

# PARAMETRIZATION OF THE BILINEAR ORBIT-LATTICE INTERACTION

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A group theoretical parametrization scheme of the bilinear orbit-lattice interaction is presented. Using this scheme a general analytical form of this interaction in the point-charge electrostatic model has been obtained. Based on this general analytical form the second-order parameters of the bilinear orbit-lattice interaction have been calculated for a tetrahedral complex. For cubic complexes a microscopic interpretation of the  $G$ -tensor components in the long-wavelength approximation of acoustic waves is given for the first time. The presented scheme of parametrization as well as the method of calculations of the interaction parameters may be extended to other models of the crystal field.

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## 1. Introduction

A magnetic ion placed in a diamagnetic crystal host is subjected to the electric field produced by lattice. In the simplest model of a crystal field the assumption is made that the nuclear framework of the complex is stationary. This static approach of the crystal field theory has been often used (see e.g. [1-4]) and is widely known.

When the thermal crystalline vibrations or the acoustic waves are considered, ion displacements from the equilibrium positions must be taken into account. These displacements of ions positions modulate the crystal field acting on a magnetic ion and change the crystal field energy. To account for these changes the crystal field operator is expanded into a Taylor series in terms of normal (or symmetry) coordinates, what can be schematically written as:

$$V_c = V^{(0)} + V^{(1)} + V^{(2)} + \dots, \quad (1.1)$$

where  $V^{(0)}$  is the static crystal field Hamiltonian with ligands at equilibrium positions,  $V^{(1)}$  is called the orbit-lattice interaction and is linearly dependent on the deformation [5-9],  $V^{(2)}$  is a term bilinear in the deformation, etc. (from the mathematical point of view the  $V^{(2)}$  can be either the bilinear form or the quadratic form).

As the bilinear term will be the main subject of our further considerations, let us give its explicit form:

$$V^{(2)} = \frac{1}{2} \sum_{\delta A \lambda, \delta' A' \lambda'} \left[ \frac{\partial^2 V_c}{\partial Q_{\delta A \lambda} \partial Q_{\delta' A' \lambda'}} \right]_0 Q_{\delta A \lambda} Q_{\delta' A' \lambda'}, \quad (1.2)$$

where  $Q_{\delta A \lambda}$  is the normal coordinate transforming according to the  $\lambda$ -th row of the irreducible representation  $A$  of a point-group (say  $G$ ) of the magnetic ion placed in a crystal field, and  $\delta$  is the repetition index of this representation. Here  $]_0$  indicates that quantities should be evaluated for equilibrium positions of the paramagnetic cluster.

The term (1.2) will be called the bilinear (with deformation) orbit-lattice interaction analogously with the orbit-lattice interaction  $V^{(1)}$  which is linearly dependent on the deformation.

Depending on definition of a "crystal field" potential, the bilinear orbit-lattice interaction may play an important role in many specific physical situations. For example in molecular approach, the quadratic vibronic constants [10] being the matrix elements of the  $\partial^2 V_c / \partial Q_{\delta A \lambda} \partial Q_{\delta' A' \lambda'}$  operator are introduced as the molecular dynamic structure parameters. As yet another example consider a magnetic ion subjected to the crystal field modulated by lattice vibrations [5, 6]. In this particular case the bilinear orbit-lattice interaction is responsible for such important two-phonon phenomena as the spin-lattice relaxation [9, 11] and the dynamical Jahn-Teller effect [12].

Despite an obvious importance of the bilinear orbit-lattice interaction in molecular physics and in solid state physics, a marked progress in its theory — particularly in microscopic formulation — has not been achieved yet. We believe this paper opens a possible way to develop a theory of that type.

In the first place we consider a group-theoretical approach to the problem of parametrization of the bilinear orbit-lattice interaction based on previously developed scheme [13] of the dynamic crystal field Hamiltonian. Classifying the interaction parameters according to the irreducible representations of a point-symmetry group of the crystal field and expressing an interaction Hamiltonian in a form appropriate to its transformation properties we create a general framework for description, which is independent of the assumed crystal field model.

Based on the presented group-theoretical description and using the two-center expansion [14] of the dynamic crystal field Hamiltonian, a general analytical form of the introduced parameters has been found for the point-charge electrostatic model. The generality of this analytical form is understood in this sense that it is valid for any point-symmetry of the crystal field and for any coordination of the magnetic ion.

Analytical expressions for the discussed parameters allowed us to find out the bilinear orbit-lattice interaction parameters for the tetrahedral complex and in the

long-wavelength limit of acoustic waves for the eight-fold cubic coordination. For both of these cases we were able for the first time to give microscopic interpretation of the above mentioned interaction parameters.

## 2. Group-Theoretical approach to parametrization of the bilinear orbit-lattice interaction

In order to parametrize the bilinear orbit-lattice interaction let us discuss transformation properties of the expression (1.2) according to symmetry of a point group  $G$  of the crystal field. Each element of this group acts on the product  $Q_{\delta A \lambda} Q_{\delta' A' \lambda'}$  of the normal coordinates. The tensor (Kronecker) product of two representations will give another representation, which will usually be reducible, the term  $Q_{\delta A \lambda} Q_{\delta' A' \lambda'}$  decomposing into components of each of the irreducible spaces of the product space [15]:

$$Q_{\delta A \lambda} Q_{\delta' A' \lambda'} = \sum_{\bar{\delta} \bar{\lambda}} \begin{bmatrix} \Lambda & \Lambda' & \bar{\Lambda} & \bar{\delta} \\ \lambda & \lambda' & \bar{\lambda} & \bar{\delta} \end{bmatrix}^* Q_{(\delta A, \delta' A') \bar{\delta} \bar{\lambda}}, \quad (2.1)$$

where  $[\dots]$  is the Clebsch-Gordan coefficient in Lulek notation [16], and asterisk designate complex conjugation. As a consequence of transformation (2.1) the quantities  $Q_{(\delta A, \delta' A') \bar{\delta} \bar{\lambda}}$  span spaces for the irreducible representations  $\bar{\Lambda}$  with  $\bar{\delta}$  being the repetition index of this representation.

The second derivative with respect to normal coordinates which appear in (1.2) is an explicit function of the electron coordinates and the elements of group  $G$  are acting only on electron coordinates. Thus we may factorize these derivatives in such a way, that

$$\frac{1}{2} \sum_{\lambda \lambda'} \frac{\partial^2 V_c}{\partial Q_{\delta A \lambda} \partial Q_{\delta' A' \lambda'}} \begin{bmatrix} \Lambda & \Lambda' & \bar{\Lambda} & \bar{\delta} \\ \lambda & \lambda' & \bar{\lambda} & \bar{\delta} \end{bmatrix}^* = f_{(\delta A, \delta' A') \bar{\delta} \bar{\lambda}} g_{\bar{\lambda}}^*(r_0, \theta_0, \phi_0), \quad (2.2)$$

where  $r_0, \theta_0, \phi_0$  are electron coordinates, and  $f$  is a scalar, real quantity. The asterisk by function  $g$  means complex conjugate so this function transforms according to the  $\bar{\Lambda}^*$  representation complex conjugated with  $\bar{\Lambda}$ .

This simple conclusion forms a group-theoretical base for parametrization of the bilinear orbit-lattice interaction Hamiltonian. Now this Hamiltonian will take the form:

$$V^{(2)} = \sum_{\delta A} \sum_{\delta' A'} \sum_{\bar{\delta} \bar{\lambda}} f_{(\delta A, \delta' A') \bar{\delta} \bar{\lambda}} g_{\bar{\lambda}}^*(r_0, \theta_0, \phi_0) Q_{(\delta A, \delta' A') \bar{\delta} \bar{\lambda}}, \quad (2.3)$$

where  $f$  is the interaction parameter, and  $g$  is an operator acting in the electron space.

It should be stressed that the operator  $g_{\bar{\lambda}}$  is defined by the transformation properties of quantities appearing on the left side of (2.2). So it may happen that this operator will be a sum of the operators transforming in the same way, i.e.

$$g_{\bar{\lambda}} = \sum_{\bar{\delta}'} f_{\bar{\delta}' \bar{\lambda}}^{\prime} g_{\bar{\delta}' \bar{\lambda}}^{\prime}, \quad (2.4)$$

where  $f'$  is a scalar quantity and the repetition index numbers the operators  $g'$  transforming in the same manner. If we are faced with such a situation it is suitable to define the interaction parameters in the following way:

$$f'_{(\delta A, \delta' A') \bar{\delta}' \bar{\delta A}} \equiv f_{(\delta A, \delta' A') \bar{\delta A}} f'_{\bar{\delta}' \bar{A}} \quad (2.5)$$

and rewrite the bilinear orbit-lattice coupling operators in the form:

$$V^{(2)} = \sum_{\delta A} \sum_{\delta' A'} \sum_{\bar{\delta A} \lambda} \sum_{\bar{\delta}'} f'_{(\delta A, \delta' A') \bar{\delta}' \bar{\delta A}} g'^*_{\bar{\delta}' \bar{A} \lambda}(r_0, \theta_0, \phi_0) Q_{(\delta A, \delta' A') \bar{\delta A} \lambda}. \quad (2.6)$$

If we make no assumption whatsoever concerning the nature of the crystal field interaction, the Hamiltonian of the bilinear orbit-lattice interaction (2.3) or (2.6) may be regarded as a purely phenomenological one. However, if an explicit form of the crystal field potential  $V_c$  is known, the Hamiltonian and its parameters may be found explicitly. This will be shown for a point-charge electrostatic model of the crystal field in the next Section.

### 3. The theory of the bilinear orbit-lattice interaction

The dynamic Hamiltonian in a point-charge electrostatic model of the crystal field has the form:

$$V_c = - \sum_l \frac{Z_l e^2}{|\mathbf{R}_l + \mathbf{r}_l - \mathbf{r}_0|}, \quad (3.1)$$

where  $Z_l$  is the  $l$ -th ligand charge,  $\mathbf{R}_l$  is a radius vector of the equilibrium position of the  $l$ -th ligand,  $\mathbf{r}_l$  is the displacement vector for the  $l$ -th ligand, and  $\mathbf{r}_0$  is a radius vector of an electron (see Fig. 1 in Ref. [13]).

A general framework of parametrization of the Hamiltonian (3.1) has been given earlier [13]. Applying that parametrization scheme and taking into account results of the previous Section we find that the Hamiltonian (3.1) takes the form:

$$V^{(2)} = \sum_{\delta A} \sum_{\delta' A'} \sum_{\bar{\delta A} \lambda} \sum_{\bar{\delta}' K} A_{(\delta A, \delta' A') \bar{\delta}' \bar{\delta A}}^{(2, K)} r_0^K C_{\bar{\delta}' \bar{A} \lambda}^{(K)*}(\theta_0, \phi_0) Q_{(\delta A, \delta' A') \bar{\delta A} \lambda}, \quad (3.2)$$

where  $A_{(\delta A, \delta' A') \bar{\delta}' \bar{\delta A}}^{(2, K)}$  is the interaction parameter and  $C_{\bar{\delta}' \bar{A} \lambda}^{(K)}$  is a symmetry adapted linear combination of the components of spherical tensor of rank  $K$  related to the spherical harmonics  $Y_Q^{(K)}$  by the relation:

$$C_Q^{(K)} = \sqrt{\frac{4\pi}{2K+1}} Y_Q^{(K)}. \quad (3.3)$$

Similarity of structure of the Hamiltonian (3.2) and the expression (2.6) is obvious. Only the repetition indices  $\bar{\delta}'$  and  $\bar{\delta}'$  appearing in these expressions need further comments. Since  $V^{(2)}$  is expanded in terms of the spherical harmonics of

rank  $K$ , the index  $K$  quite naturally distinguishes bases transforming in the same way but originating from different representations  $D^{(K)}$  of the full rotation group. On the other hand in decomposition of the representation  $D^{(K)}$  on irreducible representations of a point group of the paramagnetic complex some of these irreducible representations may appear more than once. And just these repeating themselves representations are distinguished by the index  $\delta'$ . As a consequence a pair of indices in (3.2) corresponds to the index  $\bar{\delta}'$  in (2.6)

$$\bar{\delta}' = \{K, \delta'\}. \quad (3.4)$$

Parameters of the bilinear coupling can be calculated by using the two-center expansion [14] of the crystal field dynamic Hamiltonian in a manner similar to the one used in calculation of the linear parameters of the orbit-lattice coupling [13]. Thus we get

$$\begin{aligned} A_{(\delta\lambda, \delta'\lambda')}^{(2,K)} \bar{\delta}' \bar{\delta}\lambda = & -\frac{\sqrt{\pi}}{[\Lambda]} e^2 \sum_i \sum_{\bar{\lambda}} \sum_{\lambda\lambda'} \sum_Q Z_1 \frac{(2K+1)(2K+3)}{\sqrt{3(2K+5)}} \\ & \times \begin{bmatrix} K & 2 & K+2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \Lambda & \Lambda' & \bar{\Lambda} & \bar{\delta} \end{bmatrix}^* a_{\delta'\bar{\lambda}\lambda}^{KQ} \frac{r_0^{K+2}}{R_i^{K+3}} \left\{ \frac{\partial x_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial x_i}{Q_{\delta'\Lambda'\lambda'}} \right. \\ & \times \left[ \begin{bmatrix} K & 2 & K+2 \\ Q & 2 & Q+2 \end{bmatrix} Y_{K+2, Q+2}(\theta_i, \varphi_i) - \frac{2}{3} \begin{bmatrix} K & 2 & K+2 \\ Q & 0 & Q \end{bmatrix} Y_{K+2, Q}(\theta_i, \varphi_i) \right. \\ & + \left. \left. \begin{bmatrix} K & 2 & K+2 \\ Q & -2 & Q-2 \end{bmatrix} Y_{K+2, Q-2}(\theta_i, \varphi_i) \right] - \frac{\partial y_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial y_i}{\partial Q_{\delta'\Lambda'\lambda'}} \right. \\ & \times \left[ \begin{bmatrix} K & 2 & K+2 \\ Q & 2 & Q+2 \end{bmatrix} Y_{K+2, Q+2}(\theta_i, \varphi_i) + \sqrt{\frac{2}{3}} \begin{bmatrix} K & 2 & K+2 \\ Q & 0 & Q \end{bmatrix} \right. \\ & \times Y_{K+2, Q}(\theta_i, \varphi_i) + \left. \left. \begin{bmatrix} K & 2 & K+2 \\ Q & -2 & Q-2 \end{bmatrix} Y_{K+2, Q-2}(\theta_i, \varphi_i) \right] \right. \\ & + \sqrt{\frac{8}{3}} \frac{\partial z_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial z_i}{\partial Q_{\delta'\Lambda'\lambda'}} \left. \begin{bmatrix} K & 2 & K+2 \\ Q & 0 & Q \end{bmatrix} Y_{K+2, Q}(\theta_i, \varphi_i) \right. \\ & - i \left[ \frac{\partial x_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial y_i}{\partial Q_{\delta'\Lambda'\lambda'}} + \frac{\partial y_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial x_i}{\partial Q_{\delta'\Lambda'\lambda'}} \right] \left[ \begin{bmatrix} K & 2 & K+2 \\ Q & 2 & Q+2 \end{bmatrix} \right. \\ & \times Y_{K+2, Q+2}(\theta_i, \varphi_i) - \left. \begin{bmatrix} K & 2 & K+2 \\ Q & -2 & Q-2 \end{bmatrix} Y_{K+2, Q-2}(\theta_i, \varphi_i) \right] \\ & - \left[ \frac{\partial x_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial z_i}{\partial Q_{\delta'\Lambda'\lambda'}} + \frac{\partial z_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial x_i}{\partial Q_{\delta'\Lambda'\lambda'}} \right] \left[ \begin{bmatrix} K & 2 & K+2 \\ Q & 1 & Q+1 \end{bmatrix} \right. \\ & \times Y_{K+2, Q+1}(\theta_i, \varphi_i) - \left. \begin{bmatrix} K & 2 & K+2 \\ Q & -2 & Q-1 \end{bmatrix} Y_{K+2, Q-1}(\theta_i, \varphi_i) \right] \\ & + i \left[ \frac{\partial y_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial z_i}{\partial Q_{\delta'\Lambda'\lambda'}} + \frac{\partial z_i}{\partial Q_{\delta\lambda\lambda}} \frac{\partial y_i}{\partial Q_{\delta'\Lambda'\lambda'}} \right] \left[ \begin{bmatrix} K & 2 & K+2 \\ Q & 1 & Q+1 \end{bmatrix} \right. \\ & \times Y_{K+2, Q+1}(\theta_i, \varphi_i) + \left. \left. \begin{bmatrix} K & 2 & K+2 \\ Q & -1 & Q-1 \end{bmatrix} Y_{K+2, Q-1}(\theta_i, \varphi_i) \right] \right\}, \quad (3.5) \end{aligned}$$

where the summation over  $l$  corresponds to the summation over all ions producing the electric field,  $[[::]]$  are the Clebsch-Gordan coefficients for a rotational group in Yutsis notation [17], and  $a_{\delta'\Lambda\lambda}^{KQ}$  are the decomposition coefficients defined by means of the equation:

$$C_{\delta'\Lambda\lambda}^{(K)} = \sum_Q a_{\delta'\Lambda\lambda}^{KQ} C_Q^{(K)}. \quad (3.6)$$

Moreover  $[\bar{A}]$  is the dimension of  $\bar{A}$ .

Using the relation (3.5) and taking the normal coordinates from [13] and the expansion coefficients and the Clebsch-Gordan coefficients for the cubic group from [1], the second-order ( $K = 2$ ) bilinear orbit-lattice coupling parameters for a regular tetrahedron were calculated. We obtain:

$$\begin{aligned} A_{(A_1, E)E}^{(2,2)} &= 4, & A_{(A_1, aT_2)}^{(2,2)} &= \frac{8}{3}, \\ A_{(A_1, bT_2)}^{(2,2)} &= -2\sqrt{10}/3, & A_{(E, E)E}^{(2,2)} &= 1, \\ A_{(E, aT_2)T_2}^{(2,2)} &= 2\sqrt{2}, & A_{(E, bT_2)T_2}^{(2,2)} &= 0, \\ A_{(aT_2, aT_2)E}^{(2,2)} &= 17/2\sqrt{3}, & A_{(aT_2, aT_2)T_2}^{(2,2)} &= 2\sqrt{2}, \\ A_{(aT_2, bT_2)E}^{(2,2)} &= \sqrt{30}/6, & A_{(aT_2, bT_2)T_2}^{(2,2)} &= 14\sqrt{3}/45. \end{aligned} \quad (3.7)$$

All the above parameters must be multiplied by  $|Ze^2|/R^5$ , where  $R$  is the metal-ligand distance.

Inspecting the general form of parameters  $A_{(\delta A, \delta' A')\delta\bar{\delta}\bar{A}}^{(2,K)}$  one can observe that their properties by interchange of the indices  $\delta A$  and  $\delta' A'$  are the same as the properties of interchange of the first two columns in the Clebsch-Gordan coefficient  $\begin{bmatrix} A & A' & \bar{A} & \bar{\delta} \\ \lambda & \lambda' & \bar{\lambda} & \bar{\delta} \end{bmatrix}$ . Because the Clebsch-Gordan coefficients used by us are symmetrical to this operation [1], the parameters (3.7) must also be, i.e.

$$A_{(\delta A, \delta' A')\delta\bar{\delta}\bar{A}}^{(2,2)} = A_{(\delta' A', \delta A)\delta\bar{\delta}\bar{A}}^{(2,2)}. \quad (3.8)$$

#### 4. Special cases of the bilinear orbit-lattice coupling

##### 4.1. The long-wavelength limit of acoustic waves in cubic complexes

In the long-wavelength limit the acoustic waves can be expressed in terms of the strains. The three normal coordinates  $Q_7$ ,  $Q_8$ , and  $Q_9$  from the nine active normal coordinates for tetrahedral [18] or cubic [19] complex cannot be expressed in terms of the strains [18] and do not contribute to the long-wavelength

acoustic phonons. The others six normal coordinates for the cubic complex are expressed in terms of the strains in the following way (instead of numbers 1, 2, ... 6, a group-theoretical labeling scheme was used for the normal coordinates):

$$\begin{aligned}
 Q_{A_1 a_1} &= (2\sqrt{2}/3)R(e_{xx} + e_{yy} + e_{zz}), \\
 Q_{E\theta} &= (2/3)R(2e_{zz} - e_{xx} - e_{yy}), \\
 Q_{E\epsilon} &= (2/\sqrt{3})R(e_{xx} - e_{yy}), \\
 Q_{aT_{2x}} &= -(4/\sqrt{3})Re_{yz}, \\
 Q_{aT_{2y}} &= -(4/\sqrt{3})Re_{xz}, \\
 Q_{aT_{2z}} &= -(4/\sqrt{3})Re_{xy},
 \end{aligned} \tag{4.1}$$

where  $R$  is the metal-ligand distance, and

$$e_{ij} = (\varepsilon_{ij} + \varepsilon_{ji})/2, \tag{4.2}$$

where  $i, j = x, y, z$ , and  $\varepsilon_{ij}$  is a component of the strain tensor [19].

Interaction of a spin of the paramagnetic complex with the crystal deformation field can be described in this particular case by the phenomenological Hamiltonian of the form [20]:

$$\begin{aligned}
 V_{\text{fen}}^{(2)} &= \frac{3}{2}O_2^0 \left\{ G_{111} \left[ e_{zz}^2 - \frac{1}{2}(e_{xx}^2 + e_{yy}^2) \right] + 2G_{112} \left[ \frac{1}{2}e_{zz}(e_{xx} + e_{yy}) - e_{xx}e_{yy} \right] \right. \\
 &+ 4G_{166}(e_{xz}^2 + e_{yz}^2 - 2e_{xy}^2) \left. \right\} + 2\sqrt{3}O_2^2 \left\{ \frac{1}{4}G_{111}(e_{xx}^2 - e_{yy}^2) + G_{112}(e_{xx} + e_{yy})e_{zz} \right. \\
 &+ 2G_{166}(e_{xz}^2 - e_{yz}^2) \left. \right\} + 4\Omega_2^2 \left\{ G_{661}(e_{xx} + e_{yy})e_{xy} + G_{663}e_{zz}e_{xy} + 2G_{456}e_{xz}e_{yz} \right\} \\
 &+ 4O_2' \left\{ G_{661}(e_{xx} + e_{zz})e_{xz} + G_{663}e_{yy}e_{xz} + 2G_{456}e_{yz}e_{xy} \right\} \\
 &+ 4\Omega_2' \left\{ G_{661}(e_{yy} + e_{zz})e_{yz} + G_{663}e_{xx}e_{yz} + 2G_{456}e_{xz}e_{xy} \right\},
 \end{aligned} \tag{4.3}$$

where operators  $O$  and  $\Omega$  are linear combinations of products of the spin operator components  $S_i S_j$  ( $i, j = x, y, z$ ) [20] (the above Hamiltonian contains minor corrections as compared to the Hamiltonian given by Koloskova).

Since the second-order spin Hamiltonian (4.3) was obtained by symmetry considerations, the Hamiltonian of the orbit-lattice deformation field coupling is established by replacing spin operators by the operators acting in the orbital states spaces of an electron, because they have the same transformation properties. The following substitutions for the operators:

$$\begin{aligned}
 O_2^0 &\Rightarrow C_{E\theta}^{(2)} = C_0^{(2)}, \\
 O_2^2 &\Rightarrow C_{E\epsilon}^{(2)} = (C_{-2}^{(2)} + C_2^{(2)})\sqrt{2}, \\
 O_2' &\Rightarrow C_{T_{2y}}^{(2)} = (C_1^{(2)} - C_2^{(2)})/\sqrt{2}, \\
 \Omega_2^2 &\Rightarrow C_{T_{2x}}^{(2)} = i(C_{-1}^{(2)} + C_1^{(2)})/\sqrt{2}, \\
 \Omega_2' &\Rightarrow C_{T_{2z}}^{(2)} = i(C_{-2}^{(2)} - C_2^{(2)})/\sqrt{2}
 \end{aligned} \tag{4.4}$$

and for the coupling parameters

$$G_{ijk} \Rightarrow G'_{ijk} \quad (4.5)$$

have been made.

Of course, parameters  $G'_{ijk}$  — similarly to  $G_{ijk}$  — can be treated as purely phenomenological parameters, but if an explicit form of the crystal field energy operator is known, then these parameters can be fully calculated. According to the presented microscopic theory of the bilinear orbit–lattice interaction, the parameters  $G'_{ijk}$  can be expressed by the parameters  $A_{(\delta\Lambda, \delta'\Lambda')\delta'\delta\Lambda}^{(2,2)}$ . Next, the parameters  $A_{(\delta\Lambda, \delta'\Lambda')\delta'\delta\Lambda}^{(2,2)}$  for a cubic system with the 8-fold coordination can be calculated from the parameters obtained for a tetrahedron and given by the equation (3.7). Performing the suitable calculations we have obtained the following values of the microscopic parameters  $G'_{ijk}$  for the  $XY_8$  cubic cluster:

$$\begin{aligned} G'_{111} &= 224\sqrt{2}, & G'_{112} &= 80\sqrt{2}, \\ G'_{116} &= 34\sqrt{2}, & G'_{661} &= -8\sqrt{6}, \\ G'_{663} &= -80\sqrt{6}, & G'_{456} &= -56\sqrt{6}. \end{aligned} \quad (4.6)$$

All of these parameters must be multiplied by the constant factor  $|Ze^2|r_0^2/27R^3$ .

#### 4.2. Zero cross terms cases

It is often stated that in case of a magnetic ion interacting with the crystal field modulated by lattice vibrations [5, 6] the terms containing products of the normal coordinates  $Q_{\delta\Lambda\lambda}Q_{\delta'\Lambda'\lambda'}$  with  $\Lambda\lambda \neq \Lambda'\lambda'$  are equal to zero [18, 20–22]. In that situation it is useful to modify the above expressions in such a way that the quantity  $Q_{(\delta\Lambda, \delta'\Lambda')\delta'\delta\Lambda\lambda}$  defined by equation (2.1) becomes an invariant. To this end let us make in (2.1) and in other appropriate expressions the following substitutions:

$$Q_{\delta'\Lambda'\lambda'} = Q_{\delta'\Lambda\lambda}^* \quad (4.7)$$

Since  $Q_{\delta'\Lambda\lambda}^*$  transforms according to the representation  $\Lambda^*$ , which is complex conjugated to the representation  $\Lambda$ , the quantity

$$Q_{(\delta\Lambda, \delta'\Lambda^*)A_1a_1} = \sum_{\lambda} \begin{bmatrix} \Lambda & \Lambda^* & A_1 \\ \lambda & \lambda & a_1 \end{bmatrix} Q_{\delta\Lambda\lambda} Q_{\delta'\Lambda^*\lambda} \quad (4.8)$$

is invariant under all operations of a point-group symmetry of the crystal field. The Clebsch–Gordan coefficient equals (with the phase factor accuracy):

$$\begin{bmatrix} \Lambda & \Lambda^* & A_1 \\ \lambda & \lambda & a_1 \end{bmatrix} = 1/\sqrt{[\Lambda]}, \quad (4.9)$$

where  $[\Lambda]$  is the dimension of the  $\Lambda$  representation.



## 5. Summary

In this paper a scheme of parametrization of the bilinear orbit-lattice coupling has been presented. This scheme is based on group-theoretical analysis of the orbit-lattice interaction operator and lead to an elegant and comprehensive classification of the coupling parameters. The analytical form for magnitude of the interaction parameters in the point-charge model has been derived. This allowed us to calculate, in a relatively simple manner, the parameters  $A_{(\delta A, \delta' A') \delta' \delta A}^{(2, K)}$  of any order in  $K$  and for any symmetry of the paramagnetic complex. Up to now this was almost an impossible task requiring very complicated and time consuming calculations.

The analytical form of the  $A_{(\delta A, \delta' A') \delta' \delta A}^{(2, K)}$  parameters has been calculated in the point-charge model. Therefore, the values of these parameters are a superposition of some terms each of which is proportional to the electric charge of a ligand  $Z_l e$ . Only slight modifications would extend substantially the range of applications of the result obtained. For example, the replacement of the nominal charge of a ligand by its effective charge is the operation frequently used in the theory of crystal field. This simple modification when carried out for the calculations presented above would lead us to a semiempirical model which should, in many cases, improve the consistency between the result derived from theory and from experiment. However, from the practical point of view it is most essential that the here presented results allow the classification of the parameters describing the bilinear orbit-lattice interaction in a simple and unique manner.

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