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 the Hund’s rule, for such 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 eight fold 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 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, the 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 we deal in the present paper with, the ground state is split into three levels, doublet, quartet and doublet. In accordance with the group theory, the effective spin Hamiltonian describing the splitting caused by the ion’s crystal environment is of the form

$$H = \frac{b_4}{60}(O_d^2 + 5O_4^2) + \frac{b_6}{1260}(O_6^6 - 21O_6^4)$$

(1)

where the operators equivalents $O_n^m$ for spin $S=7/2$ are $8 \times 8$ matrices defined, for example, in Ref. 4. The energy levels of Hamiltonian (1) are $b_4 > 0$ and $b_4 < 0$. The energy diagrams in Fig. 1 correspond to the splittings of Eu$^{2+}$ and Gd$^{3+}$ ions in PbTe. This compound is an example we will often refer in the present paper to, but the calculational methods and the general predictions of the theory may be applied to any semiconductor containing RE $^S$ ions. From the literature we know, that for Eu ion $b_4=129$ MHz, while for Gd ion $b_4=-110.16$ MHz. 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 the first sight, except for the small relative difference of nuclear charges these two ions are very similar and their crystal neighbourhoods are the same (six tellurium atoms placed in the vertices of regular octahedron).

The problem of the ground state splitting of rare earth $^8S_{7/2}$ ions is very old. Very comprehensive discussion of the possible physical mechanisms leading to the splitting is due to Wybourne. In Ref. 4 using perturbation theory and results of numerical calculations he analyzed the case of Gd$^{3+}$ ion in the crystal environment of $D_{3d}$ symmetry. The main idea is, that due to strong spin-orbit
interaction for 4f electrons the higher energy 4f
states 2S + 1/2L7/2 with different L and S are mixed into the ion’s
ground state

\[ |8S_7/2⟩ → s|6S_7/2⟩ + p|6P_7/2⟩ + d|6D_7/2⟩ \ldots \] (2)

where s, p, d, ... are numerical coefficients. Due to
nonzero p, d, ... the ion is no longer in pure 8S7/2 state,
it may interact with the crystal field and this interaction
leads to the ground state splitting.

The results obtained by Wybourne have been recently
improved by Smientek et. al. On the basis of ex-
tensive numerical relativistic calculations for Gd3+ ion they
derived the effective spin Hamiltonian for this ion in the
crystal neighborhood of arbitrary symmetry (relativistic
theory of RE ions). In particular, for 4f symmetry the
effective spin Hamiltonian may be written in the form of
Eq. (1) where the coefficient \( b_4 \) reads

\[ b_4 = \frac{A_4^0 U(4)}{6\sqrt{154}} \left( \frac{1}{\sqrt{2}} b_4(04) + b_4(13)X^{(13)}4 + b_4(15)X^{(15)}4 \right) \] (3)

The definitions and numerical values of \( U(4) \), \( b_4(k\ell t) \)
and \( X^{(k\ell t)}4 \) may be found in Ref. 10. \( A_4^0 \) is the crystal
field coefficient, which, in the simplest six point charge
model, is equal \( A_4^0 = \frac{7\epsilon^2 a_0}{2d} \), where \( a_0 \approx 0.5 \) Å is the
atomic length unit, \( d \) is the distance between cation and
anion and \( \epsilon \) is the electron’s charge. Taking Eu and Gd
in PbTe as example, we see that the relativistic crystal
field theory alone cannot simultaneously explain ground
state splitting for both ions because the experimentally
determined signs of \( b_4 \) are opposite. It is very improbable
that replacing Eu ion by Gd ion we change the sign of
\( A_4^0 \) because the neighborhoods of two ions are the
same. We also do not expect significant changes of the
parameters \( U(4) \), \( b_4(k\ell t) \) and \( X^{(k\ell t)}4 \) because these two
ions are very similar.

The inadequacy of a model in which the RE ion interacts
with the environment by electrostatic crystal field poten-
tial only has been already noticed in the literature.\(^\text{12,15}^\)
In 1978 Barnes et. al.\(^\text{12}^\) analysing the ground state
splitting for Gd3+ ion in different crystals, noticed that in
insulators there is proportionality between the crystal
field coefficient \( A_4^0 \) and 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 hybridization processes. Using second order
perturbation theory with respect to the hybridization
they constructed effective spin Hamiltonian for the
ground state of Gd3+ ion. As the excited states of the
system they took into account configurations in which
the number of electrons on 4f shell changes by ±1, i. e.
4f8 configuration plus one hole in the Fermi sea or 4f6
configuration plus one additional electron in the band.
According to the Hund’s rule, in the excited states 4f8
and 4f6 the angular momentum is nonzero. Taking into
account internal spin - orbit coupling, the authors of
Ref.\(^\text{12}^\) obtained effective spin - lattice interaction leading to the
ground state splitting.

In Section IV we will rederive this model because we
think that in its derivation and solution presented in
Ref.\(^\text{12}^\) 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 4f
shell, in the literature, it is very often assumed that it is
very small. For example in calculations of the exchange
integral between 4f spin and band carriers in PbEuTe,
Dietl at. al.\(^\text{10}^\) found that the contribution to the final
result resulting from the hybridization 4f - band states
processes 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 mag-
etic 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 5d - band states hybridization.

For instance, using such a model, in 1970 Kasuya\(^\text{11}^\) explained the Eu-Eu exchange constant in EuO. The
Kasuya mechanism was used also, as a starting point,
by Story et. al.\(^\text{16}^\) in the theory explaining the Fermi
level dependence of the Gd-Gd exchange constant in
SnGdTe mixed crystals. The 4f - 5d interaction was also invoked by Dietl et. al.\(^\text{10}^\) in calculation of sp - f
exchange integral between localized Eu spin and the
band carriers in PbEuTe.

In the present paper we generalize this mechanism
by including spin-orbit coupling and crystal field poten-
tial 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 combined effect of the intra-
atomic, Heisenberg type, 4f-5d exchange interaction,
spin-orbit interaction on 5d orbitals and the hybridiza-
tion of RE 5d levels with the valence band states. Our
model takes automatically the spin-orbit interaction in
the semiconductor host band states. It turns out that the
functional dependence of \( b_4 \) on 5d spin-orbit constant is
different for semiconductors with strong band spin-orbit
interaction from those for which this interaction may be
neglected. For semiconductors with strong band spin-
orbit effects one may expect that the proposed mecha-
nism is more effective. One of the important parameters
of the model is \( \epsilon_0 \), the energy necessary to transfer an
electron from the valence band to the 5d shell. The magni-
itude of the resulting 4f ground state splitting decreases
very quickly with \( \epsilon_0 \). That is why the position of 5d level
with respect to the Fermi energy decides whether the
magnetism is important or not. For example, as it will
be discussed in Section III, for Gd in PbTe this energy
is small, of the order of 0.5 eV\(^\text{18}^\) and the resulting \( b_4 \) is
of the order of the one observed in experiment, while for
Eu \( \epsilon_0 \) is a few times larger and the calculated splitting is...
much smaller. In the next Section we describe the model and we derive approximate, analytical result for $b_4$. This formula enables us to discuss the salient features of the model, in particular the dependencies of $b_4$ on the parameters of the theory. In Section III we present details of numerical calculations and Section IV is devoted to rederivation and discussion of the model by Barnes et. al. Some additional remarks are contained in the last Section.

II. THE EFFECTIVE SPIN HAMILTONIAN

Let us consider a semiconductor crystal with one cation replaced by 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 5$d$ - band states hybridization, which we treat here as a perturbation. Below, we describe these two parts of 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 RE atom. In our model RE atom is treated as the host cation atom with additional 4$f$ and 5$d$ orbitals. There are seven electrons on 4$f$ orbitals and 5$d$ shell is empty. Assuming validity of the 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 eight fold degenerate and is described by $M$, the projection of spin on a quantization axis.

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

$$H_{4f^7 5d^1} = -JS \cdot S + \lambda_I L_I \cdot S + \lambda_e L_e \cdot S + V_{cr}$$

(4)

The first term describes the exchange interaction between the 4$f$ spin $S$ and the spin $s = \frac{1}{2} \sigma$ of the 5$d$ electron. The second and the third terms describe the spin orbit interaction on the 5$d$ shell. The operators $L_{ei}$ ($i = x, y, z$) are the angular momentum operators between the 5$d$ states of $t_{2g}$ symmetry and $L_{ei}$ between the $t_{2g}$ and $e_g$ states respectively. For the definition of $t_{2g}$ ($d_{xz}, d_{yz}, d_{xy}$) and $e_g$ ($d_{xz}, d_{x^2-y^2}$) states according to Ref. 7 they have following form:

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

(5)

In the case of free ion two spin orbit constants $\lambda_I$ and $\lambda_e$ are equal, however if the ion is placed into the crystal they are in general different. Finally, the last term in the Eq. describes the influence of the crystal field on the 5$d$ energy levels and it has the form

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

(7)

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

$$|Md_i\rangle = \sum_{M\delta, \sigma} |Md_i\rangle \langle Md_i|R\rangle$$

(8)

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

In our model we assume that the 5$d$ levels of RE hybridize with the band states. (The hybridization of the 4$f$ 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 ground state $|M\rangle$ to excited state $|R, q\rangle$ with $h$ being one-electron hybridization Hamiltonian and the quantum number $q \equiv n|k|$ describes the band state of an electron with the corresponding energy $\epsilon_q$ transferred to 5$d$ shell. The wave vector $k$ belongs

In Section III we present details of numerical calculations and Section IV is devoted to rederivation and discussion of the model by Barnes et. al. Some additional remarks are contained in the last Section.
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 electron’s spin.

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

\[
H_{M'M'} = -\sum_{R,q} \sum_{d_1,σ_1, d_2,σ_2} \langle \{d_2σ_2|h|q\}\langle q|h|d_1σ_1\rangle\langle \{M|d_1σ_1|R\}\langle R|M'd_2σ_2\rangle \rangle / (ε_0 + ε_R - ε_q)
\]

Eq. (11) is the main result of the present paper. If we know the values of matrix elements \( H_{M'M'} \) then, comparing them to Eq. (11), we obtain the coefficient \( b_q \). In the next section we present details and results of numerical calculations for the example case of PbTe semiconductor, here we derive approximate, but analytical formula for \( b_q \) 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 \( b_q \) on different parameters of the model.

Let us take an arbitrary state characterized by wave vector \( k_0 \) from the first Brillouin zone and let us denote by \( \{k_0\} \) the set of states which may be obtained from \( k_0 \) by symmetry transformations of \( O_h \), including Kramers conjugation. More precisely, we take an arbitrary wave vector \( k_0 \) from the first Brillouin zone, we find all the wave vectors which may be obtained from \( k_0 \) by symmetry operations and the set \( \{k_0\} \) contains the Kramers conjugate pairs corresponding to these vectors. On the symmetry ground, the matrix \( Z_{d_1,σ_1,d_2,σ_2} = \sum_{q∈\{k_0\}} \langle d_1σ_1|h|q\rangle\langle q|h|d_2σ_2\rangle \), appearing in Eq. (11), must have following form:

\[
Z_{d_1,σ_1,d_2,σ_2} = p_I t_I + p_e I_e + q_I L_I \cdot σ + q_e L_e \cdot σ
\]

where the matrices \( I_I \) and \( I_e \) are unit operators in \( t_{2g} \) and \( e_g \) subspaces, respectively, i. e. :

\[
I_I = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}, \quad I_e = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}
\]

The coefficients \( p_I,p_e,q_I,q_e \) depend on the band structure and on the quantum number \( k_0 \). If we neglect the band spin-orbit interaction than \( q_I \) and \( q_e \) disappear. However, in many cases, for example for PbTe, such an assumption is unjustified and, as we will see below, \( q_I \) and \( q_e \), in some sense, play the role of ion’s spin-orbit constants.

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 \( ε_q \) denotes the energy necessary to transfer an electron from the Fermi level, which we assume to be zero of the energy scale, to the lowest energy state of \( 4f^75d^1 \) configuration.

Using Eq. (5) and the fact that

\[
(Md_1σq|h|M') = δ_{MM'}\langle d_iσ|h|q\rangle
\]

Eq. (9) may be rewritten in the form

\[
H_{M'M'} = \frac{1}{48} \sum_{k_0} \text{Tr}_{d_Iσ} ZQ(M,M')
\]

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

\[
Q_{d_1σ_1,d_2σ_2}(M,M') = -\sum_R \langle \{Md_1σ_1|R\}\langle R|M'd_2σ_2\rangle \rangle / (ε_0 + ε_R - ε_{k_0})
\]

and the factor 1/48 is necessary to take into account multiple counting of states (the \( O_h \) group has 48 elements). Eq. (11) may be expanded in the series of \( λ_I \) and \( λ_e \). Denoting \( H_λ = λ_I L_I \cdot σ + λ_e L_e \cdot σ \) the expansion is according to the formula:

\[
\frac{1}{\left(E - \frac{1}{2}JS \cdot σ + V_{cr} + H_λ\right)} = G_0 \sum_{n=0}^{∞} (-H_λ G_0)^n
\]

where \( E = ε_0 - ε_q + 7/4J + 4Dq \). Notice that the lowest eigenvalue of the operator \(-\frac{1}{2}JS \cdot σ + V_{cr} \) equals \(-7/4J + 4Dq \) and the subtraction of this term is in accordance with the definition of \( ε_0 \). The operator \( G_0 \equiv 1/(E - \frac{1}{2}JS \cdot σ + V_{cr}) \) is equal:

\[
G_0 = (A_I + B_I S \cdot σ) I_I + (A_e + B_e S \cdot σ) I_e
\]

with

\[
A_I = \frac{ε_0 - ε_q + \frac{3}{2}J}{(ε_0 - ε_q)(ε_0 - ε_q + 4J)}
\]
\[
B_1 = \frac{J}{2(\epsilon_0 - \epsilon_q)(\epsilon_0 - \epsilon_q + 4J)}
\]

\[
A_c = \frac{\epsilon_0 - \epsilon_q + 10Dq + \frac{4}{3}J}{(\epsilon_0 - \epsilon_q + 10Dq)(\epsilon_0 - \epsilon_q + 10Dq + 4J)}
\]

\[
B_c = \frac{J}{2(\epsilon_0 - \epsilon_q + 10Dq)(\epsilon_0 - \epsilon_q + 10Dq + 4J)}
\]

Calculations 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

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

and we obtain the coefficient \(b_4\), up to the fourth power in ion’s spin-orbit coupling:

\[
b_4 = -\frac{3}{2} \sum_{k_0} B_c^2 B_e \lambda_c \left( q_t B_t \lambda_t \lambda_c + q_c \left( B_t \lambda_t^2 - 2B_c \lambda_c^2 \right) \right) - \frac{1}{2} \lambda_c \left( 2q_t (A_t - A_c) B_t \lambda_t^2 + 8q_c (A_t B_t - A_t B_e) \lambda_t \lambda_c + p_t A_t \left( 3B_t \lambda_t^2 - 2B_c \lambda_c^2 \right) + p_c A_c \left( B_t \lambda_t^2 - 2B_c \lambda_c^2 \right) \right)
\]

Let us discuss the main features of the obtained formula. First, let us notice that \(b_1 = 0\) for \(\lambda_c = 0\). This is the general result valid for all orders of perturbation theory. It is connected with the fact that if \(\lambda_c = 0\) 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 \(H_{\lambda}\). The operator \(G_0\), Eq. (17) does not mix \(t_{2g}\) and \(e_g\) states too and, consequently, the same holds for operator \(Q_{d_{i1}, \sigma, d_{i2}, \sigma}(M, M')\), see Eqs. (15, 16). Notice, that for \(\lambda_c = 0\), in Eq. (18), 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 \(O_4\) symmetry. Moreover, due to this decoupling, the trace in Eq. (14) does not depend on \(q_c\). 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 operations of full rotational group because \(L_{ix}, L_{iy}, L_{iz}\) satisfy the angular momentum commutation relations for \(L=1\) and there is no reason to obtain \(O_4\) terms in the effective Hamiltonian. We conclude that the nonzero spin-orbit coupling \(\lambda_c\) connecting the \(t_{2g}\) and \(e_g\) states is the most important parameter of the model. Secondly, notice that the order of ion’s spin-orbit coupling, \(\lambda\), in which we obtain nonzero \(b_4\) depends on the band spin-orbit coupling. If the spin-orbit coupling is absent in the band, \(q_t = q_c = 0\), the lowest order terms are proportional to \(\lambda^4\). For nonzero band spin-orbit coupling they are proportional to \(\lambda^3\). In this sense the band spin-orbit coupling plays the role of ion’s spin-orbit coupling. The formulas for \(A_t, B_t, A_c, B_c\) show that the coefficient \(b_4\) very quickly decays with the excitation energy \(\epsilon_0\). 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 from the vicinity of the Fermi level.

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

### III. RESULTS

In this Section we show the example numerical calculations for RE ion in PbTe semiconductor. The electron band wave functions and band energies \(\epsilon_q\) are calculated according to the tight binding model developed in Ref. 12. In this model the band states are build from \(p\) and \(s\) orbitals of Pb and Te. For a given momentum \(k\) belonging to the first Brillouin zone, the tight binding Hamiltonian is diagonalized in the basis of 16 functions of the form

\[
\psi_{c/a}(r) = \frac{1}{\sqrt{N_c}} \sum_{R_{c/a}} e^{ikR_{c/a}} \varphi_{c/a}(r-R_{c/a}) |\sigma\rangle,
\]

where \(\varphi_{c/a}(r-R_{c/a})\) with \(i = px, py, pz, s\) are the cation or anion atomic orbitals centered on the lattice sites \(R_c\) or \(R_a\), 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 \(k\) we obtain the band energies \(\epsilon_{n,k}\) and corresponding eigenfunctions

\[
|q_i| = |n,k| = \sum_i \sum_{\sigma} \sum_{p=c,a} a_{ki\sigma}^p \psi_{ki\sigma}(r),
\]

where index \(n = 1, 2, \ldots, 16\) labels the band number.

The knowledge of the amplitudes \(a_{ki\sigma}^p\) enables us to calculate the hybridization matrix elements \(\langle d_i \sigma | h | q_i \rangle\). We assume that there is only an overlap of \(5d\) RE orbitals with six neighboring anions. The necessary values of inter atomic matrix elements \(\langle d_i | h | \varphi_j^q \rangle\) are calculated according to Table 20-1 of Ref. 12 and can be expressed using three constants \(V_{sd\sigma}, V_{pdx}, V_{pd\pi}\) defined as in Ref. 12

\[
V_{edm} = \eta_{edm} \frac{\hbar^2 r_d^3/2}{m_0 d^3/2}
\]

where \(\eta_{sd} = -3.13\), \(\eta_{pdx} = -2.95\) 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 \(5d\) RE orbital and it is of the order of 1 Å. In calculations we put \(r_d = 2.5\) Å and we obtain \(V_{edm} = -1.62\) eV, \(V_{pdx} = -1.51\) eV and \(V_{pd\pi} = 0.70\) eV. These values are
find data are not very consistent, however. In Ref. 19 we
Fig. 2 we present the results for 20 to more recent theoretical relativistic calculations
of 0.06 eV. In our calculations we take
spin orbit constant for free lanthanide ions is of the order
of 10
close to the ones used in Ref. 16 in calculations of EuTe
band structure.17
The summation over \( k_0 \) in Eq. (11) is replaced by the
integration over the Brillouin zone according to the for-
\[
\sum_{k_0} \rightarrow V \int_{BZ} \frac{d^3k}{(2\pi)^3}
\]
where \( V \) is the volume of the crystal.
The value of \( \epsilon_0 \), the energy necessary to transfer an
electron from the top of the valence band to the 5d level of
RE ion is one of the most important parameters of the
theory. According to Ref. 13 the 5d level of Gd in PbTe
lies about 0.2 eV above the bottom of 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 photo-emission spectroscopy experiments18 we
know that 4f level of Eu in PbTe lies near the top of
the valence band while for Gd it is placed about 10 eV
below. That is why we expect that \( \epsilon_0 \) for Eu is larger
than for Gd. The precise value is not important because
as we will see the value of the coefficient \( b_4 \) decays very
quickly with increasing \( \epsilon_0 \) and if it is bigger than 1 eV the
contribution to \( b_4 \) from the present mechanism becomes
negligible.

In the literature we haven’t found the values for the spin
orbit constants \( \lambda_t \) and \( \lambda_e \) for RE ions in PbTe. One may
find only value of single spin orbit constant \( \lambda \). The exist-
ing data are not very consistent, however. In Ref. 19 we
find \( \lambda = 0.08 \) eV for Eu and \( \lambda = 0.13 \) eV for Gd. According
to more recent theoretical relativistic calculations20, 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 \( \lambda_t \)
for \( \epsilon_0 = 0.35 \) eV, \( J = 0.25 \) eV and for two different values
of \( 10Dq = 0 \) and \( 10Dq = 0.5 \) eV. We clearly see that the
nonzero crystal field splitting of 5d strongly decreases \( b_4 \).
Taking into account the theoretical calculations21 of \( \lambda_t \)
and \( \lambda_e \) performed for 3d ions in crystals of NaCl crystal
structure, we expect that also in the present case the real
\( \lambda_t \) should be less than \( \lambda_e \).

In Fig. 3 we show the decay of \( b_4 \) with increasing of \( \epsilon_0 \) for
\( \lambda_e = 0.1 \) eV, \( \lambda_e = 0.05 \) eV, \( J = 0.25 \) eV and for two values of crystal field parameter \( 10Dq \).
As it is clear from the above discussion the main prob-
lem in calculations is the lack of knowledge of precise
values of number of necessary parameters of the model.
However, it seems that the estimations made above sug-
gest that the proposed mechanism gives the ground state
splitting of the right order of magnitude and, moreover,
in the case of Gd in PbTe it gives proper sign of the co-
efficient \( b_4 \). Also, from Fig. 3 we see that it is enough
to increase \( \epsilon_0 \) less than 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 positive sign of \( b_4 \).

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

IV. BARNES, BABERSCHKE AND
HARDIMAN MODEL

As it has been discussed in the Introduction the main
idea of the model proposed by Barnes et. al is to con-
sider the excited states of the system in which the number
of electrons on the ion’s 4f shell changes by \( \pm 1 \). Let us
concentrate in this Section on processes which lead to
\( 4f^7 \leftrightarrow 4f^6 \) transitions. The ground state of the system,
\( \mid 8S(J_z) \rangle \), is the same as in Section II, namely the RE
ion in \( 4f^7 \) configuration plus the Fermi sea of electrons.
This eight fold degenerate state of the system is characterized by $-7/2 \leq M \leq 7/2$ - the projection of $4f$ spin $7/2$ on a quantization axis which we take along the (001) crystallographic direction. In the excited states we have the ion in $4f^{10}$ configuration plus one additional electron above the Fermi level characterized, like in Section II, by the quantum number $q$. Assuming the validity of the Hund’s rule for $4f^{10}$ configuration, $L=3$ and $S=3$, the Hamiltonian for the ion in excited state reads:

$$H = (\lambda_4 L_4 + \lambda_5 L_5 + \lambda_{25} L_{25} + \lambda_{45} L_{45}) \cdot S + V_{cr}$$

(26)

In the above equation the indices 2,4,5 correspond to the decomposition of the $D^3$ representation into irreducible representation $\Gamma_2$, $\Gamma_4$ and $\Gamma_5$ of the cubic group. For example $L_4$ is the angular momentum operator between base functions of $\Gamma_4$ representation and $L_{15}$ between $\Gamma_4$ and $\Gamma_5$ base functions. $S$ is the spin operator of the length $S=3$ and $V_{cr}$ is diagonal matrix describing the crystal field potential.

Let us stress that from the physical point of view this is rather unreasonable to describe spin - orbit interaction using four different constants $\lambda_4$, $\lambda_5$, $\lambda_{25}$ and $\lambda_{45}$. The $4f$ shell is very localized and contrary to $5d$ orbitals the influence of the neighbourhood should be negligible. The only reason of 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. is in the form of hybridization elements. We propose that

$$\langle L_2 S_2 q|H| M \rangle = (27)$$

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

The state $|L_2 S_2 q\rangle$ 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 $\langle q | \phi_{-L_z, \sigma} \rangle$ describes hybridization between 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. 8, may be derived using explicit forms of antisymmetric many electron functions for ion’s states $|L_z S_z\rangle$ and $|M\rangle$. 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 Section II. That is why the conclusions are based on numerical calculations only, performed for PbTe crystal, the example semiconductor we use in the present paper.

In general, the results are similar to those for the model described in Section II. First, we observe decrease of modulus of $b_4$ with the increase of $\epsilon_0$, see Fig. 4. In this Section $\epsilon_0$ denotes the energy necessary to transfer an electron from $4f$ shell to the Fermi energy level. Secondly, for $\epsilon_0$ and other parameters of the model kept constant, $b_4$ changes with the crystal field potential parameter $\Delta_{cr}$, however as we see in the insert of Fig. 4 these changes are not very fast. $\Delta_{cr}$ is defined here as the total splitting of $4f^{16}$ manifold in the crystal field, i.e. $\Delta_{cr} = E_{f_4} - E_{f_5}$. The mechanism of changes of $b_4$ with $\Delta_{cr}$ is similar to the one analysed in Section II. From the performed numerical analysis it turns out that $b_4 \equiv 0$ for $\lambda_{45} = 0$. The relative energy positions of $\Gamma_2$, $\Gamma_4$ and $\Gamma_5$ states, which change with $\Delta_{cr}$ are important, because they decide about the effectiveness of the transitions between them caused by spin orbit interaction. However, comparing to $5d$, in the case of $4f$ shell this influence is rather small. This is connected with completely different ratio of 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.

This main difference between our results and those by Barnes et. al. is that the authors of Ref. 8 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 $V_{jk}$, (see Ref. 8) then, apart from the crystal field potential, the rest of the system’s Hamiltonian is invariant with respect to operations of 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. 8.

On the basis of our analysis, see Fig. 4 it is clear that in the case of $4f$ - band states hybridization, the most important parameter of the model is not $\Delta_{cr}$ but $\epsilon_0$, the energy necessary to transfer an electron from $4f$ shell to the conduction band.

V. CONCLUSIONS

In this paper we have proposed the 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 their hybridization with the band states. The numerical calculations have been performed for PbTe, a semiconductor from IV-VI group of compounds. We have also limited considerations to the $O_h$ symmetry of the ion’s neighbourhood. Of course, the model may be applied to any semiconductor and, with slight modifications in hybridization matrix elements, to lower symmetry cases.

In Section IV we have discussed the model proposed by Barnes et. al. In particular, we have shown the impor-
FIG. 4: Dependence of $b_4$ on the transfer energy $\varepsilon_0$ for $\lambda_4 = 0.0276$ 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 insert shows the dependence of $b_4$ on $\Delta_{cr}$ for $\varepsilon_0 = 0.5$ eV.

The general conclusion resulting from the analysis of both models is in accordance with the point of view presented in Ref. 9, 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. The model introduced in Section II, applied to Gd$^{3+}$ and Eu$^{2+}$ ions in PbTe explains origin of opposite signs of the coefficients $b_4$ observed in experiment.

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