JOURNAL OF SOLID STATE CHEMISTRY 115, 92–97 (1995)

On a Distinguished Quality of the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ Parameter Ratios in the Multipole Expansions of the Crystal Field Potentials

J. Mulak

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, P.O. Box 937, Poland

Received February 7, 1994; in revised form May 19, 1994; accepted May 24, 1994

It is demonstrated that for crystal field potentials having complex parameterizations characterized by low symmetry and large number of independent parameters, the formulas for the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios, i.e., for the parameters of the same k and $|q|$, correspond to a more general superposition model requiring the local metal–ligand symmetry to be v instead of $C_{\infty v}$ if the scaling factors alone are treated phenomenologically. A formal expression revealing the mutual interplay of both the distance and the nonaxial scaling factors has been obtained which allows the ratios $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ to be estimated more adequately. The generalization is substantial indeed; the corresponding number of independent intrinsic parameters of kth degree rises from one to $k + 1$. The distinguished quality of these ratios allows them to be treated in a distinguished way during the fitting of the potentials to experimental data. The proper fitting is then easier, since the number of independent parameters can be reduced. © 1995 Academic Press, Inc.

INTRODUCTION

The great number of independent B_q^k parameters required for the description of low symmetry crystal fields is the main hindrance to be overcome during the parameterization of their potentials. The effective form of the potential, confined to the intraconfiguration interactions only, i.e., for $k = 2$, 4 and 6, contains as many as 27 parameters for the C_1 point symmetry including 3 axial ($q = 0$) real, and 12 pairs of off-axial ($q \neq 0$) complex ones. Following the development of the central ion point symmetry, up to the cubic symmetry, the number drops. This is not an exclusively academic problem. Many of the known laser materials, quantum counters and radiation up and down converters which have found important applications are characterized by low symmetry crystal fields (1) and interpretation of their electronic energy spectra cannot avoid the problem. An important place among these materials is occupied by both stoichiometric solid compounds and crystal matrices with C_2 or C_s symmetry of the metal ion, such as LaF_3, ReF_3, Y_2O_3, YF_3, Re_2O_3, and $YAlO_3$, the crystal field potentials of which are described with 14 parameters including 5 imaginary ones, $\mathrm{Im}B_2^4$, $\mathrm{Im}B_4^4$, $\mathrm{Im}B_2^6$, $\mathrm{Im}B_4^6$, and $\mathrm{Im}B_6^6$, as well as the $CaWO_4$ and $LiYF_4$ matrices of S_4 coordination symmetry of the doped metal, the potential of which requires only one independent imaginary parameter, $\mathrm{Im}B_4^6$.

Knowledge of interrelations between the crystal field parameters is equivalent to reduction of their number. Some values of the ratios between the parameters of a given kth degree can be obtained from the superposition model (2) in which they result from the coordination geometry only. However, the assumption of the axial symmetry $C_{\infty v}$ of the local fields generated by individual ligands, which is crucial for the model, does not warrant the needed accuracy. On the other hand, there is a conviction, supported by some findings (3, 4), that in the case of crystal field potentials with complex parameterizations the ratios of the parameters of the same k and $|q|$, i.e., the ratios of type $\mathrm{Im}B_q^k/ReB_q^k$, play a distinguished role in the superposition approach, since their formulas correspond *de facto* to a model more general than that of $C_{\infty v}$ local symmetry.

The validity of this hypothesis in the case of S_4 central ion point symmetry has recently been proved (5). Thus, the assumption of the local symmetry v, instead of $C_{\infty v}$, is enough to obtain for the $\mathrm{Im}B_4^6/\mathrm{Re}B_4^6$ ratio (the only one for this symmetry) an expression phenomenologically equivalent to that for the axial $C_{\infty v}$ superposition model. The scaling factors responsible for the differentiation of the ligands now take into account both distance (radial) and nonaxial corrections. Moreover, the modification of the scaling factors resulting from the generalization is *explicitly* defined within the frame of the generalized superposition model. It is easy to show that the generalization is substantial; there are $k + 1$ intrinsic parameters of the kth degree (seven in this case) for the v model instead of one for the conventional $C_{\infty v}$ model.

In this work the general validity, i.e., for an arbitrary symmetry of the central ion, of the thesis on a distinguished quality of the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios in the multipole expansion of the crystal field potentials has been demonstrated. This property allows the ratios to be introduced a priori into the phenomenological fitting procedures for

0022-4596/95 $6.00

the low symmetry crystal field potentials to reduce the number of the independent parameters.

FORMALISM

1. *Crystal Field Potentials of Complex Parameterization*

The crystal field potential has to be real but its parameters can be complex. The reality and Hermitianness of the crystal field Hamiltonian given in the tensor notation according to Wybourne (6) as

$$H_{\mathrm{cf}} = \sum_j \sum_k \sum_q B_q^k C_q^{(k)}(\vartheta_j, \varphi_j), \qquad [1]$$

where j runs over all unpaired electrons of the metal ion, and k and q over all effective q components of the normalized spherical tensor operators of rank k, $C_q^{(k)}(\vartheta_j, \varphi_j)$, require, according to the Condon–Shortley phase convention (7), the following relation between the parameters to be fulfilled:

$$(B_q^k)^* = (-1)^q B_{-q}^k. \qquad [2]$$

Consequently, in the general case, the crystal field parameters, except the axial ones, are complex conjugate in pairs. Instead of using the pairs of the B_q^k and B_{-q}^k parameters, it is more practical to apply their symmetrical and antisymmetrical combinations, i.e., their real and imaginary components:

$$\mathrm{Re}B_q^k = \frac{1}{2}(B_q^k + (-1)^q B_{-q}^k) \qquad [3]$$

$$\mathrm{Im}B_q^k = \frac{1}{2i}(B_q^k - (-1)^q B_{-q}^k). \qquad [4]$$

For most actual crystal fields the parameters B_q^k are real, i.e., $B_q^k = (B_q^k)^* = (-1)^q B_{-q}^k$, and only $\mathrm{Re}B_q^k = B_q^k$ occur in expansion [1]. The presence of a vertical v plane in the central ion point symmetry group is the necessary and sufficient condition for the reality of all the B_q^k parameters in Eq. [1]. Besides, for the potentials composed of multipoles of k even the presence of a two-fold axis C_2 in the plane perpendicular to the main axis (at least C_2) ensures the reality of the parameters too.

Among the 32 crystal field potentials of different point symmetry, 15 for $k = 2$, 4, and 6 and 10 for $k = 1$, 3, and 5 require complex parameters (8). They are, for k even, $C_1(12)$, $C_i(12)$, $C_2(6)$, $C_s(6)$, $C_{2h}(6)$, $C_3(3)$, $C_{3i} = S_6(3)$, $D_3(2)$, $D_{3d}(2)$, $C_4(2)$, $S_4(2)$, $C_{4h}(2)$, $C_6(1)$, $C_{3h}(1)$, and $C_{6h}(1)$, and for k odd, $C_1(9)$, $C_s(6)$, $C_2(3)$, $D_2(3)$, $C_3(2)$, $C_{3h}(2)$, $C_4(1)$, $S_4(1)$, $D_{2d}(2)$, and $D_4(1)$. In the parentheses after the Schoenflies symbols of the groups, the numbers of the imaginary parameters, Eq. [4], are given. These numbers may always be reduced by one—see further.

Ignoring all the interconfiguration interactions, i.e., considering only the potentials with k even and equal to 2, 4, and 6, each potential with complex parameters may be described by means of three real axial parameters and a certain number of pairs of the complex conjugate parameters resulting from the point symmetry; i.e., the number of the parameters in sum is odd. However, such a parameterization is an excessive one. Any rotation of the reference system about the z axis does not alter the qualitative form of the potential (Eq. [1]), leading simultaneously to realizations that are equivalent, although differing in the off-axial parameters. Obviously, the axial parameters are invariant with respect to the rotations. There are certain particular rotations among them for which any arbitrarily chosen $\mathrm{Im}B_q^k$ parameter vanishes. The corresponding χ_{kq} angle is given by

$$\tan(q\chi_{kq}) = \frac{\mathrm{Im}B_q^k}{\mathrm{Re}B_q^k}. \qquad [5]$$

After rotation, the new parameter $[B_q^k]$ becomes real and

$$[B_q^k] = [(\mathrm{Re}B_q^k)^2 + (\mathrm{Im}B_q^k)^2]^{1/2}. \qquad [6]$$

Consistently, the remaining off-axial parameters transform themselves according to the two-dimensional rotation matrix

$$\begin{aligned}[\mathrm{Re}B_{q'}^{k'}] &= \cos(q'\chi_{kq})\mathrm{Re}B_{q'}^{k'} + \sin(q'\chi_{kq})\mathrm{Im}B_{q'}^{k'} \\ [\mathrm{Im}B_{q'}^{k'}] &= -\sin(q'\chi_{kq})\mathrm{Re}B_{q'}^{k'} + \cos(q'\chi_{kq})\mathrm{Im}B_{q'}^{k'}.\end{aligned} \qquad [7]$$

The elimination of a chosen imaginary parameter is equivalent to the strict localization of the reference system. After that all the parameters and ratios between them are determined uniquely. The so-called standardization procedure for the potentials consists just in rotation (9, 10). Usually, the parameter $\mathrm{Im}B_q^k$ of the lowest k and q indices is eliminated; e.g., in the case of S_4 symmetry this is done for the $\mathrm{Im}B_4^4$ parameter. In the light of the results of this paper the method finds a deeper justification (see the Discussion).

2. *The* $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ *Ratios in the Generalized Superposition Model*

The conviction that the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios take a special place among the parameter ratios in expansions of the crystal field potentials is derived from the close similarity of the transformation properties of the corresponding operators. Of course, the uniqueness of the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios cannot be demonstrated in the framework of the conventional superposition model in which

$$B_q^k = \sum_i C_q^{(k)*}(\beta_i, \alpha_i) f_{k,i} b_k^0, \qquad [8]$$

where β_i, α_i are the spherical coordinates of the ith ligand in the central reference system, $f_{k,i}$ is the distance factor scaling the parameters of kth degree according to differences in the metal–ligand distances R_i in relation to a certain average reference distance R_0, and b_k^0 is the intrinsic parameter common in the model for all the kth degree parameters.

The essential characteristic of the model is that the ratios of arbitrary crystal field parameters of the same kth degree depend only on the coordination geometry and the scaling factor, which is independent of q:

$$\frac{B_q^k}{B_{q'}^k} = \frac{\sum_i C_q^{(k)*}(\beta_i, \alpha_i) f_{k,i}}{\sum_i C_{q'}^{(k)*}(\beta_i, \alpha_i) f_{k,i}}. \qquad [9]$$

Due to the simplifying assumptions of the model, expressions [9] for all the q and q' are equivalent, considering their formal adequacy.

To demonstrate the specific character of the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios, we will consider the generalized superposition model in which the assumption of the $C_{\infty v}$ symmetry of the local fields is rejected and as a consequence the counterpart of expression [8] takes the more general form

$$\begin{aligned} B_q^k &= \sum_i \sum_{q'} D_{q'q}^{(k)*}(\alpha_i, \beta_i, \gamma_i) f_{k,i} b_k^{q'} \\ &= \sum_i \sum_{q'} \exp(-iq'\gamma_i) d_{q'q}^{(k)}(\beta_i) \exp(-iq\alpha_i) f_{k,i} b_k^{q'}, \end{aligned} \qquad [10]$$

where $D_{q'q}^{(k)}(\alpha_i, \beta_i, \gamma_i)$ is the element of the rotation matrix of rank $2k + 1$ (7), $d_{q'q}^{(k)}(\beta_i)$ is the real core of the element dependent on the β_i angle only, α_i, β_i, and γ_i are the three Euler angles defining the transformation of the local ith system to the central one, and $b_k^{q'}$ are the intrinsic parameters, which are as many as required by the local symmetry.

There is a complete equivalence between the rotations performed in relation to the frame of reference carried with the moving object and those referred to the initial fixed frame of axes. The first method is intuitively more clear, the first rotation being by α ($0 \le \alpha < 2\pi$) about the initial z axis, the second by β ($0 \le \beta < \pi$) about the new y' axis, and the third rotation by γ ($0 \le \gamma < 2\pi$) about the z axis in its last position z''. The equivalent rotation, in the original frame, is accomplished as follows: rotation by γ about the z axis, rotation by β about the y axis, and repeated rotation about the z axis by α, i.e., in the reverse order to the previous. Thus, β_i and α_i are the angles between the z_i axis, i.e., the axis joining the central ion with the ith ligand, and the z and x axes of the central system, respectively, whereas the γ_i angle fixes the local x_i and y_i axes.

This generalized model, due to the number of free parameters involved, has no application from a practical point of view. However, the point is not in the model itself but in the mere statement that there is a "virtual" version of the superposition model which is more accurate due to the degree of its generality, in which only the formulas for the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios keep their conventional model form.

For clarity, we state the following: the intrinsic parameters met in expressions [8], [10] and further always refer to the so-called local systems of the z axis joining the central ion with a chosen ith ligand but with the center in the central ion position, i.e., after the translation of the actual local system of the ligand with the center in its nucleus by $-R$. The relations between the parameters corresponding to both these local systems will be mentioned later.

From the Euler angles definition results that if a vertical symmetry plane v exists in the central ion point group, expression [10] for the B_q^k is invariant in relation to the α_i sign. In other words, each ligand of the α_i coordinate has to have its partner of the $-\alpha_i$ coordinate. In turn, the presence of a vertical symmetry plane in the local system is equivalent to the invariance of expression [10] in respect of the γ_i sign. This means that the values B_q^k for γ_i and $-\gamma_i$ angles are simply identical.

3. *The Proof of the Overmodel Adequacy of the* $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ *Ratios*

Hereafter, making use of the symmetry properties of the rotation matrices (7), it will be demonstrated that for the local symmetry v instead of $C_{\infty v}$ the expressions for the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios take the identical phenomenological forms with those for the axial model, in which the B_q^k are defined by Eq. [8]. Only the scaling factors $f_{k,i}$ undergo certain, strictly defined, modifications and their effective values can now depend on $|q|$.

Thus, for the local symmetry v, considering the invariance of expression [10] with respect to the sign of γ_i it can be presented in the form

$$\begin{aligned} B_q^k &= \sum_i \sum_{q'} \left[\frac{1}{2}\exp(-iq'\gamma_i) + \frac{1}{2}\exp(iq'\gamma_i)\right] \\ &\quad \times d_{q'q}^{(k)}(\beta_i) \exp(-iq\alpha_i) f_{k,i} b_k^{q'} \\ &= \sum_i \sum_{q'} \cos(q'\gamma_i)\, d_{q'q}^{(k)}(\beta_i) \exp(-iq\alpha_i) f_{k,i} b_k^{q'} \end{aligned} \qquad [11]$$

and similarly

$$B^k{}_{-q} = \sum_i \sum_{q'} \cos(q'\gamma_i)\, d_{q'-q}^{(k)}(\beta_i) \exp(iq\alpha_i) f_{k,i} b_k^{q'}, \qquad [12]$$

where $\exp(-iq'\gamma_i)$ (or $\exp(iq'\gamma_i)$) is replaced by $\cos(q'\gamma_i)$ which is equivalent under the symmetry.

Taking into consideration one of the symmetry properties of the rotation matrix,

$$d^{(k)}_{q'q}(\beta) = (-1)^{q'-q} d^{(k)}_{-q'-q}(\beta), \qquad [13]$$

and the reality of the intrinsic parameters (v local symmetry),

$$b_k^{-q'} = (-1)^{q'} b_k^{q'}, \qquad [14]$$

formula [12] can easily be transformed to the form

$$B^k_{\pm q} = (-1)^q \sum_i \sum_{q'} \cos(-q'\gamma_i)\, d^{(k)}_{\pm q'q}(\beta_i) \exp(iq\alpha_i) f_{k,i} b_k^{-q'}, \qquad [15]$$

and since the summation runs over all q' from $-k$ to k, we get

$$B^k_{\pm q} = (-1)^q \sum_i \sum_{q'} \cos(q'\gamma_i)\, d^{(k)}_{q'q}(\beta_i) \exp(iq\alpha_i) f_{k,i} b_k^{q'}. \qquad [16]$$

Expressions [11] and [16] of course obey relation [2] and have the desired form, i.e., the phases of the intrinsic contributions (for each individual ligand i) depend only on the α_i angles, as in the $C_{\infty v}$ model, and the whole modification resulting from the nonaxial components of the local fields concerns the absolute values of the contributions. They may be transformed to the form revealing their modification compared to that for the simplified axial model:

$$\sum_{q'} \cos(q'\gamma_i) d^{(k)}_{q'q}(\beta_i) f_{k,i} b_k^{q'} = \left[1 + \sum_{q' \neq 0} \cos(q'\gamma_i) \frac{d^{(k)}_{q'q}(\beta_i)}{d^{(k)}_{0q}(\beta_i)} \frac{b_k^{q'}}{b_k^0}\right] f_{k,i} b_k^0 d^{(k)}_{0q}(\beta_i). \qquad [17]$$

Introducing the designation

$$\bar{f}_{k,q,i} = \left[1 + \sum_{q' \neq 0} \cos(q'\gamma_i) \frac{d^{(k)}_{q'q}(\beta_i)}{d^{(k)}_{0q}(\beta_i)} \frac{b_k^{q'}}{b_k^0}\right] f_{k,i} \qquad [18]$$

for the effective scaling factor $\bar{f}_{k,q,i}$, we get

$$B^k_q = \sum_i C^{(k)*}_q(\beta_i, \alpha_i) \bar{f}_{k,q,i} b_k^0$$
$$B^k_{-q} = (-1)^q \sum_i C^{(k)*}_{-q}(\beta_i, \alpha_i) \bar{f}_{k,q,i} b_k^0, \qquad [19]$$

since

$$C^{(k)*}_{\pm q}(\beta_i, \alpha_i) = D^{(k)*}_{0\pm q}(\alpha_i, \beta_i, \gamma_i) = d^{(k)}_{0q}(\beta_i) \exp(\mp iq\alpha_i). \qquad [20]$$

This completes the proof of the postulated thesis.

In conclusion, for an arbitrary point symmetry of the *central ion (only the contribution of an individual ligand* has been considered) and for the v symmetry of the local fields, the expressions for the $\mathrm{Im}B^k_q/\mathrm{Re}B^k_q$ ratios are of the same form as those for the conventional axial model and only the phenomenological, in practical approach, scaling factors (Eq. [18]) are subjected to definite modifications. Their analysis allows the factors, under certain conditions, to be estimated more adequately.

The result obtained may be interpreted otherwise by introducing an effective intrinsic parameter of axial character dependent on $|q|$ and kind of ligand (i) according to

$$b_k^0(|q|, i) = b_k^0 + \sum_{q' \neq 0} \cos(q'\gamma_i) \frac{d^{(k)}_{q'q}(\beta_i)}{d^{(k)}_{0q}(\beta_i)} b_k^{q'}. \qquad [21]$$

In general, the requirement of a vertical symmetry plane for each ligand confines to a certain degree the permissible forms of the local potentials, since it reduces the number of independent intrinsic parameters from $2k + 1$ to $k + 1$ (see Eq. [21]), but a proper measure of the generalization is rather the $k + 1$ parameters compared to one. In the $C_{\infty v}$ model we have at our disposal only one intrinsic parameter for each kth degree of the potential.

4. *The Reality of the Crystal Field Parameters ($\mathrm{Im}B^k_q \equiv 0$) in the Generalized Superposition Model as a Consequence of the Central Ion v Symmetry*

When a vertical symmetry plane v occurs in the central ion point group of symmetry the reality of the crystal field parameters is implicitly ensured. However, the v plane has to be chosen as the xz plane of the central reference system. Nevertheless, it is instructive to trace, in the frame of the generalized superposition model, the mechanism of vanishing of all the $\mathrm{Im}B^k_q$ parameters under the condition. Obviously, the local v symmetry is not required now.

The global symmetry v forces the third Euler angles γ for the corresponding ligands of coordinates α_i and $-\alpha_i$, respectively, to be of equal modulus but of opposite sign. In addition, because of the change of orientation of the local reference system due to the reflection, the intrinsic parameters for both the ligands are mutually complex conjugate.

Starting from definition [4] and general formula [10] and considering only one pair of ligands as being symmetrical in respect to the v plane, one gets

$$
\begin{aligned}
2i\,\mathrm{Im}B_q^k &= \sum_{q'} \exp(-iq'\gamma_i) d^{(k)}_{q'q}(\beta_i) \exp(-iq\alpha_i) f_{k,i} b_k^{q'} \\
&- (-1)^q \sum_{q'} \exp(-iq'\gamma_i) d^{(k)}_{q'-q}(\beta_i) \exp(iq\alpha_i) f_{k,i} b_k^{q'} \\
&+ \sum_{q'} \exp(iq'\gamma_i) d^{(k)}_{q'q}(\beta_i) \exp(iq\alpha_i) f_{k,i} (b_k^{q'})^* \\
&- (-1)^q \sum_{q'} \exp(iq'\gamma_i) d^{(k)}_{q'-q}(\beta_i) \exp(-iq\alpha_i) f_{k,i} (b_k^{q'})^*.
\end{aligned} \qquad [22]
$$

The first two sums describe the contribution of the ligand of coordinates (R_i, β_i, α_i), and the remaining two that of its partner $(R_i, \beta_i, -\alpha_i)$.

Using property [13], the equivalent of formula [2] for the intrinsic parameters,

$$(b_k^{q'})^* = (-1)^{q'} b_k^{-q'}, \qquad [23]$$

and remembering that the summation runs over all q' from $-k$ to k, it is easy to show that the first and fourth sums in Eq. [22], as well as the second and third are mutually compensated and hence the identity $\mathrm{Im}B_q^k \equiv 0$ is always valid.

DISCUSSION

The generalized effective scaling factor (Eq. [18]) turns out to be a product of the distance factor, taking into account a differentiation in the distances R_i by the nonaxial factor responsible for the nonaxial components of the local fields.

The distance scaling factor in the classical axial model has been usually presented phenomenologically in the form of a power law $(R_0/R_i)^{t_k}$ with the power coefficients t_k taking rather large positive values, e.g., six or more (2, 11, 12). Obviously, for the closer ligands ($R_i < R_0$), the factor is greater than one, whereas for the remaining it is smaller. For comparison, in the point charge model, the crystal field parameters vary with the metal–ligand distance R as $R^{-(k+1)}$, i.e., as R^{-3}, R^{-5}, and R^{-7} for $k = 2$, 4, and 6, respectively.

On the other hand, since the signs of the small $b_k^{q'}/b_k^0$ ratios may in principle be found from the ligand coordination geometry, the nonaxial factors, according to the signs of $\cos(q'\gamma_i)$ and $d^{(k)}_{q'q}(\beta_i)/d^{(k)}_{0q}(\beta_i)$, can also be either a little larger or a little smaller than one amplifying or reducing the scaling factor effect according to their product. The result of the mutual interplay of both the subfactors can be qualitatively estimated based on the coordination geometry only. However, what still remains is the problem of the $b_k^{q'}/b_k^0$ values, which are rather unknown. Fortunately, with a good approximation, only the terms with $q' = 1$ and 2 can be considered. This is a consequence of the transformation properties of the multipolar components of the potential for the translation of the reference system along the z axis by R. After such a translation the multipolar components of the potential become transformed according to the scheme (13)

$$\beta_q^k(r) C_q^{(k)}(\vartheta, \varphi) \rightarrow \sum_{k'=|q|}^{\infty} \beta_q^{k'}(r') C_q^{(k')}(\vartheta', \varphi), \qquad [24]$$

where the superscript prime refers to the system after the translation, and $\beta_q^k(r)$ and $\beta_q^{k'}(r')$ are the initial and the final radial coefficients, which are correlated by the Sharma formula (13). If $\beta_q^k(r) \sim r^{-(k+1)}$ as for the 2^k-pole moment, $\beta_q^{k'}(r') \sim R^{-(k+k'+1)}$ and is discriminated when $k + k'$ is large. As is seen, each q component of the local 2^k-pole moment is transformed into the superposition of the q components of all the $2^{k'}$-pole moments of $k' > |q|$ with the corresponding Sharma coefficients $\beta_q^{k'}(r')$. The main contribution to the axial parameters ($q' = 0$) comes from the ligand point change $(\beta_0^0(r) C_0^{(0)}(\vartheta, \varphi) = \beta_0^0(r))$. In addition, an essential contribution can be given by the moments with $k = 1$ and 2 for which the dipolar and quadrupolar polarizations of the ligand are responsible. On the other hand, for higher q's only the respective high moments are effective (see Eq. [24]). Therefore, a distinct domination of the axial parameters is expected, and among the off-axial ones of those with $q' = 1$ and 2. Consequently, the higher the k and q indices, the more negligible the correction for the nonaxiality, and the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios are more exactly described by the axial model formulas. This is why the elimination of the $\mathrm{Im}B_q^k$ parameter of the lowest k and q is well founded. A more penetrating analysis of the mutual interplay of both the subfactors in the generalized scaling factor allows the conventional formulas for the $\mathrm{Im}B_q^k/\mathrm{Re}B_q^k$ ratios to be applied for the wide class of crystal fields of v local symmetry (perfect or approximate). Moreover, we are able then to estimate the adequacy of the formulas better and to understand the values which are incomprehensible in the axial model.

The generalization of the scaling factor concept is equivalent to extending its phenomenological power form without any limitation for the power law coefficients t_k, even up to (or down to) nonphysical (from the axial model point of view) negative values, when the nonaxial factor that is opposed to the distance one dominates. Some symptoms of this situation, such as artificially low power coefficients t_k in the phenomenological distance factors, have been reported for the Yb^{3+} ion in the scheelite matrix (11).

REFERENCES

1. C. A. Morrison and R. P. Leavitt in "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gschneider, Jr., and L. Eyring, Eds.), Vol. 5, Chap. 46. North-Holland, Amsterdam, 1982.
2. D. J. Newman, *Adv. Phys.* **20,** 197 (1971).
3. J. Mulak and Z. Gajek, *Polish J. Chem.* **67,** 1489 (1993).
4. J. Mulak, *Polish J. Chem.* **67,** 2053 (1993).
5. J. Mulak, *Polish J. Chem.*, in press.
6. B. G. Wybourne, "Spectroscopic Properties of Rare Earths." Wiley, New York, 1965.
7. A. R. Edmonds, "Angular Momentum in Quantum Mechanics," Chaps. 2 and 4. Princeton Univ. Press, Princeton, NJ, 1957.
8. M. Sachs, "Solid State Theory," Chap. 4. McGraw–Hill, New York, 1963.
9. C. Rudowicz, *Chem. Phys.* **97,** 43 (1985).
10. C. Rudowicz, *J. Chem. Phys.* **84,** 5045 (1986).
11. Vishwamittar and S. P. Puri, *J. Chem. Phys.* **61,** 3720 (1974).
12. M. M. Curtis and D. J. Newman, *Chem. Phys. Lett.* **9,** 606 (1971).
13. R. R. Sharma, *Phys. Rev.* **A 13,** 517 (1976).