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Gd³⁺ crystal-field effects in low-symmetric centres

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Abstract. A correlation between collections of the experimental values of the crystal-field parameters $\{P_2^0, b_2^0, A_2^0\}$ characterizing the nuclear quadrupole interaction, the ground-state and excited-state splitting for $^{157}\text{Gd}^{3+}$ in various ionic crystals with the same type of anions has been established. The correlation consists of a tendency towards a decrease in P_2^0 and an increase in A_2^0 through a series of these collections provided that they are arranged according to descending values of b_2^0 . The great variety of the centres involved and the considerable magnitudes of the intervals within which the parameters of the collections obeying the correlation fall suggest that this correlation is a highly general characteristic of the collections $\{P_2^0, b_2^0, A_2^0\}$ and its explanation may be regarded as an important criterion of validity for microtheory crystal-field models. We have developed a model to interpret the correlation mentioned and some cases of deviation from it. The phenomenological values of the Sternheimer antiscreening coefficient γ_x have been determined in different ways. These values agree with each other and with the value of γ_x for Pr^{3+} calculated by Ahmad and Newman taking the interelectron correlation into account in addition to the interactions considered by Sternheimer originally.

1. Introduction

The phenomenological Hamiltonians describing the Stark structure of energy levels for rare-earth ions in non-cubic centres in ionic crystals include the second-rank crystal-field terms

$$H_2 = \frac{1}{2} \sum_m Z_2^m O_2^m \quad (1)$$

where Z_2^m are the crystal-field parameters and O_2^m are the Stevens operators. We shall be interested only in $^{157}\text{Gd}^{3+}$ centres where there is one independent parameter of the second rank in accordance with the site symmetry, this parameter being Z_2^0 when the principal axes are used. For each centre of this kind, three types of Z_2^0 (P_2^0 , b_2^0 and A_2^0) may be experimentally obtained, and they are concerned respectively with the nuclear quadrupole interaction, the ground-state splitting and the effective single-particle crystal-field potential. In the latter case the relation $Z_2^0 = 3\alpha A_2^0$ is generally used, where α is a coefficient defined by the quantum numbers of the excited states of the $^{157}\text{Gd}^{3+}$ ground-state configuration upon which the operator (1) acts, but we accept formally that $3\alpha = 1$ to preserve the designation Z_2^0 for all types of second-rank parameter.

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Until now no regularity covering a large number of the various types of Z_2^0 in various crystals has been found. Therefore, it is difficult to ascertain for which centres the Stark splittings are generated by the same fundamental mechanisms, and to what extent a specific theoretical model of the crystal fields furnishes an interpretation of experimental data.

In the present paper a large number of collections $\{Z_2^0\} = \{P_2^0, b_2^0, A_2^0\}$ for $^{157}\text{Gd}^{3+}$ in different centres is considered and a correlation among these collections is established. We also propose a model to explain this correlation.

2. Collections $\{Z_2^0\}$ for oxide crystals

2.1. Description of the experimental data

Here we shall consider the available experimental data on the parameters P_2^0 , b_2^0 and A_2^0 in the principal axes for $^{157}\text{Gd}^{3+}$ centres in crystals which have only the O^{2-} type of anions (tables 1 and 2). For comparison, two known collections $\{Z_2^0\}$ for centres of rare-earth ions in crystals which have anions of other types are also given (table 2). As there is a lack of relevant published data, some of the collections $\{Z_2^0\}$ in tables 1 and 2 include values of b_2^0 for impurity crystals, where a small number of the lattice Y^{3+} ions are replaced by the $^{157}\text{Gd}^{3+}$ ions, together with values of P_2^0 for $^{155}\text{Gd}^{3+}$ in isomorphous crystals, where the $^{155}\text{Gd}^{3+}$ ions are lattice ions instead of the Y^{3+} ions, these P_2^0 being multiplied by the ratio $Q(^{157}\text{Gd})/Q(^{155}\text{Gd})$ of quadrupole moments of the isotopes [36]. The values of A_2^0 are taken for trivalent rare-earth ions RE^{3+} . If the value of A_2^0 for Gd^{3+} is not known, we use the value for Eu^{3+} or Tb^{3+} . The collections $\{Z_2^0\}$ where the only unknown entity is the parameter A_2^0 (for Gd^{3+} , Eu^{3+} or Tb^{3+}) are complemented by values of A_2^0 for another RE^{3+} and for similar centres in isomorphous crystals, if such values are available. When only the absolute value of the parameter Z_2^0 is known, two different signs are indicated before this Z_2^0 . A number of values of P_2^0 and b_2^0 have been determined experimentally at 2 K in this work. They are presented in the tables with the experimental errors in parentheses.

2.2. Correlation between collections $\{Z_2^0\}$

Collections $\{Z_2^0\}$ with known signs of b_2^0 are arranged in table 1 according to descending values of b_2^0 . Under this arrangement the series of parameters A_2^0 from these collections shows a tendency to increase, i.e. if we consider any pair of the neighbouring collections of this kind (I and II) and if $b_2^0(\text{I}) > b_2^0(\text{II})$ then either $A_2^0(\text{I}) < A_2^0(\text{II})$ for the greater part of the pairs or

$$\left| |A_2^0(\text{I})| - |A_2^0(\text{II})| \right| < 0.1 (|A_2^0(\text{I})| + |A_2^0(\text{II})|) \quad (2)$$

for the other pairs. The corresponding series of values of P_2^0 with known signs shows a similar tendency to decrease. Later we shall be referring to these tendencies in relations between the collections $\{Z_2^0\}$ as the correlation, and the magnitude of the left-hand side of the inequality (2) we shall call the deviation from monotonicity. The two remaining collections with unknown signs of b_2^0 (but with known signs of A_2^0 or P_2^0) are placed in table 1 corresponding to the supposition that they must not violate the correlation. There is only one way to assign signs where they are unknown in these two collections to satisfy the supposition given. On applying a similar supposition to the first collection in table

Table 1. Collections $\{Z_{ij}^2\}$ in crystals with O²⁻ anions.

Crystal	Space group	Site symmetry	$P_{ij}^2 (10^{-4} \text{ cm}^{-1})$	$b_{ij}^2 (10^{-4} \text{ cm}^{-1})$	$A_{ij}^2 (\text{cm}^{-1})$	RE ³⁺	References
Y ₂ O ₃	<i>Ia</i> $\bar{3}$	3	$\pm 63.7^a$	1604	-850	Gd ³⁺	[1-3]
La ₂ O ₃	<i>P</i> $\bar{3}m1$	3 <i>m</i>		± 1310	-350	Eu ³⁺	[4, 5]
LiNbO ₃	<i>R</i> $\bar{3}c$	3 (site 2)		1260	-417	Eu ³⁺	[6, 7]
LiNbO ₃	<i>R</i> $\bar{3}c$	3 (site 1)		1185	-350	Eu ³⁺	[6, 7]
LaAlO ₃	<i>R</i> $\bar{3}m$	3 <i>m</i>		479	-110	Eu ³⁺	[8, 9]
ZrSiO ₄	<i>I</i> ₄ / <i>a</i> <i>md</i>	4 <i>2m</i>		-352	-60	Eu ³⁺	[10, 11]
YVO ₄	<i>I</i> ₄ / <i>a</i> <i>md</i>	4 <i>2m</i>	+15.3 ^a	-479	-54	Eu ³⁺	[12-14]
YPO ₄	<i>I</i> ₄ / <i>a</i> <i>md</i>	4 <i>2m</i>	∓ 17.9	-728	181	Eu ³⁺	[14, 15]
PbMoO ₄	<i>I</i> ₄ / <i>a</i>	4	-16.7(4) ^b	-800	214	Eu ³⁺	[16, 17]
CaMoO ₄	<i>I</i> ₄ / <i>a</i>	4	-23.8(4) ^b	-855	247	Yb ³⁺	[18, 19]
CaWO ₄	<i>I</i> ₄ / <i>a</i>	4	-21.09(2) ^b	-919.6(8) ^b	233	Tb ³⁺	[20]
Y ₂ Ti ₂ O ₇	<i>Fd</i> $\bar{3}m$	3 <i>m</i>	-(63.2-69.2) ^a	∓ 1409	$\pm (340-620)^c$	Gd ³⁺	[21-23]

^a Obtained for ¹⁵⁵Gd in an isomorphous crystal (where ¹⁵⁵Gd³⁺ is the lattice ion instead of Y³⁺) and multiplied by $Q(^{157}\text{Gd})/Q(^{155}\text{Gd})$.

^b This work.

^c Estimated for isomorphous Gd₂Ce₂O₇.

Table 2. Examples of the collections $\{Z_i^0\}$ which violate the correlation in table 1.

Crystal	Space group	Site symmetry	$P_2^0 (10^{-4} \text{ cm}^{-1})$	$b_2^0 (10^{-4} \text{ cm}^{-1})$	$A_2^0 (\text{cm}^{-1})$	RE^{3+}	References
$\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	$F6_3/m$	$\bar{6}$	-17.71	201	80 ^a	Eu^{3+}	[24, 25]
$\text{Bi}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	$R3$	3	8.848	124	-30 ^b	Sm^{3+}	[26, 27]
$\text{Y}(\text{OH})_3$	$F6_3/m$	$\bar{6}$	$\pm 20.0^c$	-135	175	Gd^{3+}	[28, 29]
$\text{Pb}_3(\text{GeO}_4)(\text{Ge}_2\text{O}_7)$	$P3_1$	3	-73.7	307			[30, 31]
$\text{La}_2\text{O}_2\text{S}$	$P3m$	$3m$		462	53	Eu^{3+}	[32, 33]
LaCl_3	$F6_3/m$	$\bar{6}$	-10.775	17.7	108	Gd^{3+}	[30, 34, 35]

^a For $\text{Eu}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

^b For $\text{Sm}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$.

^c Obtained for ^{155}Gd in an isomeric $\text{Gd}(\text{OH})_3$ crystal and multiplied by $Q(^{157}\text{Gd})/Q(^{155}\text{Gd})$.

Table 3. Collections $\{Z_i^0\}$ in crystals with F^- anions.

Crystal	Space group	Site symmetry	$P_2^0 (10^{-4} \text{ cm}^{-1})$	$b_2^0 (10^{-4} \text{ cm}^{-1})$	$A_2^0 (\text{cm}^{-1})$	RE^{3+}	References
KY_3F_{10}	$Fm3m$	$4mm$		± 809	-264	Eu^{3+}	[37, 38]
SrF_2	$Fm3m$	$3m^a$	-11.16(1) ^b	-153.8(8) ^b	103	Dy^{3+}	[39]
LiYF_4	$I4_1/a$	4		-830	180	Eu^{3+}	[40, 41]
SrF_2	$Fm3m$	$4mm^a$	-9.553(5) ^b	-1222(1) ^b	200	Gd^{3+}	[42]
CaF_2	$Fm3m$	$4mm^a$	-21.046(7) ^b	-1570(1) ^b	332	Gd^{3+}	[42]

^a Centre with nearby charge compensator F^- .

^b This work.

1, a definite sign of P_2^0 in this collection may also be assigned. All these assigned signs are the upper signs in table 1 and we shall be considering them as true. It should be noted that the absolute value of P_2^0 for $\text{YPO}_4: {}^{157}\text{Gd}^{3+}$ satisfies the correlation irrespective of the sign chosen. Thus all the collections of table 1 obey the correlation if the assigned signs are taken into account.

Examples of the collections $\{Z_2^0\}$ both for oxide crystals and for other crystals which could not be placed in table 1 without substantial violation of the correlation are presented in table 2. Collections of this type for crystals with F^- anions (CaF_2 and SrF_2) are also shown in table 3. The collections for oxide crystals from table 2 are conventionally separated from the collections of table 1, which violate the monotonicity of Z_2^0 series, for two reasons. Firstly, the numerical factor 0.1 in the inequality (2) corresponds to the usual relative error in values of A_2^0 . We believe that some deviations from monotonicity in table 1 may be influenced by these errors. Secondly, it is noteworthy that, for the oxide crystals in table 2, oxygen is included in the molecular groups not occurring in the crystals from table 1. Therefore, it is possible that the causes responsible for the violation of the correlation by the collections from table 2 differ from the causes responsible for the violation of the monotonicity of Z_2^0 series in table 1.

2.3. A number of considerations about the correlation

Now we would like to discuss some of our considerations in connection with the correlation. First, the existence of the correlation suggests that each type of parameter Z_2^0 is influenced by the same fundamental mechanisms for all the centres which give the collections $\{Z_2^0\}$ obeying the correlation. Secondly, the large variety of crystals presented in table 1 show that the correlation does not depend on the types of cation entering these crystals while the last two collections in table 2 and the collections for CaF_2 and SrF_2 in table 3 show that the properties of anions may substantially influence whether there is a correlation. On the other hand, it is natural to suppose that the electron density distribution in ionic crystals is influenced by cations and anions to the same extent. These considerations may be included in the common concept of the crystal fields, if we assume that a crystal with a ${}^{157}\text{Gd}^{3+}$ ion may be conventionally divided into two parts which play different roles in producing the crystal fields. One part is confined to a sphere with ${}^{157}\text{Gd}^{3+}$ as the centre. The radius of the sphere is of the same order of magnitude as the distance between ${}^{157}\text{Gd}^{3+}$ and the nearest cation. The anions located within this sphere (the ligands) define the values of Z_2^0 to a great degree and the existence of the correlation. The rest of the crystal gives contributions to Z_2^0 which are either negligible or not violating the correlation.

3. Model

3.1. Approaches to interpretation of the correlation

The data in table 1 may be presented graphically in $Z_2^0 - Z_2^{00}$ coordinates (where Z_2^0 and Z_2^{00} are parameters of different types). However, without any additional approximations, neither the tabulated nor the graphical presentation of the data allows one to interpret the correlation confidently. Therefore, in considering the correlation we shall use as a starting point the model of the crystal fields $A_2^0 O_2^0$ and $b_2^0 O_2^0$ which was developed in [43–45] and based on two fundamental approximations.

The superposition approximation of Newman gives

$$Z_2^0 = \sum_d \bar{Z}_2(R_d) K_2^0(\vartheta_d, \varphi_d) \quad (3)$$

where R_d , ϑ_d and φ_d are the spherical coordinates of the d th ligand in relation to the nucleus of Gd^{3+} and $K_2^0(\vartheta_d, \varphi_d) = (3 \cos^2 \vartheta_d - 1)/2$ [46].

In accordance with another approximation concerned with the exchange model of crystal-field screening for rare-earth ions [44] we may write

$$\bar{Z}_2(R) = \bar{Z}_{2p}(R_0)(R_0/R)^3 + \bar{Z}_{2s}(R_0)(R_0/R)^{10} \quad (4)$$

where $\bar{Z}_{2p}(R_0)$ and $\bar{Z}_{2s}(R_0)$ are the contributions to $\bar{Z}_2(R_0)$ due to the electrostatic field of the ligand 'point' charge and to the short-range metal-ligand interaction respectively, $R_0 = 0.234$ nm being chosen for the pair $\text{Gd}^{3+}-\text{O}^{2-}$. It should be noted that $\bar{A}_{2p}(R_0)/\bar{A}_{2s}(R_0) \neq \bar{b}_{2p}(R_0)/\bar{b}_{2s}(R_0)$ [43].

Combining equations (3) and (4), we have

$$Z_2^0 = \sum_g K_2^0(t_g) \bar{Z}_{2g}(R_0) \quad (5)$$

where

$$K_2^0(t_g) = \sum_d K_2^0(\vartheta_d, \varphi_d) \left(\frac{R_0}{R}\right)^{t_g} \quad g = p, s \quad t_g = 3, 10. \quad (6)$$

3.2. Probability model

Equations (3)–(5) may be considered as a particular example of the more general class of hypothetical expressions for A_2^0 , b_2^0 and P_2^0 :

$$Z_2^0 = \sum_{g=1,2} Z_g K_g \quad (7)$$

where K_g are functions of nuclear coordinates of the crystal in adiabatic approximation, and arrows and columns of the (3×2) matrix of the numerical coefficients Z_g are non-proportional to each other. Hereafter the symbol Z without a subscript 2 and superscript 0 may take the values P , b and A , indicating the connection to the types of parameter Z_2^0 . Now we shall show that, if any expression of the type (7) holds true for two different types of parameter Z_2^{i0} and Z_2^{j0} , then, irrespective of what kind this expression is, the same way of describing the correlation may be developed; we shall be referring further to this as a probability model of the correlation.

Suppose that we have a finite set S of more than two centres of $^{157}\text{Gd}^{3+}$ in crystals and corresponding sets of pairs of values $\{(Z_2^{i0}, Z_2^{j0})\}$ and $\{K\} = \{(K_1, K_2)\}$ where all values of Z_2^{i0} , Z_2^{j0} and all elements (K_1, K_2) are different. We shall seek conditions under which the elements of $\{(Z_2^{i0}, Z_2^{j0})\}$ may be arranged according to the monotonic change in values of both types of parameter.

Let us consider the elements of $\{K\}$ as the points on the plane K_1OK_2 (figure 1). The relation between the values Z_2^0 (Z_2^{i0} or Z_2^{j0}) at the points K^i and K^j depends exclusively on the angle of the vector $K^j \equiv K^iK^j$ with the straight line l_z determined in the plane K_1OK_2 by the equation $K_2 = C_z K_1$, where $C_z = -Z_1/Z_2$. This becomes obvious if one bears in mind that the surface M_z determined by equation (7) in a three-dimensional

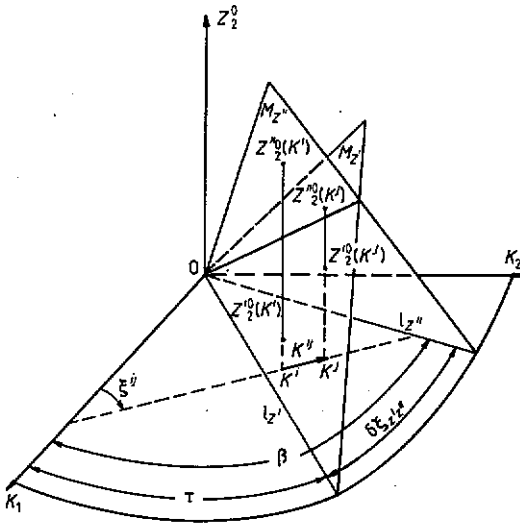


Figure 1. Example of the relative position of the vector K^{ij} and the planes M_Z and M_Z^0 , in the case when $Z_2^{i0}(K^i) < Z_2^{j0}(K^j)$ and $Z_2^{m0}(K^i) > Z_2^{n0}(K^j)$.

space $K_1 K_2 Z_2^0$ is a plane which intersects the plane $K_1 O K_2$ along the line l_Z . To characterize the K^{ij} direction we introduce an angle

$$\xi^{ij} = \begin{cases} \tan^{-1}[(K_2^i - K_2^j)/(K_1^i - K_1^j)] & \text{for } \begin{cases} K_1^i - K_1^j \neq 0 \\ K_1^i - K_1^j = 0. \end{cases} \end{cases} \quad (8)$$

We shall regard the values ξ^{ij} for all possible vectors by which the points from $\{K\}$ may be joined as a set $\{\xi\}$. Given that Z_g values are fixed, a definite relation between $Z_2^{n0}(K^i)$ and $Z_2^{m0}(K^j)$ follows from the relation between $Z_2^{i0}(K^i)$ and $Z_2^{j0}(K^j)$ and vice versa. If the elements of $\{(Z_2^{i0}, Z_2^{j0})\}$ are arranged according to the monotonic change in Z_2^{i0} , then the relationship between neighbouring values of Z_2^{j0} in this series will depend on the values ξ^{ij} for the vectors K^{ij} corresponding to the neighbouring terms of the series. Thus the validity of the following statement becomes clear. In order that the elements of $\{(Z_2^{i0}, Z_2^{j0})\}$ may be arranged according to the monotonic change in the values of both types of parameter, it is necessary and sufficient that all elements of $\{\xi\}$ must be contained either in an interval $\Delta_1 \xi_{Z^i Z^j} = (\tau, \beta)$ or in the union of two intervals $\Delta_2 \xi_{Z^i Z^j} = (\beta, \pi/2] \cup (-\pi/2, \tau)$ (the first of them being half-open) where

$$\tau = \tan^{-1}(\min\{C_{Z^i}, C_{Z^j}\}) \quad \beta = \tan^{-1}(\max\{C_{Z^i}, C_{Z^j}\}). \quad (9)$$

It follows from the statement above that, if the elements of $\{\xi\}$ are distributed evenly along the interval $(-\pi/2, \pi/2]$, then the greatest fraction $\rho_{Z^i Z^j}$ of the centres from S for which the pairs (Z_2^{i0}, Z_2^{j0}) may be arranged according to the monotonic change in the values of both types of parameter is equal to $(\pi - \delta \xi_{Z^i Z^j})/\pi$, where $\delta \xi_{Z^i Z^j} = \min\{\beta - \tau, \pi + \tau - \beta\}$ and increases from 0.5 to 1 with $\delta \xi_{Z^i Z^j}$ decreasing from the maximum $\pi/2$ to the minimum 0 value. The phenomenological values $\rho_{AB}^{phen} = \frac{5}{8}$, $\rho_{AP}^{phen} = \frac{6}{7}$ and $\rho_{BP}^{phen} = \frac{5}{7}$ may be easily obtained for the set of collections in table 1.

Thus, we may obtain a description of the correlation and the small deviations from monotonicity in table 1 as a corollary of the assumption that the values $\delta \xi_{Z^i Z^j}$ for any pair of the parameters P_2^0 , b_2^0 and A_2^0 are small enough and the values $\{\xi\}$ for the centres of table 1 are distributed sufficiently evenly along the interval $(-\pi/2, \pi/2]$, few values from $\{\xi\}$ being outside the limits of $\Delta_1 \xi_{Z^i Z^j}$ or $\Delta_2 \xi_{Z^i Z^j}$ where the greater part of the values

$\{\xi\}$ is contained. It is to be noted that in this model of the correlation there is a significant approximation where the centres S should be looked upon as a set, and not separately, and this approximation consists in modelling a probability density function for the number of angles ξ^j per length unit along the interval $(-\pi/2, \pi/2]$. In other approximations the parameters Z_2^0 and Z_g are treated by themselves (for a separate centre). Therefore, the probability model, on the whole, does not coincide with any model of the crystal fields.

3.3. Extended probability model for A_2^0 and b_2^0

Identifying K_g with $K_2^0(t_g)$ and Z_g with $\bar{A}_{2g}(R_0)$ as well as $\bar{b}_{2g}(R_0)$ for the pair $\text{Gd}^{3+}-\text{O}^{2-}$ [43], we obtain $\delta\xi_{Ab} = 0.03\pi$ and the theoretical value $\rho_{Ab}^{\text{theor}} = 0.97$. Since ρ_{Ab}^{theor} is even greater than ρ_{Ab}^{phen} , we may consider that the probability model of the correlation extended with the particular model for the crystal fields $A_2^0O_2^0$ and $b_2^0O_2^0$ furnishes not only a description of the relationship between the incomplete collections $\{b_2^0, A_2^0\}$ in table 1 but a certain explanation as well. Some quantitative discordance between ρ_{Ab}^{theor} and ρ_{Ab}^{phen} may be caused both by the errors in the magnitudes involved in the consideration and by the approximations used and, in particular, by the supposition that the values $\{\xi\}$ for the collections in table 1 are distributed evenly along the interval $(-\pi/2, \pi/2)$.

Another possible extension to the probability model will be discussed in section 5.

4. Nuclear quadrupole interaction

4.1. Extended probability model for P_2^0

We believe that at present there is not a sufficient measure of certainty in the contributions of various mechanisms to the nuclear quadrupole interaction (in particular, for $^{157}\text{Gd}^{3+}$ in oxide crystals). Therefore, suggesting a particular extension to the probability model for P_2^0 , we shall not calculate the values of ρ_{ZP}^{theor} and compare them with ρ_{ZP}^{phen} . On the contrary, we shall be looking for some characteristics of the nuclear quadrupole interaction, using the data in table 1, and shall compare these with the results determined earlier.

Considering that the P_2^0 -, b_2^0 - and A_2^0 -dependences are similar, we extend equations (3)–(5) to the parameters P_2^0 . To determine the phenomenological values of $\bar{P}_{2g}(R_0)$, first we substituted the experimental values of b_2^0 and A_2^0 in equation (5) for all complete collections $\{Z_2^0\}$ from table 1, then considered these expressions as a system of equations in $K_2^0(t_g)$ and, upon solving it, thereby found phenomenological structure factors. Then, varying $\bar{P}_{2g}(R_0)$, we sought a minimum of the sum of differences between the experimental parameters P_2^0 and those obtained with the help of the phenomenological factors $K_2^0(t_g)$ and $\bar{P}_{2g}(R_0)$. However, we did not obtain any sharp minimum because some of the experimental values Z_2^0 are not as accurate as we had hoped. Therefore, another method is considered below to estimate $\bar{P}_{2g}(R_0)$.

If the collection $\{Z_2^0\}$ for YPO_4 with an unknown sign of P_2^0 is ignored, it is seen that in the columns for P_2^0 and A_2^0 in table 1 the change in sign occurs for the same centres (differing from those for which the change in sign occurs in the column for b_2^0). In this connection, we may accept $C_p = C_A$ and the columns for P_2^0 and A_2^0 are approximately proportional. Then, consequently, the ratio P_2^0/A_2^0 may be represented as $k = \bar{P}_{2p9}(R_0)/$

$\bar{A}_{2p}(R_0)$. Writing $\bar{P}_{2p}(R_0)$ in accordance with the Sternheimer parametrization of the nuclear quadrupole interaction [47] and $\bar{A}_{2p}(R_0)$ as in [43], we obtain

$$k = - (1 - \gamma_x) Q / \langle r^2 \rangle_{4f4f} \quad (10)$$

where γ_x is the Sternheimer antiscreening coefficient. The Steinheimer screening factor $1 - \sigma_2$ [47] does not appear in equation (10) because the present consideration and equation (4), in particular, are based on the exchange model of the crystal-field screening [44] as has been mentioned above. Phenomenological values of k may be used to obtain γ_x and then $\bar{P}_{2g}(R_0)$. We shall determine these values k^{phen} as ratios of the experimental values of P_2^0 and A_2^0 for the centres in table 1. We omit the most inaccurate data related to the centre in $\text{Y}_2\text{Ti}_2\text{O}_7$. For centres in Y_2O_3 and scheelite crystals, k^{phen} varies from -7.5×10^{-6} to -9.6×10^{-6} , the relative error ε_1 in the mean value being of the order of 10%. The value $k^{\text{phen}} = -28 \times 10^{-6}$ for the centre in YVO_4 by far exceeds the bounds of this interval. We shall not be taking this value into account, supposing that its substantial difference from the other values k^{phen} is generated by a strong compensation between the contributions $\bar{Z}_{2g}(R_0)K_2^0(t_g)$ in Z_2^0 when the approximation $C_p \approx C_A$ may give rise to a considerable error in k^{phen} while using the above-described method of determination.

The most precise value of A_2^0 is available for the centre in CaWO_4 . This value of A_2^0 has been determined for the Tb^{3+} ion which is neighbouring to Gd^{3+} in the lanthanide series. Differences between the values of A_2^0 for a number of RE^{3+} in CaWO_4 are not more than 10% (compare for example with A_2^0 for RE^{3+} in other crystals with scheelite and zircon structures) [14]. Various methods of obtaining A_2^0 for Tb^{3+} in CaWO_4 (the result for one of these being used in table 1) give a disagreement of not more than 5% [20]. So the error ε_2 in A_2^0 and k^{phen} is of the order of 10% for $^{157}\text{Gd}^{3+}$ in CaWO_4 , because the error in P_2^0 is only 0.1% (see table 1).

We consider that the value ε_1 is less reliable than ε_2 since the errors in A_2^0 or P_2^0 for centres other than RE^{3+} in CaWO_4 involved in calculation of ε_1 are probably greater than ε_1 . Therefore, we shall be using only k^{phen} for $^{157}\text{Gd}^{3+}$ in CaWO_4 . Substituting this k^{phen} in equation (10), we have $\gamma_x = -147$ and hence $\bar{P}_{2p}(R_0) = -182 \times 10^{-4} \text{ cm}^{-1}$ (using [47]) and $\bar{P}_{2s}(R_0) \approx C_A \bar{P}_{2p}(R_0) = 75.1 \times 10^{-4} \text{ cm}^{-1}$, the error being 10% presumably. This value of γ_x is substantially different from the theoretical value of -61 for Gd^{3+} (and -64 for Pr^{3+}) calculated with the help of the Sternheimer approach [48], but it is in agreement with another theoretical value for Pr^{3+} , $\gamma_x = -172$, calculated by Ahmad and Newman [49] taking the interelectronic correlation into account in addition to the interactions considered by Sternheimer originally. We believe that the difference between the γ_x -value from [49] and that from our work is less than the sum of the errors in both of these values and the difference between the γ_x -values for Gd^{3+} and Pr^{3+} .

It is noteworthy that the value of $\bar{P}_{2s}(R_0)$ obtained here agrees within an order of magnitude with the contributions to the nuclear quadrupole interaction due to the effects of overlap and exchange calculated for Pr^{3+} in a Cl^- environment [50, 51].

4.2. On the violation of the correlation

Now, we can calculate the values of P_2^0 for YPO_4 and the first three crystals in table 2 with the help of the phenomenological values of $\bar{P}_{2g}(R_0)$ and $K_2^0(t_g)$. These P_2^0 are equal to $-16.2 \times 10^{-4} \text{ cm}^{-1}$, $-15.8 \times 10^{-4} \text{ cm}^{-1}$, $-7.3 \times 10^{-4} \text{ cm}^{-1}$ and $2.8 \times 10^{-4} \text{ cm}^{-1}$, respectively. If an error of 10% is allowed in $\bar{P}_{2g}(R_0)$, the corresponding intervals for these calculated values of P_2^0 include the experimental values provided that the negative

sign of P_2^0 for YPO_4 and $\text{Y}(\text{OH})_3$ is chosen. Thus the negative sign of P_2^0 for YPO_4 may be considered to be true, in line with the supposition that $C_p \approx C_A$ for oxide crystals. As to the non-correspondence of the first three collections from table 2 to the correlation in table 1, the present examination cannot yet answer the question of whether this violation is influenced by some particular values of $K_2^0(t_g)$, the extended probability model being valid for these centres, or whether this violation is caused by invalidity of the model for these types of chemical compound.

5. Phenomenological and calculated structure factors

The phenomenological factors obtained here differ from those that we have tried to calculate by substitution of the ligand coordinates into equation (6). This difference may be due to the uncertainty of the atomic coordinates of the pure crystal, distortion of structure caused by impurity or to errors in $\bar{Z}_{2g}(R_0)$. However, this difference may also be influenced by 'absorbing' contributions from the interactions between ligands and between Gd^{3+} and the rest of the crystal into $K_2^0(t_g)$. Suppose there are, for example, contributions to Z_2^0 from the electrostatic field caused by charges other than the ligand 'point' charges and 'external' with reference to Gd^{3+} . In our model these contributions may be collected together with $\bar{Z}_{2p}(R_0)K_2^0(3)$ and given the form $\bar{Z}_{2p}(R_0)\bar{K}_2^0(3)$ (i.e. the form corresponding to the type (7)) where $\bar{K}_2^0(3)$ is the same magnitude for all types of Z_2^0 . As a result of such a transformation of $K_2^0(3)$ into $\bar{K}_2^0(3)$ for any set of Gd^{3+} centres, the intervals $\delta\xi_{Z^0}$ do not change and, therefore, the conditions of the correlation remain unchanged.

6. Collections $\{Z_2^0\}$ for fluoride and chloride crystals

6.1. Correlation between collections $\{Z_2^0\}$ for fluoride crystals

The number of sets of known collections $\{Z_2^0\}$ for $^{157}\text{Gd}^{3+}$ in the crystals which have only F^- anions (table 3) is not as large as in the case of the oxide crystals but these collections obey the same correlation as the collections in table 1. We accept the extended probability model for the fluoride crystals. Using $\bar{Z}_{2g}(R_0)$ for the pair $\text{Gd}^{3+}-\text{F}^-$ from [43], we obtain $\delta\xi_{Ab} \approx 0.03\pi$. So an explanation of the correlation between the incomplete collections $\{b_2^0, A_2^0\}$ may be furnished in the same way as in the case of the oxide crystals taking the small value of $\delta\xi_{Ab}$ into account.

6.2. Model parameters for fluoride crystals

In table 3, the collections $\{Z_2^0\}$ for the tetragonal centres in CaF_2 and SrF_2 are most reliable and accurate. So, to obtain values of $\bar{P}_{2g}(R_0)$ for the pair $^{157}\text{Gd}^{3+}-\text{F}^-$ and to determine γ_∞ with the help of yet another type of independent experimental datum, we find phenomenological factors for these centres, substitute these factors and the experimental values of P_2^0 in (5) and consider the two resultant expressions as a system of equations in $\bar{P}_{2g}(R_0)$ where $R_0 = 0.237$ nm is chosen [43]. As a result we have $\bar{P}_{2p}(R_0) = -89.6 \times 10^{-4} \text{ cm}^{-1}$, $\bar{P}_{2s}(R_0) = 45.5 \times 10^{-4} \text{ cm}^{-1}$ and hence $\gamma_\infty = -150$ (using [47]). These values may be in error defined by the errors in Z_2^0 (for CaF_2 and SrF_2), $b_{2g}(R_0)$ and $\bar{A}_{2g}(R_0)$. It is rather difficult to estimate the errors in the latter two values

because they were determined using substantial model approximations and the restricted collection of experimental data. We believe that the value of $\bar{A}_{2s}(R_0)$ has the maximum error. In determining this $\bar{A}_{2s}(R_0)$ the crystal-field data were extrapolated from Dy³⁺ to Gd³⁺ [43]. With such a procedure, the error in $\bar{A}_{2s}(R_0)$ and, consequently, in γ_x presumably is not less than 10% as may be concluded from the discussion of A_2^0 for Tb³⁺ in CaWO₄ in section 4.1. The errors in P_2^0 and A_2^0 are substantially smaller according to table 3 and [42, 52]. Thus the values of γ_x obtained here agree well and this argues strongly for the model proposed. However, the value of γ_x determined as a result of the consideration of the centres in fluorites is not more precise than that determined for the centre in CaWO₄.

6.3. Trigonal centre in SrF₂

Let us compare the parameters $Z_2^0(\text{trig})$ of the trigonal centre in SrF₂ with the parameters $Z_2^0(\text{tetr})$ of the tetragonal centre in the same crystal (table 3). There are substantial differences between the $Z_2^0(\text{trig})/Z_2^0(\text{tetr})$ ratios for different types of these parameters. To examine this in terms of our model, we calculate $P_2^0(\text{trig}) = (-10 \pm 3) \times 10^{-4} \text{ cm}^{-1}$ with the help of the phenomenological factors and $\bar{P}_{2g}(R_0)$. Here the error caused by the 10% errors in $\bar{P}_{2g}(R_0)$ is indicated. The calculated value of $P_2^0(\text{trig})$ is in good agreement with the experimental value. Thus the substantial differences between the $Z_2^0(\text{trig})/Z_2^0(\text{tetr})$ ratios do not contradict the possible applicability of our model to these centres.

6.4. Chloride crystal

We know of only one example of the collection Z_2^0 in a crystal with Cl⁻ anions (table 2). Using equation (5), $\bar{b}_{2g}(R_0)$ and $\bar{A}_{2g}(R_0)$ from [43], and $\gamma_x = -147$, we calculate $\bar{P}_{2p}(R_0) = -48.3 \times 10^{-4} \text{ cm}^{-1}$ and $\bar{P}_{2s}(R_0) = 34.0 \times 10^{-4} \text{ cm}^{-1}$ for the pair ¹⁵⁷Gd³⁺-Cl⁻ at $R_0 = 0.289 \text{ nm}$.

7. Conclusions

As the intervals between the minimum and maximum values of the parameters Z_2^0 from the collections obeying the correlation are quite considerable for each type of the parameter Z_2^0 , we suppose that the correlation revealed is a rather general characteristic of the collections $\{Z_2^0\}$ and its explanation may be regarded as an important criterion of validity for microtheory crystal-field models.

The extended probability model developed in this work explains the correlation and predicts that there may exist collections $\{Z_2^0\}$ not obeying the correlation but pertaining to centres with the same fundamental mechanisms of the crystal fields as is the case with centres which give the collections $\{Z_2^0\}$ obeying the correlation.

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