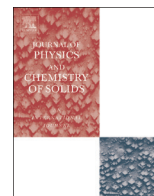




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On standardization of low symmetry crystal fields



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ABSTRACT

Standardization methods of low symmetry – orthorhombic, monoclinic and triclinic – crystal fields are formulated and discussed. Two alternative approaches are presented, the conventional one, based on the second-rank parameters and the standardization based on the fourth-rank parameters. Mainly *f*-electron systems are considered but some guidelines for *d*-electron systems and the spin Hamiltonian describing the zero-field splitting are given. The discussion focuses on premises for choosing the most suitable method, in particular on inadequacy of the conventional one. Few examples from the literature illustrate this situation.

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1. Introduction

The minimal expansion of the crystal field potential in terms of the tensor operators commonly used in the phenomenological modeling is not unique because of freedom in choosing the nominal coordinate system, implying different but equivalent sets of the coefficients of the expansion – the CF parameters. In the case of no symmetry elements apart from the inversion (i.e. for C_1 and S_1) and the symmetries which favor only one direction (i.e. C_n , S_{nh} , and S_n), there is infinite number of equivalent orientations. For the remaining point groups the number of equivalent minimal settings is finite. In each case, the phenomenological Hamiltonian requires a standardization, i.e. a convention according to which the nominal coordinate system is chosen.

Initially, the problem of the standardization did not focus much attention. The symmetry descent techniques or simplified models based on so-called intrinsic parameters (see [1,2] and references therein) allowed one to overcome it in most cases. In the last decades, however, a group of materials has been rapidly growing for which these techniques appear insufficient. Present research based on the spectroscopic, neutron, resonant, magnetic, thermal, transport and other measurements provide important details of the electronic structure which cannot be reproduced reliably without referring to the actual symmetry and the general parameterization.

The standardization was introduced originally as a convention for selecting the principal directions in description of zero field splitting observed in EPR spectra [3,4]. It was noticed that six equivalent orientations of the coordinate system in the case of

orthorhombic symmetry were related to different ranges of the *rhomnicity* – the ratio of the two parameters describing the quadrupole footprint on the EPR recordings. In 1985 this idea was extended by Rudowicz and Bramley to general spin Hamiltonian containing terms of higher rank as well as to the crystal field Hamiltonian of that symmetry [5]. Later, Rudowicz and coworkers extended the standardization to monoclinic [6] and triclinic [7] symmetries and proved its usefulness processing an amount of literature data (see Ref. [8] and references therein).

The Rudowicz and Bramley standardization (RBS) is based on the second-rank CF parameters. Below we will see that this approach can be misleading in some cases. Alternative standardization scheme presented here bases on the fourth-rank parameters. It allows one to avoid the pitfalls of RBS on the one hand but requires to handle adversely increased number of equivalent settings of the parameters on the other. Nevertheless there are still materials and experimental data for which RBS remains correct. We present both the methods as unified procedures for the three crystallographic systems: orthorhombic, monoclinic and triclinic. Apart from the crystal field Hamiltonian for *f*-electron systems, they can be applied also to *d*-electron systems and the spin Hamiltonian [9]. The methods are illustrated by examples of the CF parameters reported for realistic materials.

2. Low symmetry crystal field Hamiltonian

The conventional expansion of the crystal field (CF) potential into the normalized spherical harmonics $\hat{C}_q^{(k)}(\mathbf{r}/r)$ in the Hilbert space restricted to the single configuration f^N (or d^N), where N is the number of *f* (*d*) electrons, includes components of second,

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fourth and sixth rank:

$$H^{CF} = \sum_q B_{2q} \hat{C}_q^{(2)}(\mathbf{r}/r) + \sum_q B_{4q} \hat{C}_q^{(4)}(\mathbf{r}/r) + \sum_q B_{6q} \hat{C}_q^{(6)}(\mathbf{r}/r) \equiv \hat{V}_2 + \hat{V}_4 + \hat{V}_6 \quad (1)$$

with

$$\hat{V}_k = \sum_q B_{kq} \hat{C}_q^{(k)}(\mathbf{r}/r) \quad (2)$$

The three axial CF parameters, B_{k0} ($k=2,4,6$), are real, whereas the remaining 24 non-axial ones, B_{kq} ($q = -k, \dots, -1, 1, \dots, k$) are complex and conjugated according to the Condon–Shortley phase convention [10]:

$$B_{kq}^* = (-1)^q B_{k,-q} \quad (3)$$

to ensure hermiticity of the Hamiltonian. The six-rank terms are ineffective in the case of the d -electrons and the expansion is reduced to 14 terms. Generally, the 27(14) parameters in (1) are not independent. The redundant parameters can be eliminated by appropriate choice of the coordinate system. Following Rudowicz [11] we call it the *symmetry-adapted axis system* (SAAS).

If no direction is distinguished as for the triclinic symmetries (C_1 and $S_2 \equiv C_i$ point groups) any orientation of the coordinate system is possible and equally good. In particular it can be chosen so as to eliminate any three of 27 parameters except for the three axial parameters. This restriction results from the fact that there is no rotation dependent on only two Euler angles that would eliminate three CF parameters. In other words any selection of 24 parameters, containing one axial parameter at least, is admissible. There is no restriction in selection of the 11 parameters from 14 ones for d -electron system. The monoclinic symmetry (C_2 , C_h and C_{2h}) reduces the number of parameters to 15 (8 in the case of d -electrons) if any axis of the coordinate system coincides with the symmetry axis. Freedom in orientation of the two remaining axes allows us to eliminate one of these 15 parameters. Thus, the minimal set is reduced to 14(7). For the orthorhombic points groups (D_{2h} , D_2 , and C_{2v}) SAAS leaves 9(5) independent parameters as the minimal set. These are the real components of B_{kq} with q even.

The relations between the parameters B_{kq} in the original and rotated coordinate frames are determined by the transformation properties of the spherical harmonics under rotation. The transformation matrices can be obtained from analytic formulas given for instance in Refs. [12,13] or generated numerically [14–16]. They can be easily adapted to various forms of the CF Hamiltonian and function bases as well as to the general spin Hamiltonian describing the zero-field splitting [17,12,6].

The rotation does not mix the CF components of different k and for each k it preserves the length B_k of the “vector” of the parameters of given rank, $\vec{B}_k = (B_{k,-k}, B_{k,-k+1}, \dots, B_{k,k-1}, B_{k,k})$

$$B_k = |\vec{B}_k| = \left(\sum_q B_{kq} B_{kq}^* \right)^{1/2} = \left(\vec{B}_k \cdot \vec{B}_k^* \right)^{1/2} \quad (4)$$

The length of the vector is proportional to the quadratic rotational invariant s_k :

$$s_k = \frac{1}{2k+1} B_k \quad (5)$$

which can be determined directly from the crystal field transitions observed experimentally [18–20].

The experimental data, especially those provided by optical spectroscopy, are, in principle, capable to determine even as large number of CF parameters (CFP) as 24 (cf. Ref. [21]). However, one first has to

choose 24 parameters from 27 and second, indicate one from several different sets of the 24 parameters which represent given crystal field energy levels sequence. Equivalent CFP settings also exist for higher than triclinic symmetries. In other words, there are always several equivalent SAAS and the corresponding different sets of the parameters. These ambiguities are well known in the case of higher symmetries [22,1,2] – for example the simultaneous inversion of the signs of the B_{44} and B_{64} parameters in the case of the cubic symmetry.

The following rotations play a special role since they maintain the minimal number of CF parameters, i.e. keep the Hamiltonian in SAAS regardless an actual site symmetry:

$$R_1: (\pi/2)/Oy: B_{kq} \xrightarrow{(0,\pi/2,0)} (\dots) \quad (6a)$$

$$R_2: (\pi)/Oy: B_{kq} \xrightarrow{(0,\pi,0)} B_{kq}^* \quad (6b)$$

$$R_3: (\pi/2)/Oz: B_{kq} \xrightarrow{(\pi/2,0,0)} (i)^q B_{kq} \quad (6c)$$

$$R_4: (\pi)/Oz: B_{kq} \xrightarrow{(\pi,0,0)} (-1)^q B_{kq} \quad (6d)$$

The arrows in (6) are labeled with the corresponding Euler angles, (...) means nontrivial linear combination of B_{kq} 's which can be found in [12].

Usually we are dealing with various sets of the parameters for the same or isostructural compounds or for series of metal ions doped in given matrix. We will need to compare them taking into account various forms of SAAS including those generated by above rotations. Thus we need a measure of similarity of two sets of the parameters. For this purpose we will use the *closeness factors* c_k^{AB} , defined by Rudowicz [11] as

$$c_k^{AB} = \sum_{q=-k}^k \frac{B_{kq}^A B_{kq}^{B*}}{B_k^A B_k^B} \equiv \frac{\vec{B}_k^A \cdot \vec{B}_k^{B*}}{B_k^A B_k^B}, \quad (7)$$

where A and B denote two different sets of CF parameters which are to be compared. The *global closeness factor* c^{AB} constructed in similar way from the “vectors” \vec{B} of all CF parameters may also be useful:

$$c^{AB} = \sum_{k=2,4,6} \sum_{q=-k}^k \frac{B_{kq}^A B_{kq}^{B*}}{B_k^A B_k^B} \equiv \frac{\vec{B}^A \cdot \vec{B}^{B*}}{B^A B^B}. \quad (8)$$

All these quantities c_k^{AB} and c^{AB} vary in the range of (0, 1): zero means no correlation, one – the identical sets of the parameters. If fitting errors are known then the closeness factors could be re-defined to account for corresponding weights.

3. Following the Rudowicz and Bramley standardization (RBS)

The standardization can be formulated on the ground of the theory of little groups which allows one to foresee non-trivial symmetries of the irreducible representations of the rotation group and its finite subgroups [23]. It stems from the fact that the efficient symmetry of a part of the Hamiltonian transforming according to a given representation of the rotation group may be higher than the site symmetry, if the latter is low enough. In such a case the number of independent parameters describing the system is lower than the site symmetry implies. In order to eliminate the redundant parameters suffice to set the coordinate system appropriately, taking into account the corresponding little subgroup. In particular, the second-rank term in the crystal field expansion \hat{V}_2 transform according to the subgroup D_2 of the representation $D^{(2)}$ of the rotation group. Therefore without loss of generality all the parameters except B_{20} and $\Re B_{22}$ can be set to zero in \hat{V}_2 , no matter

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