phys. Rev. B **18**, 2409 (1978).

[14] T. Dietl, C. Śliwa, G. Bauer, and H. Pascher, Phys. Rev. B **49**, R2230 (1994).

[15] T. Kasuya, IBM J. Res. Dev. **14**, 214 (1970).

[16] T. Story, M. Górska, A. Łusakowski, M. Arciszewska, W. Dobrowolski, E. Grodzicka, Z. Gołacki, and R. R. Gałazka, Phys. Rev. Lett. **77**, 3447 (1996).

[17] T. Story, M. Arciszewska, P. Łazarczyk, A. Łusakowski, M. Górska, W. Dobrowolski, B. Witkowska, E. Grodzicka, and R. R. Gałazka, Acta Phys. Pol. A **92**, 997 (1997).

[18] M. Kriechbaum, P. Kocevar, H. Pascher, and G. Bauer, IEEE J. Quantum Electron. **24**, 1727 (1988).

[19] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[20] J. Blinowski and P. Kacman, Phys. Rev. B **64**, 045302 (2001).

[21] P. Kacman (private communication).

[22] B. J. Kowalski, Z. Gołacki, E. Guziewicz, A. Kozanecki, B. A. Orłowski, J. Ghijsen, and R. L. Johnson, J. Alloys Compd. **286**, 121 (1999).

[23] R. Denecke, L. Ley, G. Springholz, and G. Bauer, Phys. Rev. B **53**, 4534 (1996).

[24] H. Krenn, W. Herbst, H. Pascher, Y. Ueta, G. Springholz, and G. Bauer, Phys. Rev. B **60**, 8117 (1999).

[25] T. Kasuya and A. Yanase, Rev. Mod. Phys. **40**, 684 (1968).

[26] M. Dolg and H. Stoll, in *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier Science, New York, 1996), Vol. 22, Chap. 152, p. 607.

[27] E. Francisco and L. Pueyo, Phys. Rev. B **37**, 5278 (1988).

[28] Strictly speaking Barnes *et al.* in their considerations used only the matrix element for maximal spin, $\langle 33_q|H|7/2\rangle$, thus this factor was unimportant; however, in a more general treatment of the problem its presence is necessary.