Barycenter of Energy of Lanthanide 4f^{N−1}5d Configuration in Inorganic Crystals

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A semiempirical method for the evaluation of the barycenter of energy of 4f^{N−1}5d configurations is presented. The environmental factors affecting the barycenter are given to be the bond volume polarization, fractional covalence of the chemical bond between the central ion and the nearest anion, and presented charge of the nearest anion in the chemical bonds. The barycenter energies of 4f^{N−1}5d configurations of Eu^{2+} and Ce^{3+} are calculated in various crystals, and the results are in good agreement with the experimental values. A relationship is found between the barycenter of energy of the 4f^{N−1}5d configuration on Eu^{2+} and Ce^{3+} ions and environmental factors. Our method offers the advantage of applicability to a broad class of luminescence materials and initiates a link between macroscopic properties and microscopic structure.

1. Introduction

Recently the d−f transitions of lanthanides in solids have attracted much more attention because they have many practical and potential applications in the high-energy range, for example, plasma display panels (PDPs), luminescent materials, up-conversion fluorescence, and so on. For 4f^{N−1}5d configurations, there is an electron in a 5d orbital, which is poorly shielded from the environment; it is very sensitive to the environment. For example, the 5d level for Ce^{3+} doped in different hosts may split up into a wide band as much as 25 000 cm^{-1}, and the central energy of the 5d levels may shift downward by 22 000 cm^{-1}.[1] To design new luminescence materials and explore high excited energy levels in solids, it is of the utmost importance to clarify the relation between the position of the 5d levels and the environment. We have studied the dependence of crystal field splitting of 5d levels on hosts in the halide crystals and found that the 10Dq splitting width can be directly related to the homopolar part of the average energy gap, the coordination number of the central ion, the presented charge of neighboring anions, and the fractional ionicity of the chemical bond between the central ion and the nearest anions.[2]

The phenomenon that the barycenter position of the energy of lanthanide 5d levels shifts downward in hosts has for a long time been noted and attributed to the nephelauxetic effect,[3] which is related to the reduction of the repulsion between the electrons. Over the past semicentury, scientists have built several models to discuss the nephelauxetic effect from various viewpoints. Jorgensen[3] suggested the nephelauxetic effect might be caused by the covalency, which included the central-field covalency and the symmetry-restricted covalency. The work by Sugano and Shelane[4] showed similar results that the levels of Ni^{2+} in $KMgF_3$ are much influenced by these covalency effects. Other scientists[5,6] point out that the energy shift is related to the polarizability of the ligand. In 1980, Marrison[6] built a polarizable model and suggested that the central energy shift of the 4f^{N−1}5d configurations is in direct proportion to the summation of ligand polarizabilities over all nearest coordinating

anion ligands. All of these studies help to reveal the origin of the central energy shift, but a quantitative explanation of the central energy shift is still lacking.

Recently, Dorenbos[1] used the ligand polarizable model to analyze the Ce^{3+} central energy shift. He defined a parameter named spectroscopic polarizability and set up a relation between the energy shift of the 5d configuration with the spectroscopic polarizability and the average cation electronegativity for Ce^{3+} in oxides and fluorides, respectively. His work gave a clear clue that the polarizability plays an important role in the central energy shift.

In this paper, according to the experimental data and dielectric chemical bond theory,[7,8] the major factors of the environment influencing the center energy level shift are given to be the chemical bond volume polarizability, fractional covalence of the chemical bond, and presented charge of the nearest anion in the chemical bonds. The empirical expression between the barycenter position of the energy level of the 4f^{N−1}5d configuration and the major factors of the environment is obtained.

2. Theoretical Background

To calculate the three parameters mentioned above, the dielectric chemical bond theory of complex crystals is used. The detailed theory can be found in refs 7 and 8.

According to the theory, when the crystal structure is known, the "crystal formula" of complex crystals can be written as a linear combination of the subformulas of various binary crystals. The subformula of any type of chemical bond A−B in the multibond crystal $A_aB_bD_dG_g...$ can be expressed by the following formula:

$$\frac{N(B-A)a}{N_{CA}}A\frac{N(A-B)b}{N_{CB}}B \tag{1}$$

where A, B, D, G... represent the different constituent elements or different sites of the same element in the crystal formula, and *a*, *b*, *c*, *d*... represent the numbers of the corresponding element. $N(B-A)$ is the number of B ions in the coordination group of an A ion, and N_{CA} represents the nearest coordination number of the A ion. This means that the complex crystal is

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decomposed into the sum of different binary crystals like A_mB_n. Then, the presented charge Q of each ion can be obtained according to the neutral principle of the binary crystals. For any binary crystal A_mB_n, Q_A is the normal valence of the cation A, and Q_B is obtained from $Q_B = mQ_A/n$. For example, given a complex example like YPO_4, we can obtain $YPO_4 = YO_{8/3} + PO_{4/3}$ in terms of eq 1. For $YO_{8/3}$, let $Q_Y = 3.0$; then the presented charge of the O ion is $Q_O = 3/8 \times 3 = 1.125$ in the Y–O chemical bond. For $PO_{4/3}$, let $Q_P = 5.0$; the presented charge of the O ion is $Q_O = 3/4 \times 5.0 = 3.75$ in the P–O chemical bond. From that, we can find that the presented charges in various chemical bonds are different.

In this theory, the macroscopic linear susceptibility can be obtained by the following equation:

$$\chi = (\epsilon - 1)/4\pi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu \qquad (2)$$

where ϵ is the crystal dielectric constant, which can be obtained from the index of refraction, n ($\epsilon = n^2$). χ^μ is the total macroscopic susceptibility of bond type μ. F^μ is the fraction of bonds of type μ composing the actual complex crystal. χ_b^μ is the susceptibility of a single bond of type μ, and N_b^μ is the number of bonds per cubic centimeter. χ_b^μ can be written as

$$\chi^\mu = \frac{1}{4\pi}\left[\frac{\hbar\Omega_p^\mu}{E_g^\mu}\right]^2 \qquad (3)$$

where E_g^μ is the average energy band gap for the type μ bond, and Ω_p^μ is the plasma frequency obtained from the number of valence electrons of type μ per cubic centimeter N_e^μ, using

$$(\hbar\Omega_p^\mu)^2 = (4\pi N_e^\mu e^2/m)D^\mu A^\mu \qquad (4)$$

$$D^\mu(A,B) = \Delta_A^\mu \Delta_B^\mu - (\delta_A^\mu \delta_B^\mu - 1)[(Z_A^\mu)^* - (Z_B^\mu)^*]^2 \qquad (5)$$

$$A^\mu = 1 - (E_g^\mu/4E_F^\mu) + 1/3(E_g^\mu/4E_F^\mu)^2 \qquad (6)$$

Δ and δ are the periodic dependent constants tabulated in ref 9. $(Z_A^\mu)^*$ and $(Z_B^\mu)^*$ are the number of effective valence electrons on the A and B atoms of the μ bond. Taking YPO_4 as an example, we know the presented charges of the O ion are -1.125 in the Y–O chemical bond and -3.75 in the P–O chemical bond, respectively. The charges of the effective valence electron are $-1.125/2 = -0.5625$ and $-3.75/2 = -1.875$, respectively. For O atomic, there are six valence electrons; then, for the Y–O chemical bond, $(Z_Y^\mu)^* = 3$ and $(Z_O^\mu)^* = 0.5625 \times 6 = 3.375$, and for the P–O chemical bond $(Z_P^\mu)^* = 5$ and $(Z_O^\mu)^* = 1.875 \times 6 = 11.25$.

The average energy gap E_g^μ appearing in eq 3 for every type μ of bond can be separated into homopolar energy E_h^μ and heteropolar energy C^μ parts as follows:

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \qquad (7)$$

The fractional ionicity f_i^μ and covalence f_c^μ of any type of μ bond are defined as

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \qquad f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2} \qquad (8)$$

where

$$E_h^\mu = \frac{39.74}{(d^\mu)^{2.48}} \text{ (eV)} \qquad (9)$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu)\left[\left[\frac{(Z_A^\mu)^*}{r_0^\mu} - (n/m)\frac{(Z_B^\mu)^*}{r_0^\mu}\right]\right] \text{ (eV)}$$
$$\text{(if } n > m) \quad (10)$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu)\left[\left[(m/n)\frac{(Z_A^\mu)^*}{r_0^\mu} - \frac{(Z_B^\mu)^*}{r_0^\mu}\right]\right] \text{ (eV)}$$
$$\text{(if } m > n) \quad (10')$$

where

$$E_F^\mu = (h\kappa_F^\mu)^2/(2m)$$

$$\kappa_s^\mu = (4\kappa_F^\mu/\pi a_B)^{1/2}$$

$$\kappa_F^\mu = [3\pi^2(N_e^\mu)^*]^{1/3}$$

$$r_0^\mu = d^\mu/2 \qquad (11)$$

a_B is the Bohr radius, and $\exp(-k_s^\mu r_0^\mu)$ is the Thomas–Fermi screening factor; b^μ is a correction factor and is proportional to the square of the average coordination number N_C^μ.

$$b^\mu = \beta(N_C^\mu)^2$$

$$N_C^\mu = \frac{m}{m+n}N_{CA}^\mu + \frac{n}{m+n}N_{CB}^\mu \qquad (12)$$

N_{CA}^μ and N_{CB}^μ are the coordination number of atoms A and B composing the bond μ, respectively; if the refractive index of a crystal is known, the value of β can be deduced by eqs 2–12. $(N_e^\mu)^*$ is the number of effective valence electrons of the μ bond per cubic centimeter:

$$(N_e^\mu)^* = (n_e^\mu)^*/v_b^\mu \qquad (13)$$

The number of effective valence electrons $(n_e^\mu)^*$ per μ bond is

$$(n_e^\mu)^* = (Z_A^\mu)^*/N_{CA}^\mu + (Z_B^\mu)^*/N_{CB}^\mu \qquad (14)$$

The bond volume v_b^μ of the chemical bond of μ type is

$$v_b^\mu = (d^\mu)^3/\sum_v (d^\mu)^3 N_b^v \qquad (15)$$

where d^μ is the chemical bond length, and N_b^v is the number of chemical bonds of μ type per cubic centimeter, which can be obtained from the crystal structural data.

According to the Lorentz formula,

$$\frac{(\epsilon^\mu - 1)}{(\epsilon^\mu + 2)} = \frac{4}{3}\pi\alpha_0^\mu \qquad (16)$$

the polarizability coefficient α_0^μ of the μ bond in Å^3 can be obtained. The polarizability of the bond volume of the chemical bond of μ type can be written

$$\alpha_b^\mu = v_b^\mu \alpha_0^\mu \qquad (17)$$

If the crystal structure and the refractive index are known, the bond volume polarizability $\alpha(i)$, the fractional covalence

Barycenter of Energy of Lanthanide 4f^{N-1}5d Configuration

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TABLE 1: Central Energy of the 4f^{6}5d Configuration and Parameters Related to the Central Energy Calculations in Eu^{2+}-Doped Crystals

crystals	ϵ	site[a]	N	f_C	α	Q	h_e	E_{Cexp}[b]	E_{Ccal}[j]
NaF	1.7	Na$^+$	6	0.054	0.186	1	0.245	38.01	37.67
KF	1.8	K$^+$	6	0.046	0.320	1	0.297	36.76	36.72
NaCl	2.3	Na$^+$	6	0.064	0.536	1	0.454	33.96	34.34
KCl	2.2	K$^+$	6	0.049	0.708	1	0.456	33.95	34.31
RbCl	2.2	Rb$^+$	6	0.044	0.810	1	0.462	33.99	34.23
NaBr	2.6	Na$^+$	6	0.067	0.737	1	0.544	33.11	33.25
KBr	2.3	K$^+$	6	0.047	0.864	1	0.494	33.44	33.83
RbBr	2.4	Rb$^+$	6	0.045	1.020	1	0.525	33.52	33.46
NaI	3.0	Na$^+$	6	0.071	1.079	1	0.678	31.95	31.93
KI	2.7	K$^+$	6	0.052	1.270	1	0.629	32.46	32.37
RbI	2.7	Rb$^+$	6	0.046	1.425	1	0.627	32.44	32.39
CaF$_2$	2.03	Ca^{2+}	8	0.032	0.317	1	0.285	37.79	36.93
SrF$_2$	2.05	Sr^{2+}	8	0.029	0.385	1	0.299	37.34	36.68
BaF$_2$	2.15	Ba^{2+}	8	0.026	0.500	1	0.322	36.45	36.29
KMgF$_3$	2.04	K$^+$	12	0.022	0.093	0.5	0.079	41.00[c]	41.38
RbMgF$_3$	2.23[k]	Rb$^+$	12	0.021	0.094	0.5	0.077	40.80[c]	41.43
MgS	5.1	Mg^{2+}	6	0.211	0.809	2	2.02	28.30[d,e]	27.55
CaS	4.5	Ca^{2+}	6	0.093	0.986	2	1.48	27.75[e]	28.25
CaSe	5.1	Ca^{2+}	6	0.095	1.198	2	1.65	28.60[e]	27.95
CaO	3.3	Ca^{2+}	6	0.084	0.490	2	0.994	29.20[f]	29.83
EuF$_2$	2.10	Eu^{2+}	8	0.025	0.390	1	0.279	37.42[g]	37.04
EuO	4.60	Eu^{2+}	6	0.077	0.738	2	1.17	28.55[g,h]	29.09
CsI	3.20	Cs$^+$	8	0.040	1.201	1	0.620	32.68[i]	32.46
SrCl$_2$	2.72	Sr^{2+}	8	0.031	0.924	1	0.480	34.25	34.00
EuSe	4.7	Eu^{2+}	6	0.051	1.304	2	1.263	28.47[g,h]	28.79

[a] Sites occupied by Eu^{2+}. *[b]* Reference 17 unless specified. *[c]* Reference 18. *[d]* Reference 19. *[e]* Reference 20. *[f]* Reference 21. *[g]* Reference 22. *[h]* Reference 23. *[i]* Reference 24. *[j]* This work. *[k]* The dielectric constant of RbMgF$_3$ is estimated in terms of KMgF$_3$ (2.04), KMnF$_3$ (2.10), KCoF$_3$ (2.25), KNiF$_3$ (2.30), and KZnF$_3$ (2.34) crystals. A 1% error of the dielectric constant leads to 0.004 error of h_e.

$f_C(i)$ of the chemical bond between the central ion and the nearest anion numbered i, and the presented charge $Q(i)$ of the nearest anions can be calculated by the method mentioned above. In the current work, we used the average value of $\alpha(i)$ and $f_C(i)$ over all the chemical bonds and found a new factor h_e, which is written as follows:

$$h_e = (Nf_C\alpha Q^2)^{1/2} \qquad (18)$$

where N is the number of ligands, f_C is the average fractional covalence, and α is the average bond volume polarizability; h_e is named the environmental factor, which may characterize the change of the central energy of 4f^{N-1}5d configurations of rare earths. To determine the correlation between the central energy of 4f^{N-1}5d configurations and the environmental factor h_e, we calculated h_e environmental factors of 25 kinds of crystal doped with Eu^{2+} and 22 kinds of crystal doped with Ce^{3+} and discussed the relation between the central energy of 4f^{N-1}5d configurations and h_e environmental factors.

3. Result and Discussion

All parameters of various crystals are listed in Tables 1 and 2. These crystal structures have been reported.[10−14] The second column shows the values of the dielectric constant ϵ.[9,15,16] The sites occupied by Ce^{3+} or Eu^{2+} in the crystals are shown in the third column. The experimental values of the central energy of Ce^{3+} are determined by the crystal field energy levels of 5d states. For the Eu^{2+} ion, the cubic splitting leads to two bands: a 3-fold degenerate and a 2-fold degenerate (for 6-fold octahedral coordination, a low lying band is the 3-fold degenerate 5d state, and the upper is the 2-fold degenerate 5d state; in 8-fold cubic the situation is reversed). Taking the NaF:Eu^{2+} crystal as an example, Eu^{2+} is coordinated by six fluoride ions

TABLE 2: Central Energy of the 5d Configuration and Parameters Related to the Central Energy Calculations in Ce^{3+}-Doped Crystals

crystals	ϵ	site[a]	N	f_C	α	Q	h_e	E_{Cexp}[b]	E_{Ccal}[k]
KMgF$_3$	2.04	K$^+$	12	0.022	0.093	0.5	0.079	46.90	48.49
CeF$_3$	2.59	Ce^{3+}	11	0.020	0.377	1	0.286	45.75	43.88
LaF$_3$	2.56	La^{3+}	11	0.019	0.381	1	0.283	46.02	43.94
YF$_3$	2.43	Y^{3+}	9	0.029	0.404	1	0.323	45.60	43.12
LuF$_3$	2.43	Lu^{3+}	9	0.030	0.396	1	0.325	45.60	43.08
LiYF$_4$	2.11	Y^{3+}	8	0.011	0.176	1.125	0.139	45.89[b,c]	47.08
LiLuF$_4$	2.12[l]	Lu^{3+}	8	0.011	0.159	1.125	0.132	45.62	47.25
CaSO$_4$	2.52	Ca^{2+}	8	0.071	0.424	0.75	0.368	42.60[d]	42.22
SrSO$_4$	2.64	Sr^{2+}	12	0.044	0.401	0.667	0.306	43.30[d]	43.46
BaSO$_4$	2.64	Ba^{2+}	12	0.030	0.342	0.667	0.233	43.40[d]	45.00
CaF$_2$	2.03	Ca^{2+}	8	0.032	0.317	1	0.285	45.35	43.90
SrF$_2$	2.05	Sr^{2+}	8	0.029	0.385	1	0.299	43.97	43.61
BaF$_2$	2.15	Ba^{2+}	8	0.026	0.500	1	0.322	44.77	43.14
YAlO$_3$	3.71	Y^{3+}	9	0.038	0.402	1.667	0.615	38.26[e]	37.73
Y$_3$Al$_5$O$_{12}$	3.35	Y^{3+}	8	0.036	0.395	1.5	0.508	36.42[f]	39.58
LaCl$_3$	3.24	La^{3+}	9	0.028	1.201	1	0.547	38.25[g]	38.89
CaS	4.5	Ca^{2+}	6	0.093	0.986	2	1.48	27.80[h]	26.72
CaCl$_2$	2.31	Ca^{2+}	6	0.039	1.019	1	0.490	37.79[i]	39.91
BaCl$_2$	3.02	Ba^{2+}	8	0.031	1.187	1	0.540	38.32[i]	39.02
SrCl$_2$	2.72	Sr^{2+}	8	0.028	0.924	1	0.457	39.68[i]	40.51
YPO$_4$	2.99	Y^{3+}	8	0.049	0.419	1.125	0.454	41.36	40.57
CaO	3.3	Ca^{2+}	6	0.084	0.490	2	0.994	30.73[j]	32.13

[a] Sites occupied by Ce^{3+}. *[b]* Reference 25 unless specified. *[c]* Reference 26. *[d]* Reference 27. *[e]* Reference 28. *[f]* Reference 29. *[g]* Reference 30. *[h]* Reference 31. *[i]* Reference 32. *[j]* Reference 33. *[k]* This work. *[l]* The dielectric constant of LiLuF$_4$ is estimated in terms of LiYF$_4$ (2.11). A 1% error of the dielectric constant leads to 0.01 error of h_e.
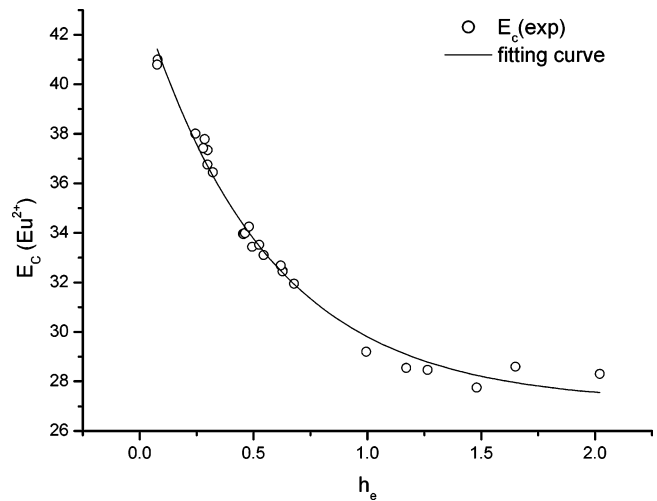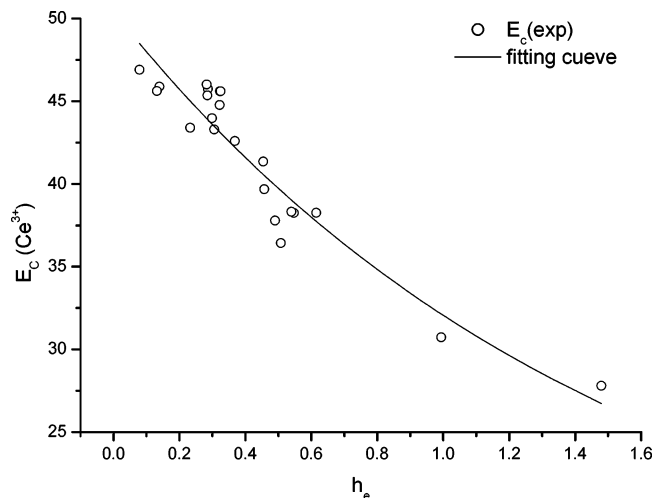

Figure 1. Central energy of the 4f^{6}5d configuration E_C as a function of the environmental factor h_e. The solid line is from eq 19.

and there are two bands at 30 675 and 49 020 cm^{-1}. So, its central energy is $(30675 \times 3 + 49020 \times 2)/5 = 38.01$ K cm^{-1}. All spectral experimental values of the central energy are shown in the ninth column.

Figure 1 shows the relation between the central energy E_C of the 4f^{6}5d configuration and the environmental factor h_e for the cubic crystals doped with Eu^{2+} from Table 1. The trend of the central energy of the 4f^{6}5d configuration in fluorides, chlorides, bromides, iodides, oxides, sulfides, and selenides can be fitted by the following exponential equation:

$$E_C = A + Be^{-kh_e} \qquad (19)$$

where $A = 27.13$, $B = 16.45$, and $k = 1.817$. It is seen that the values of the central energy E_C decrease with the increase of h_e. The data in Table 1 show that the values of E_C calculated

Figure 2. Central energy of the 5d configuration E_C as a function of the environmental factor h_e. The solid line is from eq 20.

Figure 3. Schematic energy diagram showing the energy levels of the 4f⁶5d configuration for Eu^{2+}.

by eq 19 are in good agreement with the experimental values;[17-24] the maximum error between the experimental and calculated values in CaF_2 is 0.86 K cm⁻¹. Equation 19 displays good predictive power.

Jorgensen[3] studied the central energy trend of d group compounds in the same structure and found the central energy tends to reduce as a function of the nearest-neighbor anions:

$$F^- > Cl^- > Br^- > I^- > O^{2-} > S^{2-}$$
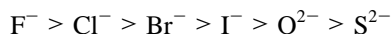
which is well-known as the nephelauxetic series. The series can be also shown by h_e. For example, the h_e values of NaF, NaCl, NaBr, NaI, CaO, and CaS increase by 0.245, 0.454, 0.544, 0.678, 0.994, and 1.48, and the position of the corresponding energy central decreases by 38.01, 33.96, 33.11, 31.95, 29.20, and 27.75 K cm⁻¹.

The environmental factor h_e not only can explain the center energy position of the 4f⁶5d configuration of rare earth ions in the nephelauxetic series but also can define subtly the trend of the center energy levels of various crystals with the same kind of anion element. For example, in fluorides, all nearest anions to Eu^{2+} are fluorions. According to the increase of the environmental factors h_e, we can obtain an order: $KMgF_3$ < $RbMgF_3$ < NaF < KF < CaF_2 < SrF_2 < BaF_2. Obviously it displays a more detailed order.

The trend between the 5d central energy of the Ce^{3+} ion[25-33] and h_e in different crystals is shown in Figure 2. It is seen that there is the same regulation with the Eu^{2+} ion. The trend between the central energy E_C and h_e for the Ce^{3+} ion is fitted with eq 20:
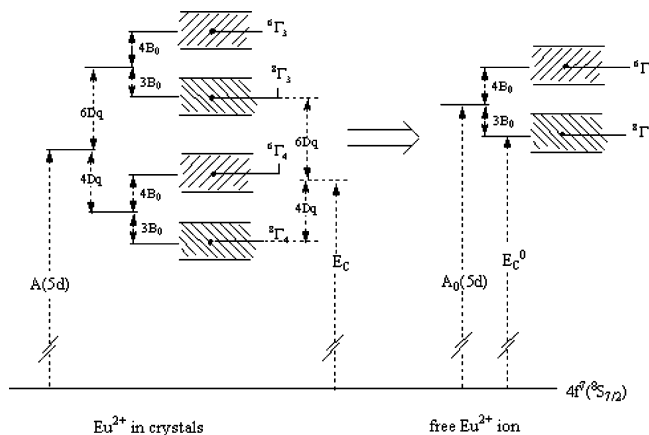
$$E_C = A + Be^{-kh_e} \qquad (20)$$

where $A = 12.49$, $B = 37.93$, and $k = 0.662$. The central energy position E_C also is the highest in the $KMgF_3$ crystal and the lowest in the CaS crystal with the Eu^{2+} ion.

For a free rare earth ion, its electron cloud is not affected by any outside factor, $f_C = 0$, and $\alpha = 0$. The central energy of Eu^{2+} and Ce^{3+} in the free state can be obtained from eqs 19 and 20:

$$E_C^0(Eu^{2+}) = 27.13 + 16.45 = 43.58 \text{ K cm}^{-1} \qquad (21)$$

$$E_C^0(Ce^{3+}) = 12.49 + 37.93 = 50.42 \text{ K cm}^{-1} \qquad (22)$$

Asano[19] has given a "real" barycenter of energy of the 4f⁶5d configuration: $A_0(5d) = 46.34$ K cm⁻¹ for a free Eu^{2+} ion. According to the work by Sugar and Spector,[34] the sketch map of the energy level is shown in Figure 3. Where $^6\Gamma_3$ and $^6\Gamma_4$ are the low spin energy levels, the transition from the $^8S_{7/2}$ state to the $^6\Gamma$ state is spin forbidden; $^8\Gamma_3$ and $^8\Gamma_4$ are high spin energy levels, and the transition from the $^8S_{7/2}$ state to the $^8\Gamma$ state is spin allowed, which are two broad bands observed in the spectra of the Eu^{2+}-doped cubic crystals. The barycenter of energy must be the barycenter position between the $^8\Gamma_3$ and $^8\Gamma_4$ energy levels. So the experimental value of the barycenter for a free Eu^{2+} ion must be $E_C^0(Eu^{2+}) = A_0(5d) - 3B_0 = 46.34 - 3.79 = 42.55$ K cm⁻¹.[19] For a free Ce^{3+} ion, the experimental value of the 5d level is 51.23 K cm⁻¹.[35] Our calculated results are in very good agreement with that.

In conclusion, for any crystal, if the structure and refractive index are known, the barycenter energy of the 4f^{n-1}5d configurations in the crystal can be calculated by our method. Three microcosmic factors should be met to confirm the barycenter energy of 4f^{n-1}5d configurations: they are the chemical bond volume polarizability, the fractional covalency of the chemical bond between the central ion and the nearest anion, and the charge presented by the nearest anion. Our method has built up a link between the barycenter energy and environment of crystals and could provide important information in the design of new luminescence materials and revealment of the high excited energy levels of Eu^{2+} and Ce^{3+} in solids. Hopefully, these relations may be extended to other rare earth ions if the spectral data are enough.

References and Notes

(1) Dorenbos, P. *Phys. Rev. B* **2002**, *65*, 235110.
(2) Shi, J. S.; Wu, Z. J.; Zhou, S. H.; Zhang, S. Y. *Chem. Phys. Lett.* **2003**, *38*, 245.
(3) Jorgenson, C. K. *Prog. Inorg. Chem.* **1962**, *4*, 73.
(4) Sugano, S.; Shulman, R. G. *Phys. Rev.* **1963**, *130*, 517.
(5) Newman, D. J. J. *Aust. Phys.* **1977**, *30*, 315.
(6) Morrison, C. A. *J. Chem. Phys.* **1980**, *72*, 1001.
(7) Zhang, S. Y.; Gao, F. M.; Wu, C. X. *J. Alloys Compd.* **1998**, *275–277*, 835.
(8) Wu, Z. J.; Zhang, S. Y. *J. Phys. Chem. A* **1999**, *103*, 4270.
(9) Levine, B. F. *Phys. Rev. B* **1973**, *7*, 2591.
(10) Wyckoff, R. W. G. *Crystal Structure*; Interscience: New York, 1964; Vols. 1 and 2.
(11) Morrison, C. A.; Leavitt, R. P. *Handbook on the Physics and Chemistry of Rare Earths*; North-Holland: New York, 1982; Vol. 46, p 461.
(12) Hawthorne, F. C.; Ferguson, R. B. *Can. Mineral.* **1975**, *13*, 289.
(13) Hawthorne, F. C.; Ferguson, R. B. *Can. Mineral.* **1975**, *13*, 181.
(14) Hill, R. J. *Can. Mineral* **1977**, *15*, 522.

(15) *Handbook of Chemistry and Physics*, 69th ed.; Weast, R. C., Astel, M. J., Beyer, W. H., Eds.; CRC Press: Boca Raton, FL, 1989; p **B**-68.

(16) Thoma, R. E.; Insley, H.; Hebert, G. M. *Inorg. Chem.* **1966**, *5*, 1222.

(17) Rubio, O. J. *J. Phys. Chem. Solids* **1991**, *52*, 101.

(18) Alcala, A.; Sardar, D. K.; Sibley, W. A. *J. Lumin.* **1982**, *27*, 273.

(19) Asano, S.; Nakao, Y. *J. Phys. C*: *Solid State Phys.* **1979**, *12*, 4095.

(20) Nakao, Y. *J. Phys. Soc. Jpn*. **1980**, *48*, 534.

(21) Yamashita, N. *J. Electrochem. Soc.* **1993**, *140*, 840.

(22) Freiser, M. J.; Methfessel, S.; Holtzberg, F. *J. Appl. Phys.* **1968**, *39*, 900.

(23) Wachter, P. *Handbook on the Physics and Chemistry of Rare Earths*; North-Holland: New York, 1979; Vol. 19, p 507.

(24) Seo, H. J.; Zhang, W. S.; Tsuboi, T.; Doh, S. H.; Lee, W. G.; Kang, H. D.; Jang, K. W. *J. Alloys Compd.* **2002**, *344*, 268.

(25) Dorenbos, P. *Phys. Rev. B* **2000**, *62*, 15640.

(26) Van Pieterson, L.; Reid, M. F.; Burdick, G. W.; Meijerink, A. *Phys. Rev B* **2002**, *65*, 045113.

(27) van der Kolk, E.; Dorenbos, P.; Vink, A. P.; Perego, R. C.; van Eijk, C. W. E. *Phys. Rev. B* **2001**, *64*, 195129.

(28) Weber, M. J. *J. Appl. Phys.* **1973**, *44*, 3205.

(29) Tomiki, T.; Kohatsu, T.; Shimabukuro, H.; Ganaha, Y. *J. Phys. Soc. Jpn.* **1992**, *61*, 2382.

(30) Andriessen, J.; Antonyak, O. T.; Dorenbos, P.; Rodnyi, P. A.; Stryganyuk, G. B.; van Eijk, C. W. E.; Voloshinovskii, A. S. *Opt. Commun.* **2000**, *178*, 355.

(31) Jia, D.; Meltzer, R. S.; Yen, W. M. *J. Lumin.* **2002**, *99*, 1.

(32) Li, W. M.; Leskela, M. *Mater. Lett.* **1996**, *28*, 491.

(33) Lehmann, W. *J. Lumin.* **1973**, *6*, 455.

(34) Sugar, J.; Spector, N. *J. Opt. Soc. Am.* **1974**, *64*, 1484.

(35) Lang, R. J. *Can. J. Res.* **1936**, *14*, 127.