Charge transfer process contribution to the zero-field splitting of the S-state transition ions

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Abstract. The zero-field splitting of the S state due to the virtual electron transfer processes from the ligands into an unfilled shell (l^n) of a paramagnetic ion has been calculated. A simple analytical formula has been deduced for the spin-Hamiltonian parameters. The paramagnetic centres: $LiCaAlF_6:Fe^{3+}$, $LiSrAlF_6:Fe^{3+}$, $Al_2O_3:Fe^{3+}$, $LiCaAlF_6:Gd^{3+}$, $LiSrAlF_6:Gd^{3+}$, $Al_2O_3:Gd^{3+}$ and $YBa_2Cu_3O_{6+y}:Gd^{3+}$ with $y = 0.91$, 0.95 have been considered as an example. In all cases the calculated values of the D-parameter are in agreement with the electron paramagnetic resonance data within an order of magnitude and in the sign as well.

1. Introduction

The question of the nature of the zero-field splitting of the S-state transition ions substituted into a diamagnetic crystal lattice is still not completely understood. An overview of the early investigations is given in [1]. Careful semiempirical analysis of the S-state splitting problem was given by Newman *et al* [2]. It is worth noting that exact numerical diagonalization of the matrix energy including Coulomb, spin–spin interactions and crystalline field was performed for the Gd^{3+} ($4f^7$) ion in [3]. All possible terms of the $4f^7$ configuration were taken into account. However the calculated splitting of ^8S states for the trigonal paramagnetic centre $SrF_2:Gd^{3+}$ was only 35% of the experimental value. Actually, it was shown in [3] that the one configuration approach is not sufficient to solve the S-state splitting problem.

Generally speaking, the several configuration approach, including the charge transfer processes from the nearest ligands into unfilled 3d shell (the covalence effect) was suggested already in [4]. Replacing 4f-electron states in Mn^{2+} (^6S) states by the molecular orbitals, the authors of [4] have examined the overlapping and covalence effects on the zero-field splitting of Mn^{2+} (^6S) states in the cubic crystals. This method is well known as a semiempirical method of the molecular orbitals (the linear combinations of the atomic orbitals) (MO-LCAO). For the problem we are interested in it is very exhausting and uneffective. Moreover, the authors of [5] have pointed out many mistakes in the calculations [4]. Thus, the question about influences of the covalence on the S-state splitting is still not clear, as yet.

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Below to solve that problem we shall use the configuration interaction method (CI) [6]. It has already been pointed out (see, i.e. [7]) that this method is equivalent to MO-LCAO, but is more applicable for many electronic problems, because it enables us to use the power of the operator techniques in the atomic spectroscopy [8]. Plenty of the numerical MO-LCAO calculations can be carried out in an analytical way and yield a simple formula, which can be applied for crystals with different symmetry.

The paper is organized as follows. We calculated the aspherical part of the magnetic dipole–dipole interaction between electrons of the central ion whose orbitals have been changed from their free ion forms by surrounding ligands. Crudely speaking there are two reasons for that. (1) There is effective repulsion between overlapping central ion and ligand electrons due to the Pauli principle. (2) Electron transfer from the ligands into the unfilled shell of paramagnetic ions (for short the covalence effect). Covalence parameters are larger than the overlap integrals in the case under consideration. Thus we start from a description of charge transfer contribution and at the end discuss corrections which appear due to the nonorthogonality wave function of the central ion and ligand electrons. We do not consider effects of nonorthogonality of ligand wave functions and hybridization between central ion orbitals.

2. Effective spin–spin interaction operator for paramagnetic S-state centres

The influence of the covalent bonding effects on the spin–spin interaction of the electrons in a paramagnetic ion can be taken into account in third order perturbation theory via the effective Hamiltonian approach [7] as follows:

$$V_{\text{eff}} = \tfrac{1}{2}[[V_1 H_2]H_2] \tag{1}$$

where

$$V_1 = \frac{1}{2}\sum \langle \eta_1 \xi_2 | g_{12} | \eta_1' \xi_2' \rangle a_\eta^+ a_\xi^+ a_{\xi'} a_{\eta'} \tag{2}$$

is an operator of spin–spin interaction expressed in a second quantization form [8]. In (2), the Greek symbols denote a set of four quantum numbers. In particular $\eta \equiv n_\eta l_\eta m_\eta \sigma_\eta$, and

$$H_2 = \sum \gamma_{\eta\zeta} a_\eta^+ c_\zeta - \sum \gamma_{\zeta\eta} c_\zeta^+ a_\eta \tag{3}$$

describes the electron transfer from a ligand into the unfilled shell of the paramagnetic ion. In the expression (3) $\gamma_{\eta\zeta} = -t_{\eta\zeta}/\Delta_{\eta\zeta}$ are dimensionless hoping integrals, or covalence parameters calculated per metal–ligand bond. Here and hereafter operators a_η and c_ζ refer to the electrons of the unfilled shell of the paramagnetic ion and to the ligands electron respectively. Substituting (3) and (2) in (1), after the calculation of the commutator we obtain

$$V_{\text{eff}} = \frac{1}{2}\sum \gamma_{\alpha\zeta} \gamma_{\zeta\xi} \langle \eta_1 \xi_2 | g_{12} | \eta_1' \xi_2' \rangle a_\eta^+ a_{\xi'} a_{\eta'} a_\alpha^+ + \text{HC} \tag{4}$$

where HC denotes a Hermite conjugated term.

Now we are interested in the angular momentum representation V_{eff} in (1). We expand the spin–spin interaction operator

$$g_{12} = g^2 \beta^2 \left[\frac{(\boldsymbol{s}_1 \boldsymbol{s}_2)}{r_{12}^3} - 3 \frac{(\boldsymbol{s}_1 \boldsymbol{r}_{12}) \times (\boldsymbol{s}_2 \boldsymbol{r}_{12})}{r_{12}^5} \right] \tag{5}$$

into the series of the irreducible tensor operators [9]. Following the standard method [9, 10], we obtain

$$g_{12} = -\frac{g^2\beta^2}{2\sqrt{5}}\left\{\sum_k(-1)^k\sqrt{\frac{(2k+5)!}{(2k)!}}\left[\frac{r_2^k}{r_1^{k+3}}(\{c_1^{(k+2)}c_2^{(k)}\}_q^{(2)}\cdot\{s_1s_2\}_q^{(2)})\right.\right.$$
$$\left.\left.+\frac{r_1^k}{r_2^{k+3}}(\{c_1^{(k)}c_2^{(k+2)}\}_q^{(2)}\cdot\{s_1s_2\}_q^{(2)})\right]\right\}. \tag{6}$$

Here the first and the second term have been derived under assumptions $r_2 < r_1$ and $r_1 < r_2$, respectively. The tensor products of the spin operators are defined by the usual rules [9, 10]:

$$\{s_1^{(1)}s_2^{(1)}\}_q^{(2)} = \sum_{\pi_1\pi_2}(-1)^q\sqrt{5}\begin{pmatrix} 1 & 1 & 2 \\ \pi_1 & \pi_2 & q \end{pmatrix}s_{\pi_1}^{(1)}s_{\pi_2}^{(2)}$$
$$\{c_1^{(k+2)}c_2^{(k)}\}_q^{(2)} = \sum_{q_1q_2}(-1)^q\sqrt{5}\begin{pmatrix} k+2 & k & 2 \\ q_1 & q_2 & -q \end{pmatrix}c_{q_1}^{(k+2)}c_{q_2}^{(k)}. \tag{7}$$

Using the expressions (2)–(7), the effective Hamiltonian V_{eff} after integrating over the radial variables and applying Wigner–Eckart theorem can be rewritten as follows:

$$V_{\text{eff}} = -\frac{g^2}{2}\sum\gamma_{\alpha\zeta}\gamma_{\zeta\xi}\left\{\sum_k(-1)^k\sqrt{\frac{(2k+5)!}{(2k)!}}M^{(k)}(-1)^{2q}\right.$$
$$\times\sqrt{5}\begin{pmatrix} 1 & 1 & 2 \\ \pi_1 & \pi_2 & -q \end{pmatrix}\langle s_\eta\sigma_\eta|s_{\pi_1}^{(1)}|s_{\eta'}\sigma_{\eta'}\rangle\langle s_\xi\sigma_\xi|s_{\pi_2}^{(2)}|s_{\xi'}\sigma_{\xi'}\rangle$$
$$\times\left[\begin{pmatrix} k+2 & k & 2 \\ q_1 & q_2 & -q \end{pmatrix}\langle l_\eta m_{l_\eta}|c_{q_1}^{(k+2)}|l_{\eta'}m_{l_{\eta'}}\rangle\langle l_\xi m_{l_\xi}|c_{q_2}^{(2)}|l_{\xi'}m_{l_{\xi'}}\rangle\right.$$
$$\left.\left.+\begin{pmatrix} k & k+2 & 2 \\ q_1 & q_2 & -q \end{pmatrix}\langle l_\eta m_{l_{\eta i}}|c_{q_1}^{(k)}|l_{\eta'}m_{\eta'}\rangle\langle l_\xi m_{l_\xi}|c_{q_2}^{(k+2)}|l_{\xi'}m_{l_{\xi'}}\rangle\right]\right\}$$
$$\times a_\eta^+ a_{\xi'} a_{\eta'} a_\alpha^+ + \text{HC}. \tag{8}$$

The reducible matrix elements of the one-electron operators are defined by the usual relations [9]:

$$(l||c^k||l) = (-1)^l\sqrt{(2l+1)(2l'+1)}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \qquad (s||s||s) = \sqrt{s(s+1)(2s+1)} \tag{9}$$

and the radial integrals:

$$M^{(k)} = \beta^2\iint\frac{r_<^k}{r_>^{k+3}}R_{nl}^2(r_1)R_{nl}^2(r^2)r_1^2r_2^2\,dr_1\,dr_2 \tag{10}$$

are known in the literature as Marvin integrals [11] and R_{nl} are the Hartree–Fock wave functions of electrons in the unfilled shell of the paramagnetic ion.

Expression (8) contains two terms. Let us consider the second one which contains the matrix element $\langle l_\xi m_{l_\xi}|c_{q_2}^{(k+2)}|l_{\xi'}m_{l_{\xi'}}\rangle$. Using the formula from [8]

$$a_\eta^+ a_{\eta'} = \sum_{\substack{\pi q \\ \chi_1 k}}(-1)^{s-\sigma_\eta}\sqrt{(2\chi_1+1)}\begin{pmatrix} s & \chi_1 & s \\ -\sigma_\eta & \pi_1 & \sigma_{\eta'} \end{pmatrix}(-1)^{l-m_\eta}\sqrt{(2k_1+1)}$$
$$\times\begin{pmatrix} l & k_1 & l \\ -m_\eta & q_1 & m_{\eta'} \end{pmatrix}\mathbf{W}_{\pi_1q_1}^{\chi_1k_1} \tag{11}$$

where $\mathbf{W}_{\pi_1 q_1}^{\chi_1 k_1}$ is a double irreducible tensor operator [8], then using the orthogonality of the $3j$-symbols and finally taking into consideration the selection rules for the covalence parameters [7] $\gamma_{\eta\zeta} = \gamma_{n_\xi l_\xi m_\xi} \delta_{\sigma_\eta \sigma_\xi} \delta_{m_\eta m_\xi}$ we obtain

$$V_{2\text{eff}} = -\frac{g^2\sqrt{5}}{2} \sum \gamma_{m_\xi} \gamma_{m_\alpha} \sum_k (-1)^k \sqrt{\frac{(2k+5)!}{(2k)!}} M^{(k)} \begin{pmatrix} k & k+2 & 2 \\ q_1 & q_2 & -q \end{pmatrix}$$
$$\times \begin{pmatrix} l_\xi & k+2 & l_{\xi'} \\ -m_\xi & q_2 & m_{\xi'} \end{pmatrix} \begin{pmatrix} 1 & 1 & 2 \\ \pi_1 & \pi_2 & -q \end{pmatrix} \begin{pmatrix} l_\xi & k_2 & l_{\xi'} \\ -m_\alpha & q_2' & m_{\xi'} \end{pmatrix}$$
$$\times \frac{\delta_{k_1 k} \delta_{q_1 q_1'} \delta_{1\chi_1} \delta_{\pi_1 \pi_1'} \delta_{1\chi_2} \delta_{\pi_2 \pi_2'}}{(2k+1) \times 3 \times 3} (l||c^{(k+2)}||l)(l||c^{(k)}||l)(s||s||s)^2$$
$$\times \sqrt{2\chi_1+1}\sqrt{2k+1}\sqrt{2\chi_2+1}\sqrt{2k_2+1}\mathbf{W}_{\pi_2 q_2'}^{1k_2}\mathbf{W}_{\pi_1 q_1'}^{1k} + \text{HC.} \tag{12}$$

In a similar manner the first part of the expression (8) can be simplified. Using the Wigner–Eckart theorem it can be proved that $V_{\text{eff}} = 0$ for the pure S states.

The expression (12) applies to the one metal ion ligand pair with the local z-axis along the bond of the pair. Before transformation of (12) to the crystallographic coordinate system it is useful to make some manipulations in it. Firstly, using the relations between the $6j$-symbols and $3j$-symbols, we can perform the following recoupling of the momenta

$$\sum_{m_\zeta m_{\zeta'}} \begin{pmatrix} l & k+2 & l \\ -m_\zeta & q_2 & m_{\zeta'} \end{pmatrix} \begin{pmatrix} k_2 & l & l \\ q_2' & -m_\zeta & m_{\zeta'} \end{pmatrix}$$
$$= \sum_{m_\zeta} (-1)^{l-m_\zeta - q_2 + k_2 + k}(2K+1) \begin{Bmatrix} l & k+2 & l \\ k_2 & l & K \end{Bmatrix}$$
$$\times \begin{pmatrix} k_2 & K & k+2 \\ -q_2' & 0 & q_2 \end{pmatrix} \begin{pmatrix} l & l & K \\ -m_\zeta & m_\zeta & 0 \end{pmatrix}. \tag{13}$$

Secondly, to define the quantities which are invariants with respect to a rotation around the bond axis:

$$J_l^{(K)}(R_{ab}) = (l||c^k||l) \sum_{m_\zeta} (-1)^{l-m_\zeta}(2K+1) \begin{pmatrix} l & l & K \\ -m_\zeta & m_\zeta & 0 \end{pmatrix} \gamma_{m_\zeta}^2. \tag{14}$$

Then the expression (12) for $V_{2\text{eff}}$ takes the form

$$V_{2\text{eff}} = -\frac{g^2\sqrt{5}}{6} \sum_k (-1)^k \sqrt{\frac{(2k+5)!}{(2k)!}} \sqrt{\frac{2k_2+1}{2k+1}} M^{(k)}(-1)^{-q_2 + k_2 + k} J_l^{(K)}$$
$$\times \begin{pmatrix} k & k+2 & 2 \\ q_1 & q_2 & -q \end{pmatrix} \begin{Bmatrix} l & k+2 & l \\ k_2 & l & K \end{Bmatrix} \begin{pmatrix} 1 & 1 & 2 \\ \pi_1 & \pi_2 & -q \end{pmatrix}$$
$$\times \begin{pmatrix} k_2 & l & k+2 \\ -q_2' & 0 & q_2 \end{pmatrix} (l||c^{(k+2)}||l)(s||s||s)^2\mathbf{W}_{\pi_2 q_2'}^{1k_2}\mathbf{W}_{\pi_1 q_1'}^{1k} + \text{HC.} \tag{15}$$

For the pure S states the expression (15) simplifies as follows:

$$V_{2\text{eff}} = -\frac{g^2\sqrt{5}}{6}\sqrt{5!} \sum_{\pi_1 \pi_2} J_l^{(2)} M^{(0)} \begin{pmatrix} 0 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} l & 2 & l \\ 0 & l & 2 \end{Bmatrix}$$
$$\times \begin{pmatrix} 1 & 1 & 2 \\ \pi_1 & \pi_2 & 0 \end{pmatrix} (l||c^{(0)}||l)(s||s||s)^2\mathbf{W}_{\pi_2 0}^{10}\mathbf{W}_{\pi_1 0}^{10} + \text{HC.} \tag{16}$$

Using the relation $\mathbf{W}_{\pi 0}^{10} = (2/(2l+1))^{1/2}\mathbf{S}_{\pi}^{(1)}$ [8] and the analytical expressions for $3j$- and $6j$-symbols we obtain the following form of the effective Hamiltonian (8):

$$V_{\text{eff}} = -\frac{g^2\sqrt{6}}{5}J_l^{(2)}M^{(0)}\frac{1}{(2l+1)^2}\{\mathbf{S}^{(1)}\mathbf{S}^{(1)}\}_0^{(2)} + \text{HC}. \tag{17}$$

The rotations of the coordinate system are done using the usual transformation rules for irreducible tensor operators [10]

$$\{\mathbf{S}^{(1)}\mathbf{S}^{(1)}\}_0^{(2)} = (\{\mathbf{S}^{(1)}\mathbf{S}^{(1)}\}^{(2)}\mathbf{C}^{(2)}(\theta_b\varphi_b)) \tag{18}$$

where $\mathbf{C}^{(2)}(\theta_b\varphi_b)$ is a spherical tensor of Euler angles, that defines the orientation of the metal–ligand pair with respect to the crystallographic coordinate system. Finally, taking into account all possible surrounding ligands by the simple summation over the index b we obtain

$$V_{\text{eff}} = -\frac{g^2\sqrt{6}}{5}M^0\frac{2}{(2l+1)^2}[\{\mathbf{S}^{(1)}\mathbf{S}^{(1)}\}_0^{(2)}\cdot\mathbf{C}_0^{(2)}(\theta_b\varphi_b)]J_l^{(2)}(R_{ab}). \tag{19}$$

Operator (19) can be easily changed into the spin-Hamiltonian form, that is usually applied for the analysis of the electron paramagnetic resonance (EPR) spectra:

$$H_{\text{eff}} = D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \cdots. \tag{20}$$

In particular, for the D-parameter we find the following expression from (19):

$$D_{\text{cov}}^l = -\frac{6}{5}\frac{g^2M^{(0)}}{(2l+1)}\sum_b J_l^{(2)}(R_{ab})\mathbf{C}_0^{(2)}(\theta_b). \tag{21}$$

The formula (21) allows us to calculate the covalence contribution to the parameter D for the different types of paramagnetic centre, e.g., cubic, octahedral, tetrahedral and others. The formula for the E_{cov}^l-parameter can be written in a similar way.

3. The general features of D_{cov} and numerical calculations

For the $3d^n$ shell of an iron group the expression (21) yields:

$$D_{\text{cov}}^d = -\frac{6}{25}g^2M^0\sum_b \mathbf{C}_0^{(2)}(\theta_b)J_d^{(2)}(R_{ab}). \tag{22}$$

In the case of $4f^n$-shell rare-earth ions we find from (21):

$$D_{\text{cov}}^l = -\frac{6}{35}g^2M^0\sum_b J_1^{(2)}(R_{ab})\mathbf{C}_0^{(2)}(\theta_b\varphi_b). \tag{23}$$

Using the formula (14), $J^{(2)}(R)$ can be written as follows:

$$J_d^{(2)} = \tfrac{10}{7}(\gamma_{d\sigma}^2 + \gamma_{d\pi}^2 + \gamma_{ds}^2) \qquad J_f^{(2)} = \tfrac{2}{3}(2\gamma_{f\sigma}^2 + 3\gamma_{f\pi}^2 + 2\gamma_{fs}^2). \tag{24}$$

As can be seen from (24) the values $J_d^{(2)}$ and $J_f^{(2)}$ are positive. Thus, the sign of the parameter D is mainly defined by $\sum_b \mathbf{C}_0^{(2)}(\theta_b) = \tfrac{1}{2}\sum_b(3\cos^2\theta_b - 1)$, the structural factor. The summation is taken over the nearest surrounding ligands only, and angle θ_b is measured from the z-axis of the paramagnetic centre. It is easy now to deduce the following rules; for the compressed octahedral surroundings $D > 0$, while for compressed cubic (eightfold) and tetrahedral (fourfold) surroundings $D < 0$. These simple rules agree with semiempirical conclusions, that were drawn on the basic of the EPR data in [1]. The relation between D_{cov} and the B_2^0 crystal field parameter can be easily obtained from the expressions (21)–(23).

The comparison of (21) with the expression of the crystal field parameter [12, 13] indicates that the signs of D and B_2^0 (here as in Newman's paper [2] we include only the contributions to B_2^0 from the nearest ligands) are opposite. Hence, within the framework of the covalent model, this conclusion is really correct for all S-state ions.

Let us touch now briefly on the overlapping effect, because the electron states at the metal ion and ligands are not orthogonal to each other. Mathematically this problem has common features with the Slater reduction parameter problem, which was discussed in [14]. In the same manner as in [14], taking into account in first and second order of perturbation theory the overlapping effects of the unfilled electronic shell of the paramagnetic ion with the ligand shells, one can deduce that $\gamma_{m_\zeta}^2$ in (14) is just changed by the expression $\gamma_{m_\zeta}^2 + 2x s_{m_\zeta} \gamma_{m_\zeta} - s_{m_\zeta}^2$, where s_{m_ζ} is an overlap integral and x is an approximation parameter, which is about 0.5.

For the more accurate comparison with the experimental data [15–21] let us consider some examples. In table 1 we collected the x-ray structure analysis data of θ-angles for different single crystals. The overlap integrals were calculated using the Hartree–Fock function [22]. The covalence parameters for some fluorides are known from the analysis of the superhyperfine interaction [23]. Small corrections of these values have been performed under the assumption that the covalence parameters are changed versus R_{ab} distance like overlap integrals. The values of γ calculated in a such way are given in table 2. In table 3 we show the results of the calculation of the D_{cov}-parameter for Fe^{3+} and Gd^{3+} ions in single crystals $LiCaAlF_6$, $LiSrAlF_6$ and Al_2O_3, as well as for the ion Gd^{3+} in $YBa_2Cu_3O_{6+y}$ for $y = 0.91$ and 0.95, together with the experimental data for D in these compounds. The calculated D_{cov} coincides in order of magnitude as well as in the signs with the experimental values of D.

Table 1. Values of the angles θ_b taken from the structural data.

Paramagnetic ion	Compounds	θ_b (°)
Fe^{3+}	$LiSrAlF_6$	53.28 [15]
	$LiCaAlF_6$	54.9 [16]
	Al_2O_3	24.75 [17]
		39.14 [17]
Gd^{3+}	$LiSrAlF_6$	49.7 [18]
	$LiCaAlF_6$	52.04 [18]
	Al_2O_3	19.82 [19]
		33.28 [19]
	$YBa_2Cu_3O_{6.91}$	57.15 [20, 21]
		63.28 [20, 21]
	$YBa_2Cu_3O_{6.93}$	56.72 [20, 21]
		63.14 [20, 21]

4. Discussion

In summary, in the present paper we have calculated the influence of the covalence (charge transfer ligand–metal processes) on the zero-field splitting of the S-state phenomena. We have obtained the simple analytical formula for the spin-Hamiltonian parameters of the unfilled 4f and 3d shells, which can be applied for the crystals with a different symmetry.

Table 2. Overlap integrals and covalence parameters. Metal–ligand distance R.

Ion		LiCaAlF$_6$ $R = 1.8$ Å	LiSrAlF$_6$ $R = 1.86$ Å	Al$_2$O$_3$ $R = 1.845$ Å	Al$_2$O$_3$ $R = 1.988$ Å	YBa$_2$Cu$_3$O$_{6.91}$ $R = 2.375$ Å	YBa$_2$Cu$_3$O$_{6.91}$ $R = 2.403$ Å	YBa$_2$Cu$_3$O$_{6.95}$ $R = 2.381$ Å	YBa$_2$Cu$_3$O$_{6.95}$ $R.2 = 406$ Å
Fe^{3+}	$S_{3d,2s}$	0.064	0.056	0.056	0.045	—	—	—	—
	$\gamma_{3d,2s}$	0.034	0.032	0.032	0.026	—	—	—	—
	$S_{3d2p,\sigma}$	0.076	0.070	0.066	0.056	—	—	—	—
	$\gamma_{3d2p,\sigma}$	0.213	0.198	0.209	0.150	—	—	—	—
	$S_{3d2p,\pi}$	0.049	0.043	0.047	0.036	—	—	—	—
	$\gamma_{3d2p,\pi}$	0.153	0.142	0.159	0.100	—	—	—	—
		$R = 2.273$ Å	$R = 2.34$ Å	$R = 2.457$ Å	$R = 2.6$ Å	$R = 2.375$ Å	$R = 2.403$ Å	$R = 2.384$ Å	$R = 2.407$ Å
Gd^{3+}	$S_{4f,2s}$	0.013	0.011	0.0095	0.0073	0.0109	0.0104	0.0107	0.0103
	$\gamma_{4f,2s}$	0.017	0.014	0.013	0.009	0.013	0.011	0.013	0.011
	$S_{4f2p,\sigma}$	0.018	0.016	0.013	0.010	0.015	0.014	0.015	0.014
	$\gamma_{4f2p,\sigma}$	0.099	0.096	0.093	0.070	0.089	0.087	0.088	0.087
	$S_{4f2p,\pi}$	0.012	0.010	0.0082	0.0062	0.0096	0.0092	0.0095	0.0091
	$\gamma_{4f2p,\pi}$	0.072	0.071	0.069	0.052	0.070	0.069	0.070	0.069

Table 3. Values of parameter D.

Paramagnetic ions	Compounds	D (MHz)	
		Experimental	Calculated
Fe^{3+}	$LiSrAlF_6$	-908 [15]	-839
	$LiCaAlF_6$	112 [16]	109
	Al_2O_3	3839 [17]	1718
Gd^{3+}	$LiSrAlF_6$	-1210 [18]	-1000
	$LiCaAlF_6$	-653 [18]	-561
	Al_2O_3	2365 [19]	1177
	$YBa_2Cu_3O_{6.91}$	-1270 [20, 21]	-1184
	$YBa_2Cu_3O_{6.95}$	-1272 [20, 21]	-1279

(a) The sign of the parameter D is defined by the structural factor $\sum_b \mathbf{C}_0^{(n)}(\theta_b\varphi_b)$.

(b) Consequently, $D > 0$ for compressed octahedral surroundings; for compressed cubic and tetrahedral surroundings $D < 0$. These simple rules agree with the semiempirical conclusions [4].

(c) In the frame of our covalent model, the signs of the crystal field parameter B_2^0 (from the nearest neighbour ligands) and of the spin-Hamiltonian parameter D are opposite.

(d) We have calculated the parameters D_{cov} for Fe^{3+} and Gd^{3+} ions in $LiCaAlF_6$, $LiSrAlF_6$ and Al_2O_3 single crystals, as well as for the ion Gd^{3+} in $YBa_2Cu_3O_{6+y}$ for $y = 0.91, 0.95$. In all cases the calculated value of D agrees in order of magnitude and signs well with EPR data. Thus, we arrive at the conclusion: the charge transfer processes contribution to the zero-field splitting of the S-state transition ions is very important at least for the crystals that we have examined in the present paper.

Acknowledgments

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