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

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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 dégénérescence 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_q^k existantes pour comparer des cristaux de structures et symétries de sites différents, et prédire les écartements 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_q^k 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_q^k according to the site symmetry of the considered crystal [1]. The crystal field Hamiltonian removing degeneracy is

$$v = \sum_{k,q,i} B_q^k (C_q^k)_i,$$

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_q^k 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

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

N_v being a norm representing a distance in the space spanned by spherical harmonics Y_q^k . 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_q^k involved in the degeneracy removal were

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included into N_v . This is given by the condition $2J \geq k$. Tentatively, we looked also for empirical relations between N_v , melting temperature and cohesive energy per bond [4, 5].

Thus having defined a field strength parameter and found a good experimental link with the maximum Stark splittings of Nd^{3+} , our purpose now is to investigate its theoretical meaning so as to ascertain its generality and its usefulness for others J -levels and other ions.

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 $E_1; E_2; \dots E_n$, obtained from a g -fold degenerate level upon introduction of a perturbation v , is given by

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

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

$$(\Delta\varepsilon)^2 = \frac{1}{g_a} \sum_i^n (E_i)^2, \quad (3)$$

where E_i is the energy of the i th Stark level with respect to the free-ion position and g_a is the degeneracy effectively removed by the field : $g_a = g$ if J is integer and $g_a = g/2$ if J is half-integer.

An *ad hoc* approximation is to take half the maximum splitting as the energy unit and to assume a symmetric repartition of levels :

$$(\Delta\varepsilon)^2 = \frac{1}{g_a} \left(\frac{\Delta E}{2} \right)^2 [1 + a_2^2 + \dots + a_{g_a-2}^2 + 1]. \quad (4)$$

With $0 < a_i < 1$, the literal sum value lies between 0 and $(g_a - 2)$. For n large enough, an approximation to this sum can be obtained by assuming a somewhat, homogeneous repartition of levels :

$$(\Delta\varepsilon)^2 = \frac{2}{g_a} \left(\frac{\Delta E}{2} \right)^2 \left[\sum_{n=1}^{g_a/2} n^2 \left(\frac{2}{g_a} \right)^2 \right], \quad (5)$$

where n is integer. Then

$$(\Delta\varepsilon)^2 = \left(\frac{\Delta E}{2} \right)^2 \left(\frac{2}{g_a} \right)^2 \frac{1}{6} \left(\frac{g_a}{2} + 1 \right) (g_a + 1),$$

and

$$(\Delta E)^2 = \frac{12 g_a^2}{g(g_a + 2)(g_a + 1)} \text{tr} (P_0 v P_0 v). \quad (6)$$

Now the trace is given by

$$\begin{aligned} \text{tr} (P_0 v P_0 v) &= \sum_M \left\langle JM \left| \sum_{M'} \left| JM' \right\rangle \left\langle JM' \left| v \sum_{M''} \left| JM'' \right\rangle \left\langle JM'' \left| v \right| JM \right\rangle \right. \right. \\ &= \sum_{M, M'} \langle JM | v | JM' \rangle \langle JM' | v | JM \rangle \end{aligned} \quad (7)$$

$$= \sum_{\substack{MM' \\ kq \\ k'q'}} B_q^k B_{q'}^{k'} \left\langle JM \left| \sum_i C_q^{(k)}(i) \right| JM' \right\rangle \left\langle JM' \left| \sum_i C_{q'}^{(k')}(i) \right| JM \right\rangle \quad (8)$$

$$\begin{aligned} &= \sum_{\substack{MM' \\ kq \\ k'q'}} (-1)^{J-M+J-M'} B_q^k B_{q'}^{k'} \begin{pmatrix} J & k & J \\ -M & q & M' \end{pmatrix} \begin{pmatrix} J & k' & J \\ -M' & q' & M \end{pmatrix} \times \\ &\quad \times \left\langle J \left\| \sum_i C_{(i)}^{(k)} \right\| J \right\rangle \left\langle J \left\| \sum_i C_{(i)}^{(k')} \right\| J \right\rangle \end{aligned} \quad (9)$$

$$= \sum_{k, q} \frac{(B_q^k)^2}{2k+1} \delta(J, J, k) \left| \left\langle J \left\| \sum_i C_{(i)}^{(k)} \right\| J \right\rangle \right|^2, \quad (10)$$

where we have used equations (3), (7), (8) of [8]; the triangular condition given by $\delta(J, J, k)$ 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

$$(\Delta E)^2 = \frac{12 g_a^2}{g(g_a + 2)(g_a + 1)} \sum_{k, q} \frac{(B_q^k)^2}{2k+1} \left| \left\langle J \left\| \sum_i C_{(i)}^{(k)} \right\| J \right\rangle \right|^2. \quad (11)$$

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

$$\sum_{k,q} \frac{(B_q^k)^2}{2k+1} \left| \left\langle J \parallel \sum_i C_{(i)}^{(k)} \parallel J \right\rangle \right|^2 \cong \sum_{k,q} \frac{(B_q^k)^2}{2k+1} \left[\prod_{k'} \left| \left\langle J \parallel \sum_i C_{(i)}^{(k')} \parallel J \right\rangle \right|^2 \right]^{1/3}, \tag{12}$$

$$= \left[\prod_{k'} \left| \left\langle J \parallel \sum_i C_{(i)}^{(k')} \parallel J \right\rangle \right|^2 \right]^{2/3} \sum_{k,q} \frac{(B_q^k)^2}{2k+1}, \tag{13}$$

$$= \frac{1}{4\pi} \left[\prod_k \left| \left\langle J \parallel \sum_i C_{(i)}^{(k)} \parallel J \right\rangle \right|^2 \right]^{2/3} N_v^2. \tag{14}$$

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

$$\Delta E = \left[\frac{3g_a^2}{g(g_a+2)(g_a+1)\pi} \right]^{1/2} \left[\prod_k \left| \left\langle J \parallel \sum_i C_{(i)}^{(k)} \parallel J \right\rangle \right|^2 \right]^{1/3} N_v. \tag{15}$$

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

$$\langle J \parallel C^{(k)} \parallel J \rangle^2 = \langle f \parallel C^{(k)} \parallel f \rangle^2 \times \langle [SLJ] \parallel U^{(k)} \parallel [SLJ] \rangle^2. \tag{16}$$

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

$$\begin{aligned} \langle f \parallel C^{(2)} \parallel f \rangle &= -1.36, \\ \langle f \parallel C^{(4)} \parallel f \rangle &= 1.13, \\ \langle f \parallel C^{(6)} \parallel f \rangle &= -1.27. \end{aligned}$$

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

$$\langle [SLJ] \parallel U^{(k)} \parallel [SLJ] \rangle = (-1)^{S+L+J+k} (2J+1) \begin{Bmatrix} L & k & L \\ J & S & J \end{Bmatrix} \langle SL \parallel U^{(k)} \parallel SL \rangle, \tag{17}$$

$$\begin{aligned} &= (-1)^{S+L+J+k} (2J+1) \begin{Bmatrix} L & k & L \\ J & S & J \end{Bmatrix} n \sum_{S_1 L_1} \langle l^{n-1}(S_1 L_1) l \mid \rangle l^n SL \rangle \times \\ &\times \langle l^{n-1}(S_1 L_1) l \mid \rangle l^n SL \rangle (-1)^{L_1+l+k} (2L+1) \begin{Bmatrix} l & l & k \\ L & L & L_1 \end{Bmatrix} \end{aligned} \tag{18}$$

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]

$$\begin{Bmatrix} L & k & L \\ J & S & J \end{Bmatrix} = \begin{Bmatrix} S & L & J \\ k & J & L \end{Bmatrix} \cong \frac{(-1)^{L+J+S} P_k(\cos \theta_1)}{[(2J+1)(2L+1)]^{1/2}}, \tag{19}$$

with

$$\cos \theta_1 = \frac{S(S+1) - J(J+1) - L(L+1)}{2[J(J+1)L(L+1)]^{1/2}}, \tag{20}$$

and

$$\begin{Bmatrix} l & l & k \\ L & L & L_1 \end{Bmatrix} = \begin{Bmatrix} L_1 & L & l \\ k & l & L \end{Bmatrix} \cong \frac{(-1)^{l+L+L_1} P_k(\cos \theta_2)}{[(2l+1)(2L+1)]^{1/2}}, \tag{21}$$

with

$$\cos \theta_2 = \frac{L_1(L_1+1) - l(l+1) - L(L+1)}{2[l(l+1)L(L+1)]^{1/2}}. \tag{22}$$

Both equations (19) and (21) are stationary with respect to k for $|\cos \theta| \cong 1$, since then $P_k(\cos \theta) \cong 1$. 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

$$S \ll L, J \quad \text{and} \quad L \cong J$$

or

$$S = L \quad \text{and} \quad L \cong J\sqrt{2}$$

or

$$S = L \quad \text{and} \quad L \cong J\sqrt{2} \quad \text{with} \quad L, J > 1.$$

For $2J > k$ these conditions generally hold. For instance, all 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 ΔE and N_v , as given by equation (15), is obtained *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_q^k 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 :

- within a given ion and crystal system, application to different J -terms;
- given J -terms of a given ion, application to different crystals differing or not by site symmetry;
- for given J -terms and crystal, application to different ions.

For point *a*) we shall consider the $J > 7/2$ terms of Nd^{3+} in LaF_3 , using the experimental results of Carnall *et al.* and their tables of $\langle \|U^k\| \rangle^2$ [12].

From them we obtain $\left(\prod_k\right)^{2/3}$ as shown in table I.

It can be seen that variations of this product follow those of ΔE except for ${}^4G_{9/2}$, ${}^2H_{11/2}$ and ${}^4G_{11/2}$ which present large variations of $\langle \|U^k\| \rangle$ with k

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

[J -term]	$\left[\frac{3g_u}{2(g_u+2)(g_u+1)\pi}\right]^{1/2}$	$\langle \ U^2\ \rangle^2$	$\langle \ U^4\ \rangle^2$	$\langle \ U^6\ \rangle^2$	$\left(\prod_k\right)^{2/3}$	ΔE_{exp} cm^{-1}	$N_{v_{\text{th}}}$ cm^{-1}
${}^4I_{9/2}$	0.24	0.12	0.17	0.7	0.38	500	3 379
${}^4I_{11/2}$	0.23	0.13	0.12	0.067	0.155	264	2 915
${}^4I_{13/2}$	0.22	0.17	0.17	0.23	0.295	374	3 129
${}^4I_{15/2}$	0.20	0.23	0.37	1.93	0.85	725	3 931
${}^4F_{9/2}$	0.24	0.14	0.096	$3 \cdot 10^{-4}$	0.025	110	2 898
${}^2H_{11/2}$	0.23	0.01	10^{-3}	0.02	9.3×10^{-3}	112	5 049
${}^4G_{9/2}$	0.24	0.042	6×10^{-3}	0.01	0.01	213	8 875
${}^2K_{13/2}$	0.22	1.6	0.5	0.02	0.389	404	2 944
${}^4G_{11/2}$	0.23	10^{-3}	0.634	0.186	0.09	460	6 666
${}^2K_{15/2}$	0.20	1.98	0.42	0.015	0.36	326	2 716

$\langle \|U^k\| \rangle^2$ matrix elements and ΔE_{exp} are taken from [12] for $\text{LaF}_3 : \text{Nd}^{3+}$. $\left(\prod_k\right)^{2/3}$ is the geometrical average of $\langle \|U^k\| \rangle^2 \langle f \| C^k \| f \rangle^2$. $N_{v_{\text{th}}}$ is calculated from the values of columns 2, 6, 7 and equation (15). From B_q^k and equation (1) : $N_v(\text{LaF}_3) = 2\,356 \text{ cm}^{-1}$.

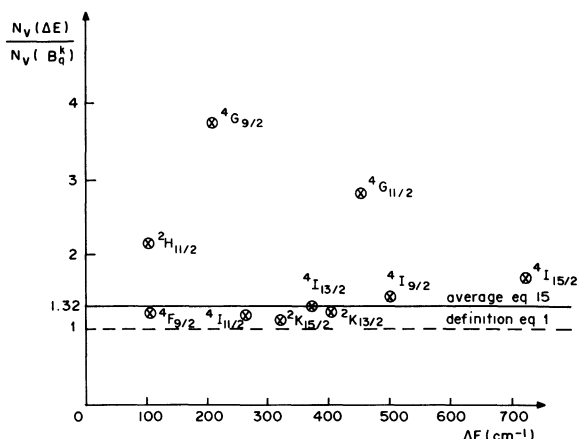


Fig. 1. — Ratio of N_v parameters obtained from ΔE (Eq. (15)) and from B_q^k (Eq. (1)) versus the maximum splitting of J -terms (ΔE) of Nd^{3+} in LaF_3 . Splittings and B_q^k are taken from [12]. The horizontal line shows the proportionality of ΔE with N_v for several J -terms according to equation (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 ΔE . 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 ΔE 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 $\langle \| U^k \| \rangle^2$ in [12] for stationarity in k shows that, the following terms should theoretically provide the best crystal field probes : $\text{Pr}^{3+}({}^3H_4, {}^3H_6)$; $\text{Sm}^{3+}({}^4I_{13/2}, {}^6H_{15/2})$; $\text{Eu}^{3+}({}^7F_5)$; $\text{Tb}^{3+}({}^7F_5)$; $\text{Dy}^{3+}({}^6F_{9/2}, {}^4F_{9/2}, {}^6F_{11/2}, {}^4I_{13/2}, {}^6H_{15/2}, {}^4H_{15/2})$;

$\text{Ho}^{3+}({}^5I_4, {}^5I_6)$; $\text{Er}^{3+}({}^4F_{9/2}, {}^4I_{11/2}, {}^4I_{13/2})$; $\text{Tm}^{3+}({}^3H_4, {}^3H_6)$.

Point *b*) is just what had been experimentally investigated in [4]. Here, we shall use equation (15) in predicting overall splittings of ${}^4I_{9/2}(\text{Nd}^{3+})$ in LaF_3 , NdCl_3 , YAG , CaWO_4 , $\text{LaP}_5\text{O}_{14}$ 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 ΔE . 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,

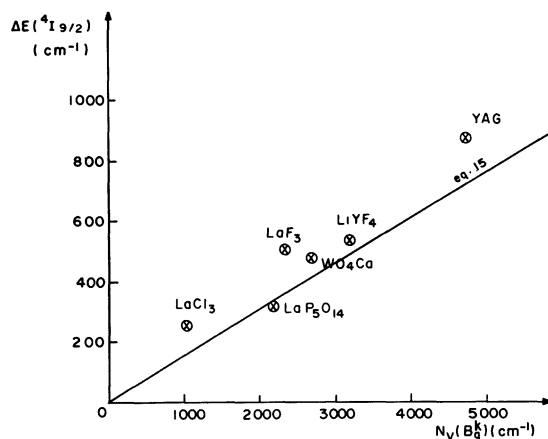


Fig. 2. — Maximum splittings of ${}^4I_{9/2}(\text{Nd}^{3+})$ in different structures and site symmetries as predicted by equation (15) compared with experimental points from the literature. Equation (15) is calculated with the first row of table I.

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

Crystals	LaCl_3	LaF_3	$\text{LaP}_5\text{O}_{14}$	CaWO_4	LiYF_4	YAG
N_v (cm^{-1}) complete	1 062	2 356	2 190	2 691	3 095	4 739
N_v (cm^{-1}) approximate [4]	928	1 841	1 406	1 860	2 194	3 691 (*)
Reference	[13]	[12]	[17]	[16]	[15]	[14]

(*) In [4], N_v approximate was given as $3\,575\text{ cm}^{-1}$ 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_q^k [12] for different ions in LaF_3 and ratio $(\Delta E_{\text{exp}}/\Delta E_{\text{th}})$ of experimental to predicted maximum splitting of ${}^4I_{13/2} : \Delta E({}^4I_{13/2})$.

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

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 ΔE_{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 be $\geq k/2$ in order that the maximum splitting can be due to every B_q^k 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 $\langle \|U^k\|^2 \rangle$ 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_q^k 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^k 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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