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Calculation of the Crystal Field Parameters of Praseodymium Ethyl Sulfate and Praseodymium Trichloride

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A method of applying the extended Hückel molecular orbital method for the evaluation of crystal field parameters in the rare earth compounds is presented. The charge distribution in the crystal field and the effect of the outer coordinated sphere on the calculation of the crystal field parameters is discussed. From the calculated charge distribution, the crystal field parameters $A_{20}\langle r^2\rangle$, $A_{40}\langle r^4\rangle$, $A_{60}\langle r^6\rangle$, and $A_{66}\langle r^6\rangle$ of praseodymium ethyl sulfate crystal and praseodymium trichloride crystal have been obtained. The calculated results are in agreement with the experimental data. Some possible sources of the error in the calculation are discussed.

Introduction

The crystal field parameterization has been very successful in fitting rare earth ion spectra. For example, a four-parameter fit of 72 levels in Er : $LaCL_3$ has been made with a root mean square deviation of only 3.8 cm^{-1} for the intralevel splitting (*1*). Such an impressive result with a symmetry-based empirical scheme has led to many attempts to calculate the crystal field parameters. A point charge approximation was used for the first calculations with poor results (*2*). Newman and co-workers have made *ab initio* calculations on $PrCl_3$ and obtained good results for two of the four parameters (*3*). They found that the covalency and exchange contributions, among others, outweighed the point charge component (*4*).

Ürland used an Angular Overlap Model approach in which the angular overlap parameters were determined from three of the crystal field parameters. The fourth crystal field parameter was then computed from the other three (*5*).

We now describe another approach to the computation of the crystal field parameters. This method involves an electrostatic model in which the charge distribution is determined by a semiempirical quantum chemical technique, the extended Hückel molecular orbital (EHMO) method (*6*). In addition to the EHMO parameters that have been validated in other calculations (*7*), a single free parameter, *AR*, is used to fit the four crystal field parameters. Although only the charges in the ML_9 skele-

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ton are used directly in the electrostatic calculation of the crystal field parameters, the effect of other atoms on the inner sphere charges is included in the EHMO treatment.

The charge distribution $\rho_j(R_j)$ plays a central role in evaluating the crystal parameters since it is used to calculate the crystal field parameters $A_{20}\langle r^2\rangle$, $A_{40}\langle r^4\rangle$, $A_{60}\langle r^6\rangle$, and $A_{66}\langle r^6\rangle$, for two different crystals, praseodymium ethyl sulfate $(Pr(C_2H_5SO_4)_3 \cdot 9H_2O)$ and praseodymium trichloride $(PrCl_3)$. The calculated results are found to be in agreement with the experimental data.

Formulation of the Crystal Field Parameters

In the parameterization scheme of the rare earth crystal field no specific assumption is made about the nature of the crystal fields, and therefore the procedure holds equally well for more and less ionic crystals. The two main assumptions in the scheme are: (i) the crystal field acts independently and equally on all of the 4*f* electrons, and (ii) the radial distribution function of the 4*f* electrons is the same for all terms (*8*). The success of the parameterization scheme shows that these approximations are justified for the 4*f* electrons, and we retain the assumptions. In an electrostatic approach an accurate charge distribution field is most important for the calculation of the crystal field parameters, whether the bonding is ionic or covalent. Therefore, the emphasis in our calculation is placed on the calculation of the charge distribution in the crystal field.

When a rare earth ion (RE^{+3}) is placed in a crystal field, it is surrounded by the coordinated atoms or molecules. The central rare earth ion and the coordinated atoms or molecules about it form a cluster that possesses a certain symmetry. For example, in a praseodymium ethyl sulfate $(Pr(C_2H_5SO_4)_3 \cdot 9H_2O)$ crystal, each Pr^{+3} ion is surrounded by nine water molecules. The site symmetry of Pr^{+3} is C_{3h}, but we have assumed that the symmetry of the $Pr(H_2O)_9$ cluster is D_{3h}, for the sake of comparing the calculated results with the experimental data.

In the crystal field of the cluster, the potential at r_i due to the *j*th coordinated atom or molecule is

$$V_j(r_i) = -\int \frac{\rho_j(R_j)}{r_{ij}}\, d\tau \qquad (1)$$

where $\rho_j(R_j)$ is the charge distribution function of the *j*th coordinated atom.

Because of the additive property of the potential, the total potential at r_i due to all the coordinated atoms is

$$V(r_i) = -\sum_{j=1}^{n} \int \frac{\rho_j(R_j)}{r_{ij}}\, d\tau \qquad (2)$$

where *n* is the number of the coordinated atoms or molecules.

If we take the position of the central rare earth ion as the coordinate origin and express the r_{ij} term by the von Neumann expansion, we obtain

$$V(r_i) = -\sum_{j=1}^{n}\sum_{k=0}^{\infty}\sum_{q=-k}^{k} (-1)^q \left(\frac{4\pi}{2k+1}\right) \int \rho_j(R_j) \frac{r_<^k}{r_>^{k+1}} Y_{kq}(\theta_i, \phi_i) Y_{k-q}(\Theta_j, \Phi_j) d\tau. \qquad (3)$$

According to convention, we define

$$C_{kq}^j(\theta_i, \phi_i) = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_{kq}(\theta_i, \phi_i) \qquad (4)$$

$$b_{kq}^j = -\left[(-1)^q \left(\frac{4\pi}{2k+1}\right)^{1/2} \int \rho_j(R_j) \frac{r_<^k}{r_>^{k+1}} Y_{k-q}(\Theta_j, \Phi_j) d\tau\right] \qquad (5)$$

Then,

$$V(r_i) = \sum_{j=1}^{n}\sum_{k=0}^{\infty}\sum_{q=-k}^{k} b_{kq}^j \cdot C_{kq}^j(\theta_i, \phi_i). \qquad (6)$$

Each of the sevenfold degenerate $4f$ wavefunctions in the free ion can be represented as $\Psi = R(r)Y_{lm}(\theta, \phi)$. In the crystal field, the angular parts of each wavefunction, $Y_c(\theta, \phi)$, will be symmetry-adapted linear combinations of $Y_{lm}(\theta, \phi)$. The radial part of all the wavefunctions, $R(r)$, is the same. Thus, each one-electron wavefunction can be represented as $\Psi_c = R(r) \times Y_c(\theta, \phi)$.

If the central rare earth ion has n_f $4f$ electrons, the crystal field interaction energy

$$E_c = n_f \sum_{j=1}^{n} \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \langle R(r_i)|b^j_{kq}|R(r_i)\rangle\langle Y_c(\theta_i, \phi_i) |C^j_{kq}(\theta_i, \phi_i)| Y_c(\theta_i, \phi_i)\rangle. \quad (7)$$

Thus, the crystal field parameters B_{kq} can be represented as

$$B_{kq} = n_f \sum_{j=1}^{n} \left[-(-1)^q \left(\frac{4\pi}{2k+1}\right)^{1/2} \int \rho_j(R_j) R^*(r_i) R(r_i) \frac{r_<^k}{r_>^{k+1}} Y_{k-q}(\Theta_j, \Phi_j) d\tau \right]. \quad (8)$$

We let $r_< = r_i$, $r_> = R_j$ where $r_i < R_j$. These are reasonable for the $4f$ electrons since the $4f$ electrons are deeply imbedded in the interior of the rare earth ion and are shielded by two closed electronic shells with larger radial expansions ($5s^2$, $5p^6$) (*9*).

B_{kq} can then be evaluated from

$$B_{kq} = -n_f \sum_{j=1}^{n} C^j_{k-q}(\Theta_j, \Phi_j) \frac{\rho_j(R_j)}{R_j^{k+1}} \langle r^k \rangle \quad (9)$$

where n_f is the number of $4f$ electrons of the central rare earth ion, and

$$C^j_{k-q}(\Theta_j, \Phi_j) = (-1)^q \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_{k-q}(\Theta_j, \Phi_j) \quad (10)$$

$$\langle r^k \rangle = \int R^*(r_i) r_i^k R(r_i) d\tau. \quad (11)$$

The $\rho_j(R_j)$ is often treated to be the charge density of the jth coordinated atom. Obviously, this is too simplistic. According to molecular orbital theory, in a molecule, all the valence electrons belong to the whole molecule system, not to a certain atom, because, when forming the molecule, all the electrons are rearranged, and the electron distribution in the molecule is determined by the occupied molecular orbitals. So, unlike the conventional concept, we shall regard $\rho_j(R_j)$ as the charge density distribution of the whole system, not as the charge density distribution of the coordinated atoms.

The EHMO method was used to obtain the coefficients of the molecular orbitals of the cluster, composed of the central rare earth ion and the coordinated atoms about it. The density matrix of the system was then calculated. The element $p_{\mu\nu}$ of the density matrix is

$$p_{\mu\nu} = 2 \sum_{k}^{n_0} C^*_{\mu k} C_{\nu k} \quad (12)$$

where n_0 is the number of the occupied molecular orbitals of the system and $C_{\mu k}$ and $C_{\nu k}$ are the coefficients of the μth and νth components of the kth occupied molecular orbital, respectively. The element S_{ij} of the overlap integral matrix of the system is

$$S_{ij} = \langle \phi_i \mid \phi_j \rangle \quad (13)$$

where ϕ_i and ϕ_j are the ith and jth atomic orbital wavefunctions, respectively.

The charge distribution, $\rho_j(R_j)$, is approximated by a discrete collection of point charges:

$$q_A = \sum_{i \varepsilon A} p_{ii} + 2 \sum_{\substack{i,j \\ i \neq j \\ i,j \varepsilon A}} p_{ij} S_{ji} \quad (14)$$

and

$$q_{AB} = 2 \sum_{\substack{i \varepsilon A \\ j \varepsilon B}} p_{ij} S_{ji} \quad (15)$$

where q_A is the charge on an atom and q_{AB}

is the overlap between atoms. The crystal field parameters, B_{kq}, are then evaluated from Eq. (9).

In performing the calculation, we made the following approximations:

(1) The charge at each coordinated atom q_A is the net charge at the atom. This takes into account the interaction between the charge of the atomic core of the coordinated atom and the 4*f* electrons in the central rare earth ion. Also, R_j (the distance between the center of the charge distribution and the central rare earth ion) is equal to $AR \cdot R_j^\circ$ (R_j° is the distance between the coordinated atom and the central rare earth ion). The factor AR, which is always less than 1.0, is discussed below. The introduction of the empirical parameter serves to include polarization effects.

(2) If $\rho_j(R_j)$ refers to the charge distribution between two coordinated atoms, q_{AB} is centered at the midpoint between A and B.

(3) If $\rho_j(R_j)$ is the charge density at the central rare earth atom or between the central rare earth ion and the coordinated atom, it is omitted in calculating the crystal field parameters. Because quantum chemical calculations show that the valence electrons between the rare earth ion and the coordinated atom, for example, between Pr and O, are mainly from the 6*s* and 5*d* electrons of the rare earth atom, especially the valence electrons at the central rare earth atom are just the 6*s* and 5*p* electrons. The interactions between the 6*s* and 5*d* electrons and the 4*f* electrons have already been included in the energy of the free rare earth atom and it is not necessary to count such interactions again. However, the interaction between the "6*s* and 5*d*" electrons in the molecule and the 4*f* electrons of the central rare earth atom must be different from the interaction between the 6*s* and 5*d* electrons and the 4*f* electrons in the free rare earth atom.

Calculations indicate that the coordinated atoms in the outer coordination sphere are so far from the central rare earth atom that direct interactions between the charge distributions at these atoms and the 4*f* electrons of the central rare earth atom are very small. However, the coordinated atoms can affect the charge distribution of the atoms in the inner coordination sphere. Therefore, only the charge distributions in the $PrCl_9$ and PrO_9 clusters were included in the calculation of the crystal field parameters, but the outer coordination sphere is included in the EHMO procedure.

D_{3h} symmetry was assumed for the $Pr(H_2O)_9$ and $PrCl_9$ cluster and there are only four crystal field parameters: B_{20}, B_{40}, B_{60}, and B_{66}. The corresponding $C^j_{k-q}(\Theta_j, \Phi_j)$ are

$$
\begin{aligned}
C^j_{20}(\Theta_j, \Phi_j) &= (-1)^0 \left(\frac{4\pi}{2 \times 2 + 1}\right)^{1/2} Y_{20}(\Theta_j, \Phi_j) \\
&= \tfrac{1}{2}(3 \cos^2\Theta - 1) \\
C^j_{40}(\Theta_j, \Phi_j) &= (-1)^0 \left(\frac{4\pi}{2 \times 4 + 1}\right)^{1/2} Y_{40}(\Theta_j, \Phi_j) \\
&= \tfrac{1}{8}(35 \cos^4\Theta_j - 30 \cos^2\Theta_j + 3) \\
C^j_{60}(\Theta_j, \Phi_j) &= (-1)^0 \left(\frac{4\pi}{2 \times 6 + 1}\right)^{1/2} Y_{60}(\Theta_j, \Phi_j) \\
&= \tfrac{1}{16}(231 \cos^6\Theta_j - 315 \cos^4\Theta_j + 105 \cos^2\Theta_j - 5) \\
C^j_{66}(\Theta_j, \Phi_j) &= (-1)^6 \left(\frac{4\pi}{2 \times 6 + 1}\right)^{1/2} Y_{66}(\Theta_j, \Phi_j) \\
&\quad + (-1)^{-6} \left(\frac{4\pi}{2 \times 6 + 1}\right)^{1/2} Y_{6-6}(\Theta_j, \Phi_j) \\
&= \frac{\sqrt{231}}{16} \sin^6\Theta_j \cos^6\Phi_j. \qquad (16)
\end{aligned}
$$

The relationships between the B_{kq} and the $A_{kq}\langle r^k \rangle$ crystal field parameters are (*8*)

$$B_{20} = 2 \cdot A_{20}\langle r^2\rangle$$
$$B_{40} = 8 \cdot A_{40}\langle r^4\rangle$$
$$B_{60} = 16 \cdot A_{60}\langle r^6\rangle$$
$$B_{66} = \frac{16}{\sqrt{231}} A_{66}\langle r^6\rangle. \quad (17)$$

Parameters and Selection of the System

In quantum chemical calculations, the valence orbitals are 6*s* and 5*d* orbitals for the rare earth atom; 2*s* and 2*p* orbitals for the oxygen atoms; 1*s* orbital for the hydrogen atom; and 3*s* and 3*p* orbitals for the chlorine atoms. The atomic parameters (Slater exponents and valence state ionization energy) used in the calculation are from Ren *et al.* (*7*). The crystallographic geometry (*10*) was used in the calculation of the praseodymium ethyl sulfate crystal field parameters. In order to compare our calculated results with other calculations, we adopted the geometry Ellis and Newman used in their calculation for the praseodymium trichloride crystal (*3*). Ellis and Newman did not include the distances between the central praseodymium atom and the praseodymium atoms outside the inner coordinated sphere in the praseodymium trichloride crystal and these data are from Zachariasen (*11*).

In EHMO quantum chemical calculations, the Wolfsberg–Helmholtz parameter K is an adjustable parameter and varies with the bond type. Generally, it is between 1.0 and 2.0. The K values used were 1.75 for H–X bonds (X = any atoms); 1.68 for O–O bonds; 1.50 for O–Pr bonds; 1.23 for Cl–Cl bonds; 1.25 for Cl–Pr and Pr–Pr bonds.

In our calculation, the factor AR was adjusted to give the best fit. For the praseodymium ethyl sulfate crystal, $AR = 0.85$; for the praseodymium trichloride crystal, $AR = 0.95$. The values of $\langle r^k\rangle$ are from Freeman and Watson (*9*). For the Pr^{+3} ion, the values are

$$\langle r^2\rangle = 1.086 \text{ au}$$
$$\langle r^4\rangle = 2.822 \text{ au}$$
$$\langle r^6\rangle = 15.726 \text{ au}.$$

In previous calculations of the crystal field parameters, the treated system was regarded as a cluster which was composed of only the central rare earth atom and the nearest-neighbor coordinated atoms. The neglect of contributions from the atoms in the outer coordination sphere is questionable. If the treatment is limited to the clusters PrO_9 or $PrCl_9$ only, the environment about the central rare earth ion is included, and the environments about the coordinated atoms are ignored. If the rare earth compounds are ionic compounds this approach might not cause very large errors, because in ionic crystals each atom can be regarded as a positive or negative point charge. But in covalent compounds, the situation is more complicated. Bonding in rare earth compounds is not purely ionic.

There are several nearest-neighbor praseodymium atoms about each chlorine atom in the praseodymium trichloride crystal (*12*) and each chlorine atom bonds not only with the central praseodymium atom in the $PrCl_9$ cluster, but also with the other praseodymium atoms outside the $PrCl_9$ cluster. In the praseodymium ethyl sulfate crystal there are the nine nearest-neighbor oxygen atoms about each praseodymium atom and each oxygen atom is surrounded by hydrogen atoms, other oxygen atoms, and the central praseodymium atom.

According to molecular orbital theory, the charge distribution at each atom is strongly affected by its environment. Although the direct interaction between the atoms outside the cluster ($PrCl_9$ or PrO_9) and the central praseodymium atom in the cluster may not be very important for evaluating the crystal field parameters, the interaction between these atoms and the coordinated atoms (the chlorine atom or the oxygen atom) inside the cluster ($PrCl_9$ or PrO_9) must affect the charge distribution at these coordinated atoms. In turn, these charge distributions must affect the interaction between these coordinated atoms and the central praseodymium atom, and the calculation of the crystal field parameters.

It is not practical to treat the entire crystal system. In practice, we can only treat a very small part of the whole crystal, for example, a cell or a larger cluster. We have selected the cluster which includes the atoms of the outer coordinated sphere. For the praseodymium ethyl sulfate crystal this cluster is $Pr(H_2O)_9$, and for praseodymium trichloride crystal, the cluster is $PrCl_9 \cdot 8Pr$.

Results and Discussion

Our calculated results are listed in Table I. For comparison, other calculated results and the experimental data are also listed.

The results show that the calculated $A_{20}\langle r^2\rangle$ and $A_{66}\langle r^6\rangle$ are in good agreement with the experimental data. The deviations between the calculated and the experimental $A_{40}\langle r^4\rangle$ or $A_{60}\langle r^6\rangle$ are slightly larger. Although some approximations were made, the calculated results are satisfactory.

The *AR* factor requires some comment. In rare earth compounds, e.g., rare earth oxides, the RE–O bond is partially covalent. In the $Pr(H_2O)_9$ cluster, the environment about each oxygen atom does not have spherical symmetry, since each oxygen atom is surrounded by two hydrogen atoms, two oxygen atoms, and the rare earth atom. The RE–O bond is partially covalent, and the extra electrons in the oxygen atom are mainly from the rare earth atom. The center of the charge distribution at each oxygen atom will be shifted toward the central rare earth atom, and is not at the center of the oxygen atom. Therefore, the distance between the center of the charge distribution at each oxygen atom and the central rare earth atom is reduced from R_j° to $R_j = AR \cdot R_j^\circ$.

AR should differ in each system. It depends not only on the covalency of the chemical bond between the central rare earth atom and the coordinated atom, but also on the symmetry of the environment about the coordinated atom. We anticipate that the higher the symmetry of the envi-

TABLE I

THE CRYSTAL FIELD PARAMETERS OF PRASEODYMIUM ETHYL SULFATE AND PRASEODYMIUM TRICHLORIDE

Compound		Crystal field parameter			
		$A_{20}\langle r^2\rangle$	$A_{40}\langle r^4\rangle$	$A_{60}\langle r^6\rangle$	$A_{66}\langle r^6\rangle$
$Pr(C_2H_5SO_4)_3 \cdot 9H_2O$	Experimental data, Hüfner (*13*)	23.0	−80	−44	695.0
	Calculated results	37.1	−99.7	−20.4	574.7
$PrCl_3$	Experimental data				
	Judd (*14*)	49.5	−39.7	−39.2	386.7
	Margolis (*15*)	47.26	−40.58	−39.62	405.4
	Calculated results				
	Hutchings and Ray (*2*)	560 (168)	−35.4	− 3.07	36.9
	Ellis and Newman (*3*)	170 (48)	−40 (−37)	−26	315
	Newman (*4*)	22	−44	−41	536
	This paper	49.9	−67.0	−14.5	367.5

ronment about the coordinated atom, the larger is the value of AR. The weaker the covalency of chemical bond between the central rare earth ion and the coordinated atom, the larger the value of AR. In the calculation, AR is a fitting parameter. AR is 0.85 for the praseodymium ethyl sulfate crystal, and 0.95 for the praseodymium trichloride crystal. These results are in concordance with the above-mentioned expectation. In the first place, the Pr–Cl bond is more ionic than the Pr–O band. Furthermore, the crystal structures show that the symmetry of the environment about the chorine atom in the praseodymium trichloride crystal is higher than that of the environment about the oxygen atom in the praseodymium ethyl sulfate crystal.

It has been noted that the errors of the calculated $A_{40}\langle r^4\rangle$ and $A_{60}\langle r^6\rangle$ are larger than for the other two parameters in both praseodymium trichloride and praseodymium ethyl sulfate. The calculated $A_{40}\langle r^4\rangle$ are always smaller and the calculated $A_{60}\langle r^6\rangle$ are always larger than the experimental values. There must be some systematic errors in the calculation. One source of error is the assumption that the overlap charge distributions are positioned at the midpoints of the connecting lines between each pair of coordinated atoms. This assumption is questionable. For example, in the $PrCl_9 \cdot 8Pr$ or $Pr(H_2O)_9$ cluster, three coplanar coordinated atoms (three oxygen atoms or three chlorine atoms) form an equilateral triangle. However, the maximum overlap between the valence orbitals ($2Px$, $2Py$ or $3Px$, $3Py$) of two atoms of these coplanar atoms may not be along the side of an equilateral triangle. Also, for bonds between two different atoms, the center of charge distribution is shifted toward the more electronegative atoms; although AR corrects for this to some extent, a single parameter is apparently inadequate for fitting all of the crystal field parameters.

Newman has discussed various contributions to the crystal field parameters (*4*). The most important contributions to $A_{20}\langle r^2\rangle$ are from the ligand point charges, remaining charges, dipolar and quadrupolar polarization, and ligand–lanthanide exchange charge. The important contributions to $A_{66}\langle r^6\rangle$ are from charge penetration, covalency, and overlap as well as exchange. The calculated results show that the agreement between the calculated and the experimental $A_{20}\langle r^2\rangle$ or $A_{66}\langle r^6\rangle$ is the most satisfactory. We believe that this implies that most of these important interactions mentioned above have been included in the treatment.

In the EHMO method, some of the important interactions, for example, covalency and overlap static, are included and the calculated charge distributions include the effects of these interactions. This may be the reason why the calculated $A_{20}\langle r^2\rangle$ and $A_{66}\langle r^6\rangle$ are very close to the experimental data.

Newman has shown that the contribution of the exchange interaction to the $A_{66}\langle r^6\rangle$ is positive (*4*). If the exchange interaction is neglected, the value of $A_{66}\langle r^6\rangle$ will be decreased. On the contrary, the contribution of the ligand–lanthanide exchange interaction to the $A_{20}\langle r^2\rangle$ is negative. If the interaction is neglected, it will make the value of $A_{20}\langle r^2\rangle$ increase. Because we have neglected the exchange interaction in the quantum chemical calculation, the calculated $A_{20}\langle r^2\rangle$ is always larger than the experimental data, and the calculated $A_{66}\langle r^6\rangle$ is always smaller than the experimental data. We have done the calculations for other rare earth compounds with the same results.

Conclusion

We have applied the EHMO quantum chemical calculation to calculate the charge distributions in the crystal fields of the rare earth compounds, and have evaluated the crystal field parameters $A_{20}\langle r^2\rangle$, $A_{40}\langle r^4\rangle$, $A_{60}\langle r^6\rangle$, and $A_{66}\langle r^6\rangle$ of the praseodymium ethyl sulfate crystal and the praseodymium trichloride crystal. The calculated results are in reasonable agreement with the experimental data and show that, except for the exchange interaction, most of the important interactions in the crystal field of the rare earths have been included in our calculation.

An accurate charge distribution, $\rho_j(R_j)$, is very important for evaluating the crystal field parameters. The $\rho_j(R_j)$ in the formulation of the crystal field parameters is not the charge distribution of the directly coordinated atoms only but is the charge distribution of the molecular system in the crystal field.

The effect of the atoms of the outer coordination sphere on the calculation of the crystal field parameters has been included in our calculation. A fitting parameter, AR, has been introduced into the calculation. This parameter, which is less than unity, is a crude measure of the extent of covalency in the rare earth–ligand bonds. The sensitivity of the calculated crystal field parameters to AR is appreciable and the sensitivity of different crystal field parameters to AR is somewhat different.

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