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Spin-dependent crystal field on f-electrons as a consequence of spin–orbit coupling renormalization due to exchange-covalent bonds with ligands

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Abstract

The problem of renormalization of the spin–orbit interaction operator of electrons of partially filled nf-shells due to exchange-covalent bonds with surrounding ligands has been solved. It is found that along with the change of the standard spin–orbit interaction parameter, new energy operators are generated, which can be interpreted as a spin-dependent crystal field operator. Simple formulas are obtained that allows to calculate its parameters via covalence parameters and overlap integrals. Numerical evaluations have been performed for multiplets $Tb^{3+}(f^8)^7F_6$ and $Er^{3+}(f^{11})^4I_{15/2}$ in fluorides with cubic symmetry. Calculated parameters were found to be of the order of 10% relative to the standard crystal field parameters.

1 Introduction

Improvement of methods of experimental investigations of energy diagrams of levels of ions with partially unfilled 4f shells in crystals stimulates the development of theoretical conceptions about the nature of splittings of energy multiplets of rare-earth ions in crystals. Relatively recently, Judd [1] and Newman et al. [2] have drawn attention to the fact that the description of multiplet splittings of some rare-earth ions in a number of crystals can be improved if one adds phenomenologically to the crystal field operator the terms depending on the spins of 4f electrons. Judd [1] proposed to include in the standard crystal field operator

$$H = \sum_{k,q} B_q^{(k)} C_q^{(k)}, \tag{1}$$

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an additional operator depending on the spin variables

$$H_1 = \sum_{k,q,i} b_q^{(k)} \left(\mathbf{S}\mathbf{s}_i\right) u_q^{(k)}(i), \tag{2}$$

where $u_q^{(k)}(i)$ and s_i—operators acting on the orbital and spin variables of the f-electron with number *i*, respectively. S is the total spin of the rare-earth ion. $B_q^{(k)}$ are the parameters of the standard crystal field [3], $C_q^{(k)}$- the components of the spherical tensor related to the unit irreducible tensor operators $U_q^{(k)} = \sum_i u_q^{(k)}$ by the relation $C_q^{(k)}{=}\left(l\|c^{(k)}\|l\right)U_q^{(k)}$, where $\left(l\|c^{(k)}\|l\right)$ is the reduced matrix element. $b_q^{(k)}$-phenomenological parameters, which are called as spin-correlated 'spin-correlated crystal field' (SCCF). This idea stimulated intensive experimental studies to detect and determine the values of $b_q^{(k)}$. The ratio of $c_k = b_q^{(k)}/B_q^{(k)}$ was introduced to characterize the relative role of $b_q^{(k)}$ in [4, 5]. Analyzing the experimental data for Gd^{3+}(f^7) and Ho^{3+}(f^{10}) ions in LaCl3, the authors of [4] reported the following values $c_2 \cong 0.02$, $c_4 \cong -0.07$, $c_6 \cong 0.13$. In Ref. [6] for Cs2NaYCl$_6$:Ln^{3+} where Ln^{3+}=Sm^{3+} and Ho^{3+} reported the following values: $c_4 \cong -0.05 \pm 0.01$, $c_6 \cong -0.11 \pm 0.06$ for Sm^{3+} and $c_4 \cong 0.03 \pm 0.02$, $c_6 \cong 0.12 \pm 0.13$ for Ho^{3+}(f^{10}). Using two-photon spectroscopic methods, the authors of [7, 8] studied compounds with cubic symmetry (Cs$_2$NaYCl$_6$:Sm, Cs$_2$NaEuCl$_6$, Cs$_2$NaYF$_6$:Eu, Cs$_2$NaTbCl$_6$, Cs$_2$NaTbBr$_6$. In particular, for the Sm^{3+}(f^5) ion, they reported in Ref. [8] the following estimates $c_4 \cong -0.01 \pm 0.01, c_6 \cong -0.09 \pm 0.03$.

Concerning the nature of the origin of the parameters $b_q^{(k)}$, the authors of [7, 8] inclined to the hypothesis of Newman [2] and Judd [9] that the origin of spin-correlation terms in the crystalline operator is somehow related to the charge transfer processes. In Ref. [10], an attempt was made to explain their origin by combining the crystal field operator with the exchange interaction operator in the second order of perturbation theory. In the literature, there are also questions to the general form of the operator (2). In particular, the authors of [8] drew attention to the problem of choosing the value of the total spin S for excited terms. The authors of [8] drew attention to the problem of choosing the value of the total spin S when analyzing splittings of excited terms. This problem is especially sharp when trying to take into account the effects of mixing of multiplets with the same values of *J* but different values of *S* and *L*. Other variants of correlation corrections to the standard crystal field operator are also discussed. In particular, the so-called correlation corrections of the form

$$H_2 = \sum_{k_1,k_2,k,q} B_q^{(k_1k_2)k} \left\{U^{(k_1)} \times U^{(k_2)}\right\}_q^{(k)}, \tag{3}$$

where curly brackets denote the Kronecker product of tensor operators. A comparative analysis of the role of correlation corrections (2) and (3), their advantages and disadvantages with respect to rare-earth compounds are given in [11, 12] and others.

The purpose of the present communication is to draw attention to the idea that spin-dependent corrections of the type (2), of approximately the same order of magnitude as those described above, are obtained due to the spin–orbit interaction, if we take into account the exchange-covalent bonds of the f-electrons with the surrounding diamagnetic ions. Most importantly, we will give simple formulas that will allow experimenters to calculate for spin-correlation parameters via overlap integrals and covalent bonding parameters. The latter are known to be measured quite accurately by magnetic resonance methods.

2 Re-normalization of the Spin–Orbit Interaction Operator Due to Exchange-Covalent Bonds

The derivation of the effective operator in the wave function basis of the electronic configuration f^N was carried out by perturbation theory using the configuration interaction method similarly as it was done in reference [13] at the analysis of renormalization of the orbital momentum. Among the excited configurations were taken the states in which one of the electrons from the outer shell of the nearest anion (2p- or 2s-shell of the fluorine ion) is transferred to the 4f-shell of the rare-earth ion. The effect of overlapping electronic orbitals of the magnetic ion and ligands within the ground configuration taken into account is the same as in the Heitler–London method and is qualified as exchange. The effect of the admixture of states with charge transfer to the states of the ground configuration, the same as in the method of molecular orbitals, is called the covalency effect. Keeping in mind both exchange and the covalency effects, one may talk about the effect of exchange-covalent bonds of the spin–orbital interaction.

It is convenient to write down the effective operator obtained by us in the form

$$H_{so} = \sum_{i} (\mathbf{ls})(\zeta_f + \Delta\zeta_f) + \sum_{k\neq 0} \Lambda_0^{(1k')k}\left(R_j\right)(-1)^q W_{-q}^{(1k')k} C_q^{(k)}\left(\vartheta_j \phi_j\right), \tag{4}$$

where $W_{-q}^{(1k')k}$ are components of the double irreducible tensor operator [14]. The summation is performed over all electrons of the partially filled shell. The sum $1+k'+k$ are odd numbers, k' takes values 3 and 5, $k=2$, 4 and 6, i.e., as in the crystal field operator for rare-earth ions. $C_q^{(k)}$—components of the spherical tensor. The Euler angles correspond to the direction of a given rare-earth ion–ligand (fluorine) pair relative to the crystallographic coordinate system. The index j in formula (4) refers to the nearest-neighbor ligands. The first term in (4) describes the renormalization of the isotropic part of the spin–orbit interaction. The modification of the one-electron parameter, due to exchange-covalent bonds is determined by the expression

$$\Delta\zeta = \sum_{j} \left\{ \zeta_f \frac{1}{7}\left[S_\sigma^2 - \gamma_\sigma^2 + S_s^2 - \gamma_s^2 + \frac{7}{3}\left(S_\pi^2 - \gamma_\pi^2\right)\right] + \zeta_p \frac{\lambda_\pi}{42}\left[\lambda_\pi + 3\sqrt{6}\lambda_\sigma\right] \right\}. \tag{5}$$

Here, $S_\sigma = \langle f0 \mid p0\rangle$, $S_s = \langle f0 \mid s0\rangle$, $S_\pi = \langle f \pm 1 \mid p \pm 1\rangle$, as in [3], are the overlap integrals. They are calculated in parallel (local) coordinate systems with z-axes directed along the metal–ligand bond line. Similar notations are adopted for the covalency parameters γ_σ, γ_s and γ_π. They have the meaning of the transfer integrals of p- or s-electrons of fluorine into the f-shell, divided by the transfer energy. As usual $\lambda_\sigma = S_\sigma + \gamma_\sigma$, $\lambda_s = S_s + \gamma_s$ and $\lambda_\pi = S_\pi + \gamma_\pi$.

The values $\Lambda^{(1k')k}\left(R_b\right)$ are calculated by the equations:

$$\Lambda_0^{(11)2}(R_j) = -\zeta_f \frac{1}{\sqrt{21}}\left[3\left(S_\sigma^2 - \gamma_\sigma^2 + S_s^2 - \gamma_s^2\right) + 2\left(S_\pi^2 - \gamma_\pi^2\right)\right] + \zeta_p \frac{\lambda_\pi}{\sqrt{21}}\left(\lambda_\pi - \sqrt{6}\lambda_\sigma\right), \tag{6}$$

$$\Lambda_0^{(13)2}(R_j) = \zeta_f \sqrt{\frac{1}{7}}\left[2(S_\sigma^2 + S_s^2 - \gamma_\sigma^2) + 3\left(S_\pi^2 - \gamma_\pi^2\right)\right] + \zeta_p \frac{\lambda_\pi}{\sqrt{7}}\left(\lambda_\pi + 2\sqrt{\frac{2}{3}}\lambda_\sigma\right), \tag{7}$$

$$\Lambda_0^{(13)4}(R_j) = \zeta_f \sqrt{\frac{1}{21}}\left[3(S_\sigma^2 + S_s^2 - \gamma_\sigma^2) + 2\left(S_\pi^2 - \gamma_\pi^2\right)\right] - \zeta_p \frac{2\lambda_\pi}{\sqrt{21}}\left(\lambda_\pi - \sqrt{\frac{3}{2}}\lambda_\sigma\right), \tag{8}$$

$$\Lambda_0^{(15)4}(R_j) = -\zeta_f \sqrt{\frac{30}{77}}\left[S_\sigma^2 + S_s^2 - \gamma_\sigma^2 + \frac{11}{6}\left(S_\pi^2 - \gamma_\pi^2\right)\right] - \zeta_p \sqrt{\frac{5}{462}}\left(5\lambda_\sigma^2 + 2\sqrt{6}\lambda_\sigma\lambda_\pi\right), \tag{9}$$

$$\Lambda_0^{(15)6}(R_j) = -\zeta_f \frac{5}{\sqrt{77}}\left[S_\sigma^2 + S_s^2 - \gamma_\sigma^2 + \frac{1}{2}\left(S_\pi^2 - \gamma_\pi^2\right)\right] + \zeta_p \frac{5}{\sqrt{77}}\left(\lambda_\pi^2 - \sqrt{\frac{2}{3}}\lambda_\pi\lambda_\sigma\right). \tag{10}$$

The distance dependence of the overlap integrals and covalency parameters in the right-hand sides of Eqs. (6)–(10) is assumed. It is not explicitly shown for shortness. ζ_p-spin–orbit coupling parameter of fluorine 2p-electrons. Note that the second terms in (4) differs from the operator (2) by its tensor structure. In Eq. (2) *k* is even numbers 2, 4, and 6, whereas in (4), k takes the values 3 and 5. In this connection, it is logical to qualify the second terms as a spin-dependent corrections to the crystal field operator (1) or may be as the energy of spin–orbit coupling modified by covalent bonds.

3 Examples of Calculations of Spin-Correlation Parameters for Some Multiplets

The energies of the multiplets of rare-earth ions are generally quite well-separated from each other. The matrix elements of both operators $W_{-q}^{(1k')k}$ and $C_q^{(k)}$ in the basis of wave functions $\left|SLJM_J\right\rangle$ are proportional to same 3-*j*-symbols (Wigner–Eckart theorem). However, the reduced matrix elements of these operators and are different. Note, that the problem of calculating the mixing effects of terms with different S and L does not appear. In the basis of states of the given multiplet states $\left|JM_J\right\rangle$, the sum of operator (1) and the second terms from (4) can be written as follows

$$H_{cf} = \sum_{k,q} \left[B_q^{(k)} + d_q^{(k)} \right] C_q^{(k)}. \tag{11}$$

As an example, we make estimates of the relative role of the values for the ground multiplets $Tb^{3+}(f^8)^7F_6$ and $Er^{3+}(f^{11})^4I_{15/2}$ in fluorides with cubic symmetry. Taking into account the relations between the reduced matrix elements of the operators $\left(SLJ\middle\|W^{(1k')k}\middle\|SLJ\right)$ and $\left(SLJ\|C^{(k)}\|SLJ\right)$ for $Tb^{3+}(f^8)^7F_6$, one gets

$$\begin{aligned} d_0^{(6)}(f^8, {}^7F_6) &= \frac{39}{10}\sqrt{\frac{11}{7}}\Lambda_0^{(15)6}S_0^{(6)}, \\ d_0^{(4)}(f^8, {}^7F_6) &= \left[\frac{11}{6}\sqrt{\frac{5}{42}}\Lambda_0^{(15)4} - \frac{11}{3}\sqrt{\frac{1}{119}}\Lambda_0^{(13)4} \right] S_0^{(4)}. \end{aligned} \tag{12}$$

For $Er^{3+}(f^{11})^4I_{15/2}$, we have

$$\begin{aligned} d_0^{(6)}(f^{11}, {}^4I_{15/2}) &= -\frac{39}{50}\sqrt{\frac{11}{7}}\Lambda_0^{(15)6}S_0^{(6)}, \\ d_0^{(4)}(f^{11}, {}^4I_{15/2}) &= \left[\sqrt{\frac{55}{42}}\Lambda_0^{(15)4} + \sqrt{\frac{121}{21}}\Lambda_0^{(13)4} \right] S_0^{(4)}. \end{aligned} \tag{13}$$

The relations between the parameters with $q = \pm 4$ and $q = 0$ remain unchanged, i.e.,

$$\left(B_{\pm 4}^{(k)} + d_{\pm 4}^{(k)}\right) / \left(B_0^{(k)} + d_0^{(k)}\right) = B_{\pm 4}^{(k)} / B_0^{(k)}. \tag{14}$$

In Eqs. (12) and (13), $S_0^{(k)} = \sum_j C_0^{(k)}(\vartheta_j \phi_j)$-structural factors.

Calculation for ions in octahedral coordination from fluorine ions yields to the following values (in cm^{-1})

$$d_0^{(4)}(f^8, {}^7F_6) = 22, d_0^{(6)}(f^8, {}^7F_6) = 13, \text{ and } d_0^{(4)}(f^{11}, {}^4I_{15/2}) = 12, d_0^{(6)}(f^{11}, {}^4I_{15/2}) = 6. \tag{15}$$

The values of covalence parameters that are required for calculation are taken according to experimental data, which were obtained by the double electron-nuclear resonance method for crystals of $KZnF_3$ activated by Er^{3+} ions [15]. Overlap integral was calculated using the same Hartree–Fock wave functions as in Ref. [15]. The spin–orbit coupling parameters of 4f-electrons were taken from the tables of [6], and $\zeta_p \cong 220\ \text{cm}^{-1}$ as in Ref. [16]. The usual crystal field parameters for this ion doped in KZnF3 are estimated in Ref. [15, 17] (in cm^{-1}) $B_0^{(4)} = 2500$ and $B_0^{(6)} = 130$. The values of covalence parameters for CaF_2:Er^{3+} are taken according to experimental data from [18]. The crystal field parameters (for the Dy^{3+} ion in CaF_2) are estimated from the absorption spectra in [19] (in cm^{-1}) $B_0^{(4)} = -2150$ and $B_0^{(6)} = 100$. It can be seen in this case, the ratio $d_0^{(6)}/B_0^{(6)}$ is even large and is about 10%.

Finally, we can estimate the modification of the spin–orbit coupling parameter when the Er^{3+} ion introduced into crystal. According to Ref. [20],

$\zeta_f(Er^{3+}) = 2407\ \mathrm{cm}^{-1}$. On the other hand, the analysis of a large number of Er^{3+} ion levels in an eightfold environment of fluorine ions has been performed in [21]. They reported the value of $\zeta_f(Er^{3+}) = 2366\mathrm{cm}^{-1}$. Comparing these values, one can say that the spin–orbit coupling parameter decreases by about 41 cm^{-1} when the Er^{3+} ion is implemented into the crystal. Calculation by Eq. (5) yields to the following value $\Delta\zeta_f(CaF_2 : Er^{3+}) = -13\ \mathrm{cm}^{-1}$. Comparing the given values, we conclude that Eq. (5) reproduces the trend of the modification and order of magnitude.

4 Concluding Remarks

In the present work, a physically based expression for the spin-dependent crystal field operator is proposed. Simple equations which allow estimation of its parameters for different multiplets of rare-earth ions are derived. The connection with the parameters of exchange-covalent bonds is elucidated. The latter are known to be measured quite accurately by magnetic resonance methods. The operator obtained by us is applicable in the regime of strong J-mixing as well, i.e., when the wave functions of the multiplet with the given J are the combinations of the states of the terms with different spins. The formulae are also applicable for 5f-shells. The values of the covalency parameters for actinide ions have not yet been practically studied. However, there is reason to expect that in actinides, they are larger than in rare-earth compounds. Therefore, it is logical to conclude that the spin-correlation terms of the crystal field operator described by us will be even more significant in actinides. It is hoped that these considerations will stimulate further spectroscopic studies of compounds with partially filled 4f- and 5f-shells.

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Data Availability No datasets were generated or analyzed during the current study.

Declarations

Conflict of Interest The authors declare no competing interests.

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