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A scalar crystal field strength parameter for rare-earth ions: meaning and usefulness

F. Auzel (*) and O. L. Malta

Departamento de Física and Departamento de Química, Universidade Federal de Pernambuco, Cidade Universitária, 50.000 Recife-PE, Brazil

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Résumé. — On étudie la signification d’un paramètre scalaire de champ cristallin défini précédemment [4, 5]. On montre pourquoi il peut être souvent utilisé comme une indication de l’amplitude totale d’une levée de dégénerescence Stark pour un terme J donné, quelle que soit la symétrie cristalline du site de l’ion étudié. On donne ainsi le moyen d’utiliser les tables de paramètres $B^k_q$ existantes pour comparer des cristaux de structures et symétries de sites différents, et prédire les écarts Stark maxima. Réciproquement, ceux-ci donnent un moyen simple pour comparer la force du champ cristallin de différents cristaux.

Abstract. — The meaning of a scalar crystal field strength parameter defined previously [4, 5] is studied. It is shown why, in many cases, it can be used as an indication of the magnitude of the maximum Stark splitting of J-terms for ions in crystals of different structures and site symmetries. It thus provides a way of making use of the existing tables of $B^k_q$ parameters for comparing crystals of different symmetries and for predicting the relative magnitude of their Stark splittings. Reciprocally, maximum Stark splittings provide a simple mean of comparing crystal field strengths of different crystals.

1. Introduction. — The degeneracy removal due to a crystal field at a given rare-earth ion site is known to be rather well described by a number of crystal field parameters $B^k_q$ according to the site symmetry of the considered crystal [1]. The crystal field Hamiltonian removing degeneracy is

$$ v = \sum_{k,q,i} B^k_q (C^k_q)_{ij}, $$

and values of the parameters are usually obtained by a least-squares fit to experimental results. The current evolution of this research is towards more refinements in the fit [2] and ab initio determination of these parameters [3]. Their use in predicting behaviour is usually restricted to a given site symmetry and often to the very crystal which produced the parameters.

Thus we felt that the published tables of phenomenological $B^k_q$ parameters, however precise they may be, were much too specialized and therefore lacked general usefulness. Being faced with the problem of predicting self-quenching of Nd$^{3+}$ in any type of crystal structure and site symmetry, we proposed the consideration of a scalar crystal field strength parameter [4], [5] given by

$$ N_v = \left[ \sum_{k,q} (B^k_q)^2 \left( \frac{4 \pi}{2 k + 1} \right) \right]^{1/2}. \quad (1) $$

$N_v$ being a norm representing a distance in the space spanned by spherical harmonics $Y^k_q$. $N_v$ is a number which can characterize the crystal field strength in any type of site symmetry. Quite recently, the same rotational invariant has been proposed in order to compare the root-mean-square error obtained for crystal fields of different strengths; however its use was restricted to comparisons of identical site symmetries [6].

Having defined a scalar strength parameter, we searched for a simple relation with experiments and found that the maximum splittings of the $^4I_{9/2},^4I_{11/2}, ^4I_{13/2}$ and $^4I_{15/2}$ levels of Nd$^{3+}$ could be rather well described by relations linear in $N_v$. The correlation coefficient was higher than 0.9 whatever the structures and site symmetries [4]. The same correlation coefficient was obtained for $^4F_{3/2}$ provided, of course, only the $B^4_q$ involved in the degeneracy removal were
2. Theoretical investigation of maximum Stark splittings. — As is shown in textbooks [7], the root-
mean-square deviation $(\Delta \varepsilon)^2$ of a number of levels $E_1; E_2; \ldots; E_n$, obtained from a $g$-fold degenerate level upon introduction of a perturbation $v$, is given by

$$(\Delta \varepsilon)^2 = \frac{1}{g} \text{tr} (P_0 v P_0 v),$$

where $P_0$ is the projector onto the subspace of the free-ion state under consideration and where it is
assumed that $v$ does not displace the gravity centre of the perturbed states from the free-ion position.

Now the maximum splitting $(\Delta E)$ and $(\Delta \varepsilon)$ can be linked using the definition

$$(\Delta \varepsilon)^2 = \frac{1}{g_a} \sum_{i=1}^{n} (E_i)^2,$$  

in which $P_0$ is the projector onto the subspace of the free-ion state under consideration and where it is
assumed that $v$ does not displace the gravity centre of the perturbed states from the free-ion position.

Now the trace is given by

$$\text{tr} (P_0 v P_0 v) = \sum_{MM'} \langle JM | v | JM' \rangle \langle JM' | v | JM \rangle$$

$$= \sum_{MM'} \langle JM | v | JM' \rangle \langle JM' | v | JM \rangle$$

$$= \sum_{MM'} B_{q_k}^k B_{q_2}^k \langle JM | \sum_{i} C_{q_i}^{(k)}(i) | JM' \rangle \langle JM' | \sum_{i} C_{q_i}^{(k)}(i) | JM \rangle$$

$$= \sum_{MM'} \left( \frac{-1}{2} \right)^{J-J'-M-J'} B_{q_k}^k B_{q_2}^k \left( \begin{array}{ccc} J & k & J' \\ M & q & M' \end{array} \right) \left( \begin{array}{ccc} J & k' & J \\ M' & q' & M \end{array} \right) \times$$

$$\times \left\langle \begin{array}{c} J \end{array} \right| \sum_{i} C_{(i)}^{(k)} \left| J \right\rangle \left\langle J \right| \sum_{i} C_{(i)}^{(k)} \left| J \right\rangle$$

$$= \sum_{k} \frac{(B_{q_k}^k)^2}{2^{k+1}} \delta(J, J, J) \left\langle \begin{array}{c} J \end{array} \right| \sum_{i} C_{(i)}^{(k)} \left| J \right\rangle \left\langle J \right| \sum_{i} C_{(i)}^{(k)} \left| J \right\rangle$$

where we have used equations (3), (7), (8) of [8]; the triangular condition given by $\delta(J, J, J)$ means $2J \geq k$
which has already been used for $N_v$. For rare-earth ions $k$ takes only the three even values 2, 4, 6. One gets

$$(\Delta E)^2 = \frac{12 g_a^2}{g(a + 2)} \sum_{k} \frac{(B_{q_k}^k)^2}{2^{k+1}} \left\langle \begin{array}{c} J \end{array} \right| \sum_{i} C_{(i)}^{(k)} \left| J \right\rangle \left\langle J \right| \sum_{i} C_{(i)}^{(k)} \left| J \right\rangle$$

An analogous relation has been recently given for $(\Delta \varepsilon)^2$ [9] in the case of negligible $J$-mixing (which is also
our case) but assuming $\langle JM | V | JM' \rangle$ to be diagonal, which is not required here.
Equation (11) can be viewed as the quadratic equation of a quadric surface (an ellipsoid centred at the origin) in the $k$-space. We replace it by a sphere of the same volume, assuming

$$\sum_{k} \frac{(B_k^2)}{2k+1} \left| \left\langle J \left| \sum_{i} C_{(i)}^{(k)} \right| J \right\rangle \right|^2 \approx \sum_{k} \frac{(B_k^2)}{2k+1} \left[ \prod_{k} \left| \left\langle J \left| \sum_{i} C_{(i)}^{(k)} \right| J \right\rangle \right|^2 \right]^{1/3},$$

(12)

$$= \prod_{k} \left| \left\langle J \left| \sum_{i} C_{(i)}^{(k)} \right| J \right\rangle \right|^{2/3} \left( \sum_{k} \frac{(B_k^2)}{2k+1} \right)^{1/3},$$

(13)

$$= \frac{1}{4\pi} \prod_{k} \left| \left\langle J \left| \sum_{i} C_{(i)}^{(k)} \right| J \right\rangle \right|^{2/3} N_{e}^{2}.$$  

(14)

From equations (14) and (11), the relation with the maximum splitting is found to be

$$\Delta E = \left[ \frac{3g_s^2}{g(g_s + 2)(g_s + 1)\pi} \right]^{1/2} \left[ \prod_{k} \left| \left\langle J \left| \sum_{i} C_{(i)}^{(k)} \right| J \right\rangle \right|^{1/3} \right] N_{e}. $$

(15)

3. Discussion of the approximation. — If we perform a geometrical average, the form of equation (15) permits the comparison of the crystal field strength and of its effects for different site symmetries. The approximation will be very good when the ellipsoid given by equation (11) is sphere-like. Let us examine the conditions for such a situation by calculating

$$\left| \left\langle J \left| \sum_{i} C_{(i)}^{(k)} \right| J \right\rangle \right|^2 = \left| \left\langle f \left| C_{(i)}^{(k)} \right| f \right\rangle \right|^2 \times$$

$$\times \left| \left\langle SLJ \left| U^{(k)} \right| SLJ \right\rangle \right|^2. $$

(16)

The first factor on the right is almost independent of $k$:

$$\left\langle f \left| C_{(i)}^{(k)} \right| f \right\rangle = -1.36, $$

$$\left\langle f \left| C_{(i)}^{(k)} \right| f \right\rangle = 1.13, $$

$$\left\langle f \left| C_{(i)}^{(k)} \right| f \right\rangle = -1.27. $$

The dependence on $k$ essentially comes from the second factor which in $L-S$ coupling is

$$\left| \left\langle SLJ \left| U^{(k)} \right| SLJ \right\rangle \right|^2 = \left[ \frac{3g_s^2}{g(g_s + 2)(g_s + 1)\pi} \right]^{1/2} \left[ \prod_{k} \left| \left\langle J \left| \sum_{i} C_{(i)}^{(k)} \right| J \right\rangle \right| \right]^{1/3} N_{e}. $$

(15)

$$\left\langle SLJ \left| U^{(k)} \right| SLJ \right\rangle = (-1)^{S+L+J+k} (2J+1) \left\{ \begin{array}{ccc} L & k & L \hline J & S & J \end{array} \right\} \left\langle SL \left| U^{(k)} \right| SL \right\rangle, $$

(17)

$$= (-1)^{S+L+J+k} (2J+1) \left\{ \begin{array}{ccc} L & k & L \hline J & S & J \end{array} \right\} \sum_{i=1}^{n} \left\langle l^{n-1}(S_{i} L_{i}) l \right| l^{n} SL \right\rangle \times$$

$$\times \left\langle l^{n-1}(S_{i} L_{i}) l \right| l^{n} SL \right\rangle (-1)^{L_{i}+L_{i}+k} (2L+1) \left\{ \begin{array}{ccc} l & l & k \hline L & L & L_{i} \end{array} \right\} $$

(18)

where we have used, for instance, equation (20) of [10] and equation (22.20) of [11], with the same notation.

The dependence on $k$ comes from the two 6-$J$ symbols which can be approximated by equation (A 2.3) of [8]

$$\left\{ \begin{array}{ccc} L & k & L \hline J & S & J \end{array} \right\} = \left\{ \begin{array}{ccc} S & L & J \hline k & J & L \end{array} \right\} \approx (-1)^{L_{i}+J+S} P_{4}(cos \theta_{1}), $$

(19)

with

$$cos \theta_{1} = \frac{S(S + 1) - J(J + 1) - L(L + 1)}{2[J(J + 1) L(L + 1)]^{1/2}}, $$

(20)

and

$$\left\{ \begin{array}{ccc} l & l & k \hline L & L & L_{i} \end{array} \right\} = \left\{ \begin{array}{ccc} L_{i} & L & l \hline k & l & L \end{array} \right\} \approx (-1)^{L_{i}+L+L_{i}} P_{4}(cos \theta_{2}), $$

(21)

with

$$cos \theta_{2} = \frac{L_{i}(L_{i} + 1) - k(k + 1) - L(L + 1)}{2[k(k + 1) L(L + 1)]^{1/2}}. $$

(22)
Both equations (19) and (21) are stationary with respect to \( k \) for \( |\cos \theta| \geq 1 \), since then \( P_k(\cos \theta) \approx 1 \). Sensitivity on \( k \) is then due more to the \( k = 6 \) term than to the \( k = 2, 4 \) ones.

The condition is fulfilled by equation (19) when

\[
S \leq L, J \quad \text{and} \quad L \equiv J
\]

or

\[
S = L \quad \text{and} \quad L \equiv J\sqrt{2}
\]

or

\[
S = L \quad \text{and} \quad L \equiv J\sqrt{2} \quad \text{with} \quad L, J > 1
\]

For \( 2J > k \) these conditions generally hold. For instance, all \( \text{Nd}^{3+} \) terms with \( J > 7/2 \) and lower than \( 26\,000 \text{ cm}^{-1} \), give a \( \cos \theta_1 \) between 0.92 and 0.99. Then equation (21) gives the essential part of the variation with \( k \). Prediction is difficult in the general case due to the sum over \( L_1 \) and the fractional parentage coefficient in equation (18) which couples only certain \( L_1 \). However, simple inspection of existing \( \langle \| U^k \| \rangle \) tables [12] permits us to make a selection of the best \( J \) terms. So equation (15) has to be considered as an approximation giving a geometrical rotational-invariant average for the maximum Stark splittings in any point symmetry. This approximation is best when equation (17) is stationary in \( k \).

4. Application to calculations of overall Stark splittings. — The proportionality coefficient between \( \Delta E \) and \( N_e \), as given by equation (15), is obtained \textit{ab initio}. In principle it can be computed for any ion and any \( J \)-term for any crystal. This generality is of course certainly at the expense of precision, since in LaF\(_3\), for instance, we replace as many as 15 \( B_k^L \) by one parameter. However, as precision is known to depend on \( J \)-terms, we propose that the best \( J \)-terms (stationary in \( k \)) be used as simple crystal field probes.

Applications of equation (15) will now be examined from three points of view:

a) within a given ion and crystal system, application to different \( J \)-terms;

b) given \( J \)-terms of a given ion, application to different crystals differing or not by site symmetry;

c) for given \( J \)-terms and crystal, application to different ions.

For point a) we shall consider the \( J > 7/2 \) terms of \( \text{Nd}^{3+} \) in LaF\(_3\), using the experimental results of Carnall \textit{et al.} and their tables of \( \langle \| U^k \| \rangle \) [12]. From them we obtain \( \langle \| U^k \| \rangle \) as shown in table I. It can be seen that variations of this product follow those of \( \Delta E \) except for \( ^4G_{9/2}, ^3H_{11/2} \) and \( ^4G_{11/2} \), which present large variations of \( \langle \| U^k \| \rangle \) with \( k \).

### Table I. — Reduced matrix elements, maximum splittings and \( N_e \) calculated equation (15) for LaF\(_3\) : \( \text{Nd}^{3+} \).

<table>
<thead>
<tr>
<th>[( J )-term]</th>
<th>( \langle | U^2 | \rangle^2 )</th>
<th>( \langle | U^4 | \rangle^2 )</th>
<th>( \langle | U^6 | \rangle^2 )</th>
<th>( \langle | U^k | \rangle ) ( ^{2/3} )</th>
<th>( \Delta E_{\exp} ) ( \text{cm}^{-1} )</th>
<th>( N_{\text{av}} ) ( \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^4I_{9/2} )</td>
<td>0.24</td>
<td>0.12</td>
<td>0.17</td>
<td>0.7</td>
<td>0.38</td>
<td>500</td>
</tr>
<tr>
<td>( ^4I_{11/2} )</td>
<td>0.23</td>
<td>0.13</td>
<td>0.12</td>
<td>0.067</td>
<td>0.155</td>
<td>264</td>
</tr>
<tr>
<td>( ^4I_{13/2} )</td>
<td>0.22</td>
<td>0.17</td>
<td>0.17</td>
<td>0.23</td>
<td>0.295</td>
<td>374</td>
</tr>
<tr>
<td>( ^4I_{15/2} )</td>
<td>0.20</td>
<td>0.23</td>
<td>0.37</td>
<td>1.93</td>
<td>0.85</td>
<td>725</td>
</tr>
<tr>
<td>( ^4F_{9/2} )</td>
<td>0.24</td>
<td>0.14</td>
<td>0.096</td>
<td>3.10( ^{-4} )</td>
<td>0.025</td>
<td>110</td>
</tr>
<tr>
<td>( ^2H_{11/2} )</td>
<td>0.23</td>
<td>0.01</td>
<td>( 10^{-3} )</td>
<td>0.02</td>
<td>9.3 ( \times 10^{-3} )</td>
<td>112</td>
</tr>
<tr>
<td>( ^4G_{9/2} )</td>
<td>0.24</td>
<td>0.042</td>
<td>( 6 \times 10^{-3} )</td>
<td>0.01</td>
<td>0.01</td>
<td>213</td>
</tr>
<tr>
<td>( ^2K_{13/2} )</td>
<td>0.22</td>
<td>1.6</td>
<td>0.5</td>
<td>0.02</td>
<td>0.389</td>
<td>404</td>
</tr>
<tr>
<td>( ^4G_{11/2} )</td>
<td>0.23</td>
<td>( 10^{-3} )</td>
<td>0.634</td>
<td>0.186</td>
<td>0.09</td>
<td>460</td>
</tr>
<tr>
<td>( ^2K_{15/2} )</td>
<td>0.20</td>
<td>1.98</td>
<td>0.42</td>
<td>0.015</td>
<td>0.36</td>
<td>326</td>
</tr>
</tbody>
</table>

\( \langle \| U^k \| \rangle^2 \) matrix elements and \( \Delta E_{\exp} \) are taken from [12] for LaF\(_3\) : \( \text{Nd}^{3+} \). \( \langle \| U^k \| \rangle \) \( ^{2/3} \) is the geometrical average of \( \langle \| U^k \| \rangle \), \( \langle f \| C^k \| f \rangle^2 \), \( N_{\text{av}} \) is calculated from the values of columns 2, 6, 7 and equation (15). From \( B_k^L \) and equation (1) :

\[ N_e(\text{LaF}_3) = 2 \, 356 \text{ cm}^{-1} \].
Fig. 1. — Ratio of $N_v$ parameters obtained from $\Delta E$ (Eq. (15)) and from $B_q^k$ (Eq. (1)) versus the maximum splitting of J-terms $(\Delta E)$ of Nd$^{3+}$ in LaF$_3$. Splittings and $B_q^k$ are taken from [12]. The horizontal line shows the proportionality of $\Delta E$ with $N_v$ for several J-terms according to equation (15).

and which are in the spectral region where strong J-mixing occurs.

Because of its $k$ independence, $^4I_{13/2}$ is proposed as a good crystal field probe; also to a lesser extent $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{15/2}$.

From table I and equation (15), $N_v$ is calculated for each term and compared with the value given by the definition of equation (1). Results are presented on figure 1 where the ratio $N_v(\Delta E)/N_v(B_q^k)$ is plotted versus $\Delta E$. All terms, except the three mentioned above, are found to have a maximum splitting proportional to $N_v$ as described by equation (15); the proportionality coefficient between $\Delta E$ and $N_v$ is given by the $ab$ initio calculation with a discrepancy factor of 1.32 on the average. Figure 1 shows also that points near the horizontal line can be used as crystal field probes, and this gives an explanation of the experimental results of [4].

For ions other than Nd$^{3+}$, inspection of tables of $\langle j | U_k | j \rangle$ in [12] for stationarity in $k$ shows that, the following terms should theoretically provide the best crystal field probes: Pr$^{3+}(^3H_4, ^3H_6)$; Sm$^{3+}(^4I_{13/2}, ^4H_{15/2})$; Eu$^{3+}(^7F_2)$; Tb$^{3+}(^7F_5)$; Dy$^{3+}(^6F_{9/2}, ^6F_{7/2}, ^6F_{5/2}, ^6F_{3/2}, ^4I_{13/2}, ^4H_{15/2}, ^4H_{13/2})$; Ho$^{3+}(^5I_4, ^5I_6)$; Er$^{3+}(^4I_{9/2}, ^4I_{11/2}, ^4I_{13/2})$; Tm$^{3+}(^3H_4, ^3H_6)$.

Point b) is just what had been experimentally investigated in [4]. Here, we shall use equation (15) in predicting overall splittings of $^4I_{9/2}$(Nd$^{3+}$) in LaF$_3$, NdCl$_3$, YAG, CaWO$_4$, LaP$_2$O$_{14}$ and LiYF$_4$.

In figure 2 experimental points for $\Delta E(^4I_{9/2})$ versus $N_v(B_q^k)$ from $B_q^k$ of the literature [12-17] are compared to the equation (15) line. One can notice that a fit would keep the slope of the line but would give a positive intercept on $\Delta E$. This is believed to be due to the neglect of a term in equation (15) arising from the assumption of coincidence between the gravity centre of splittings and the free-ion level position [7].

Such an intercept was already experimentally noticed in [4]. It should be pointed out that, to ascertain the comparison with experience, we have used here the complete form for $N_v$ (Eq. 1) and not the approximation used in [4, 5]. The complete $N_v$ and the approximate ones previously used are given in table II, in order to make comparison with results in [4, 5] easier. On the average, the ratio between the complete and the incomplete $N_v$ is 1.35.

As for point c), we shall consider, for instance, Hf$^{3+}(^5I_4, ^5I_6)$; Er$^{3+}(^4I_{9/2}, ^4I_{11/2}, ^4I_{13/2})$; Tm$^{3+}(^3H_4, ^3H_6)$.

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Table II. — $N_v$ parameters obtained from $B_q^k$ from the literature for different crystals doped with Nd$^{3+}$

<table>
<thead>
<tr>
<th>Crystals</th>
<th>LaCl$_3$</th>
<th>LaF$_3$</th>
<th>LaP$<em>2$O$</em>{14}$</th>
<th>CaWO$_4$</th>
<th>LiYF$_4$</th>
<th>YAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_v$ (cm$^{-1}$) complete</td>
<td>1 062</td>
<td>2 356</td>
<td>2 190</td>
<td>2 691</td>
<td>3 095</td>
<td>4 739</td>
</tr>
<tr>
<td>$N_v$ (cm$^{-1}$) approximate [4]</td>
<td>928</td>
<td>1 841</td>
<td>1 406</td>
<td>1 860</td>
<td>2 194</td>
<td>3 691 (*)</td>
</tr>
<tr>
<td>Reference</td>
<td>[13]</td>
<td>[12]</td>
<td>[17]</td>
<td>[16]</td>
<td>[15]</td>
<td>[14]</td>
</tr>
</tbody>
</table>

(*) In [4], $N_v$ approximate was given as 3 575 cm$^{-1}$ as computed from the $B_q^k$'s of Morrison et al. (J. Phys. C 9 (1976) L191) reproduced in [14].
Table III. — $N_v$ parameters obtained from $B_k^4$ [12] for different ions in LaF$_3$ and ratio ($\Delta E_{\text{exp}}/\Delta E_{\text{th}}$) of experimental to predicted maximum splitting of $^4I_{13/2}: \Delta E(^4I_{13/2})$.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Nd$^{3+}$</th>
<th>Sm$^{3+}$</th>
<th>Dy$^{3+}$</th>
<th>Er$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_v$ (cm$^{-1}$)</td>
<td>2 356</td>
<td>2 098</td>
<td>1 905</td>
<td>1 638</td>
</tr>
<tr>
<td>$\Delta E_{\text{exp}}$ (cm$^{-1}$)</td>
<td>374</td>
<td>142</td>
<td>312</td>
<td>219</td>
</tr>
<tr>
<td>$\Delta E_{\text{th}}$ (cm$^{-1}$)</td>
<td>282</td>
<td>144</td>
<td>274</td>
<td>197</td>
</tr>
<tr>
<td>$\frac{\Delta E_{\text{exp}}}{\Delta E_{\text{th}}}$</td>
<td>1.32</td>
<td>1.01</td>
<td>1.13</td>
<td>1.11</td>
</tr>
<tr>
<td>$\left( \frac{\prod}{k} \right)^{2/3}$</td>
<td>0.295</td>
<td>0.098</td>
<td>0.427</td>
<td>0.297</td>
</tr>
</tbody>
</table>

the $^4I_{13/2}$ term because we predicted it to be a good probe for several ions simultaneously (Nd$^{3+}$, Sm$^{3+}$, Dy$^{3+}$, Er$^{3+}$) and because we have a complete set of homogeneous results in LaF$_3$ [12].

Table III gives $N_v$ for the considered ions in LaF$_3$, and $\Delta E_{\text{theory}}$ as given by equation (15). As can be seen by the ratio $\Delta E_{\text{exp}}/\Delta E_{\text{th}}$, the prediction is even better for ions other than Nd$^{3+}$ used in the initial studies. This shows the generality of the approach given by equation (15).

5. Conclusion. — Having defined a scalar crystal field strength parameter, we have theoretically justified its uses by predicting the maximum Stark splittings of $J$-terms of rare-earth ion doped crystals of any structure and site symmetry, using a single calculated proportionality coefficient. Its generality has been verified by considering three types of situations: one ion, one crystal and various $J$-terms; one $J$-term, one ion and various crystals; one $J$-term, one crystal and various ions. The essential limitation is that $J \geq k/2$ in order that the maximum splitting can be due to every $B_k^4$ of the crystal field; this also ensures that the number of Stark levels be large enough so that the statistical coefficient containing degeneracy is more significant. Stationarity in $k$, though alleviated by the spherical approximation, in practice requires that the variations of $\langle \parallel U^k \parallel \rangle^2$ with $k$ be no larger than a factor of 10. Finally, we believe the use of the $N_v$ coefficient should widen the use of the existing $B_k^4$ tables permitting, for the first time, cross-comparison of them for crystals of different site symmetries. Further, use of selected $J$-terms as crystal field probes gives a quick quantitative measure of a crystal field strength which can be later checked by the usual $B_q$ parameters determination. Also, generality of $N_v$ permits the extension of its use to the prediction of energy-transfer properties for ions other than Nd$^{3+}$ for which it was first used.

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References