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Nephelauxetic effects in europium-doped LnOX (Ln = La, Gd, or Y; X = F, Cl, or Br) crystals: high-pressure effects

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Abstract. The free-ion parameters for Eu^{3+} in LaOF, LaOBr, GdOCl, and YOCl crystals and in LaOCl crystals at high pressure (up to 13 GPa) are calculated and fitted to the experimental 'free-ion' energy levels. The Slater parameters F_k and the spin-orbit coupling parameter ζ decrease with increasing pressure and with decreasing Eu^{3+} -ligand distances along the two host series LaOCl–GdOCl–YOCl and LaOBr–LaOCl–LaOF. The shift of the free-ion parameters along the latter series exhibits an 'anti-nephelauxetic series' and therefore has a positive correlation with the overlap integrals. On the basis of the free-ion calculations and the calculations of the overlap integrals between Eu^{3+} and the ligands, a combined cloud-expanding model is proposed to explain the behaviour of the free-ion parameters.

1. Introduction

The reduction of the free-ion parameters (Slater parameters F_k , spin-orbit coupling parameter ζ , and configuration interaction parameters α , β , and γ) in crystals has been studied for twenty years [1–5]. The reduction has been ascribed to several kinds of contribution [4–6]. The two most reasonable mechanisms that have been proposed are the covalency model [4, 6] and the dielectric-screening model [7]. According to the covalency model (also called the nephelauxetic model), the decrease of free-ion parameters is a result of the open-shell electron-cloud expansion that happens once a metal ion is incorporated in a complex. In this model, in fact, there are two types of covalency effect (expansion). The first one is called central-field covalency and is caused by the screening of the effective nuclear charge Z_{ef} due to the penetration of electron clouds of the ligands into the metal ions. The second one is called symmetry-restricted covalency and is ascribed to the admixture of the electron states of the ligands into the states of the open shells [2, 3]. In some respects (see below), the covalency model agrees well with the experimental results [3, 8, 9], but a few years ago, an *ab initio* calculation [6] showed that the covalency effect is too small to account for the observed shifts in the Slater parameters, and some researchers [4] pointed out that some conclusions of the covalency model (see section 4) are in contradiction to the experimental results.

Another mechanism, the dielectric-screening model [10], ascribed the reduction of the free-ion parameters to the screening of the Coulomb interaction in the metal ions because the surrounding crystal is a dielectric medium. A macroscopic version of this model [10] agreed reasonably well with experimental results [4] while a microscopic one [11] had trouble in

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explaining an experimental result [4]. Moreover, recently, the contribution of the dielectric screening to the reduction of Slater parameters was found to be negligible [12, 13].

Up to this stage, all the possible contributions that were believed to be important to the reduction of free-ion parameters have been ruled out by past research work. Under this circumstance, it is useful to collect additional experimental results and re-study all the possible mechanisms that could explain the variations of the free-ion parameters in crystals. Recently, high pressure was proved to be an essential and powerful condition for studying the reduction of the free-ion parameters in crystals [4, 5]. By applying hydrostatic pressure to the samples, we can obtain a continuous change in the interatomic distances, which makes it possible to study in more detail the relation between the variation of the phenomenological parameters and that of the interaction between the metal ion and the ligand.

This paper is devoted to the study of the covalency effect in the reduction of F_k and ζ for Eu^{3+} in several crystals. To this end, the free-ion parameters are fitted for $\text{Eu}^{3+}:\text{LnOX}$ systems (where $\text{Ln} = \text{La}, \text{Gd}, \text{or } \text{Y}$ and $\text{X} = \text{F}, \text{Cl}, \text{or } \text{Br}$) and for $\text{Eu}^{3+}:\text{LaOCl}$ at high pressure (up to 13 GPa) in order to describe the experimental data given by Wang *et al* [14], by Chi *et al* [15, 16] and by Hölsä and Porcher [17]. The overlap integrals between the f orbitals of Eu^{3+} and the s and p orbitals of the ligand anions (F^- , Cl^- , Br^- and O^{2-}) were calculated in order to investigate the relationship between the shift in the free-ion parameters and the variation of the overlap integrals due to different interatomic distances and pressures. The separate contributions of the two kinds of cloud-expanding mechanism are combined to avoid the weak points of each model.

2. Free-ion calculations for Eu^{3+}

The phenomenological free-ion Hamiltonian can be expressed in terms of the parameters F_2 , F_4 , F_6 , ζ , α , β , and γ [18]. However, in the present case, the number of experimental effective 'free-ion' energy levels is too small to freely vary all the phenomenological parameters in the simulations. So, in the study reported here, α , β , and γ were set to zero [4], and F_4/F_6 was fixed to their hydrogenic ratio [19]. The matrix of the free-ion Hamiltonian expressed in terms of F_2 , F_4 , and ζ was diagonalized and the eigenvalues were fitted to the observed ${}^7\text{F}_{0-4}$ and ${}^5\text{D}_{0-2}$ multiplet centroids (listed in tables 1 and 2) by an optimization program. The observed multiplet centroids of Eu^{3+} in LaOBr and in LnOCl ($\text{Ln} = \text{La}, \text{Gd}, \text{or } \text{Y}$) (table 1) and the pressure shift in the observed multiplet centroids for Eu^{3+} in LaOCl (table 2) were deduced from the experimental data in [15], [16] and [17], respectively. The multiplet centroids of Eu^{3+} in LaOF were deduced from the experimental crystal-field energy levels that will be published in a forthcoming paper [14].

The best-fit value of F_2 , F_4 , and ζ for Eu^{3+} in LaOCl at different pressures and for Eu^{3+} in GdOCl , YOCl , LaOBr , and LaOF at ambient pressure are plotted against pressure and against the Eu–ligand distance in figures 1 and 2, respectively. The RMS deviation σ ($\sigma = \{[1/(N - N_p)] \sum_{i=1}^N (E_{\text{cal}}^i - E_{\text{obs}}^i)^2\}^{1/2}$, where $N_p = 3$ is the number of free parameters in the fitting) of the fits is about 65 cm^{-1} and increases a little with increasing pressure and with decreasing interatomic distance. The small change in σ ($\pm 3 \text{ cm}^{-1}$) with different interatomic distances and with increasing pressure ensures that the shift in F_2 , F_4 , and ζ is tightly related to the shift in the observed multiplet centroids, which is confirmed by a comparison between the observed and calculated energy levels in tables 1 and 2. For example, up to 13 GPa, the shift in calculated ${}^5\text{D}_0$, ${}^5\text{D}_1$, and ${}^5\text{D}_2$ levels is -0.51% , -0.54% , and -0.62% , respectively, which are close to the shifts of -0.54% , -0.51% , and -0.54% of the observed ${}^5\text{D}_0$, ${}^5\text{D}_1$, and ${}^5\text{D}_2$ levels, respectively. Hence the shift in the free-ion

Table 1. Observed and calculated multiplet centroids (in cm^{-1}) for Eu^{3+} in LnOX ($\text{Ln}=\text{La}$, Gd , or Er) crystals at ambient pressure.

	LaOBr [15]		LaOF [13]		LaOCI [16]		GdOCI [17]		YOCI [17]	
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
	${}^7\text{F}_0$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
${}^7\text{F}_1$	389	401	379	397	384	397	379	390	374	390
${}^7\text{F}_2$	1135	1106	1052	1075	1109	1095	1064	1078	1056	1070
${}^7\text{F}_3$	1999	2008	1929	1988	1975	1990	1932	1960	1926	1956
${}^7\text{F}_4$	2981	3031	—	3003	2958	3005	2912	2964	2903	2958
${}^5\text{D}_0$	17310	17395	17259	17357	17279	17386	17217	17344	17203	17330
${}^5\text{D}_1$	19066	18959	18995	18911	19038	18941	18976	18880	18962	18870
${}^5\text{D}_2$	21531	21526	21475	21462	21503	21494	21432	21402	21428	21389

Table 2. Observed and calculated multiplet centroids (in cm^{-1}) for Eu^{3+} in LaOCl crystals at different pressures (after [16]).

	Pressure (GPa)													
	0		2		4		6		8		10		13	
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
${}^7\text{F}_0$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
${}^7\text{F}_1$	384	397	383	396	382	395	381	394	381	393	380	392	378	391
${}^7\text{F}_2$	1109	1095	1102	1092	1097	1090	1092	1087	1088	1085	1077	1082	1068	1078
${}^7\text{F}_3$	1975	1990	1969	1984	1964	1979	1958	1975	1953	1971	1946	1966	1938	1960
${}^7\text{F}_4$	2958	3005	2950	2997	2943	2991	2937	2984	2934	2979	2929	2972	2917	2963
${}^5\text{D}_0$	17279	17386	17264	17373	17249	17361	17234	17347	17220	17334	17205	17321	17185	17298
${}^5\text{D}_1$	19038	18941	19023	18924	19008	18908	18993	18892	18978	18876	18963	18860	18941	18839
${}^5\text{D}_2$	21503	21497	21482	21471	21462	21450	21450	21429	21429	21409	21421	21387	21390	21361

parameters with pressure and with interatomic distance is reliable although the deviation between the calculated and observed energy levels is seemingly too large to describe the shift in free-ion parameters (figures 1 and 2).

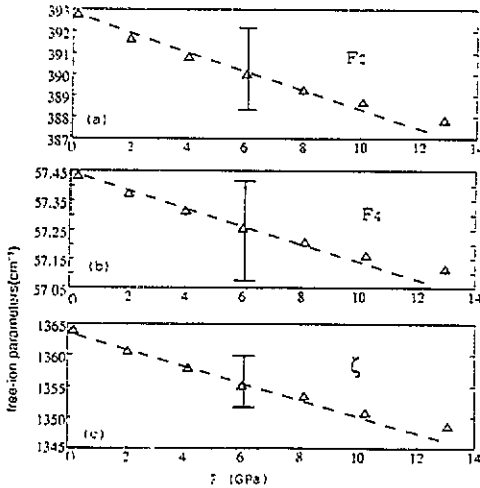


Figure 1. The best-fit F_2 , F_4 , and ζ for Eu^{3+} in LaOCl crystals as a function of pressure. The broken lines are guides for the eye. The error bars are estimated according to the RMS deviation of the fittings.

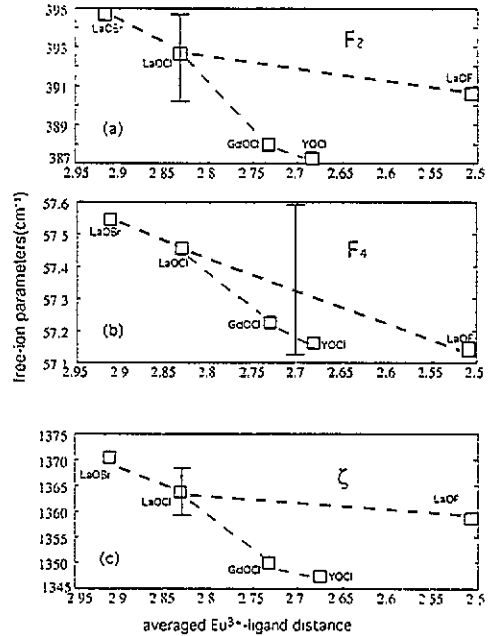


Figure 2. Shift of the best-fit F_2 , F_4 , and ζ versus averaged Eu^{3+} -ligand distance along the LnOCl ($\text{Ln} = \text{La}, \text{Gd}, \text{or Y}$) host series and the LaOX ($\text{X} = \text{Br}, \text{Cl}, \text{or F}$) host series. The broken lines are guides for the eye. The error bars are estimated according to the RMS deviation of the fittings.

As shown in figure 1, in the pressure range below 13 GPa, F_2 , F_4 , and ζ decrease with increasing pressure by 1.26%, 0.64%, and 1.18%, respectively; moreover, the pressure shift in F_2 , F_4 , and ζ exhibits a discrepancy from a linear behaviour and the shift rate diminishes distinctly with increasing pressure. A similar decrease of F_2 , F_4 , and ζ with decreasing Eu^{3+} -ligand distances is observed along the LaOCl - GdOCl - YOCl host series and the LaOBr - LaOCl - LaOF host series, as shown in figure 2. It is noteworthy that the values of the free-ion parameters for $\text{Eu}^{3+}:\text{LaOCl}$ at 10 GPa and 13 GPa approached the values for $\text{Eu}^{3+}:\text{GdOCl}$ and for $\text{Eu}^{3+}:\text{YOCl}$, respectively (compare figures 1 and 2). This fact indicates that, as far as the free-ion energy level is concerned, the pressure effect is equivalent to the effect of decreasing interatomic distance due to different isomorphous hosts, in contrast to the case in which the crystal-field energy level is concerned [5].

It should also be noted that the free-ion parameters of Eu^{3+} decrease from ligand Br^- to ligand F^- along the LaOBr - LaOCl - LaOF host series, in contrast to the observed 'nephelauxetic series' for transition-metal ions [2], according to which the reduction of free-ion parameters in crystals is positively correlated to the size of the ligand halogen anions, i.e., increases from F^- to Br^- (cf section 3). This 'anti-nephelauxetic series' of ligands for

Eu^{3+} is also clearly demonstrated by the decrease of all the observed free-ion energy levels (multiplet centroids) for Eu^{3+} along the LaOBr-LaOCl-LaOF host series (see table 1).

We have noted that there is no regularity in the variation of E_0 , E_1 , E_2 , E_3 , and ζ for Eu^{3+} , given by Hölsä and Porcher [17, 20], along the host series YOX-GdOX-LaOX ($\text{X}=\text{Cl}$ or Br), although the deviation in their calculations was smaller than that in the present work. In fact, Racah parameters E_k are equivalent to Slater parameters F_k , so there is no essential difference between the fitting procedures in [17] and those in the present work. The irregularity in the variation of E_k and ζ mentioned above, in our opinion, occurs because the number of free parameters (four in the present case) of electrostatic interaction exceeds the number of experimental manifolds ^5D , ^5G , and ^5L that were used to determine E_k , although the total number of free parameters (five in the present case) is less than the number of experimental free-ion energy levels [17]. A similar case occurred in the work carried out by Sovers and Yoshioka [21].

3. Relationship between the shift in the free-ion parameters and the shift in the overlap integrals

In order to study the relationship between the shift in F_2 , F_4 , and ζ and the shift in the overlap integrals with different interatomic distances, the overlap integrals between the f orbitals in Eu^{3+} and the s and p orbitals in ligand ions F^- , Cl^- , Br^- , and O^{2-} have been calculated according to a generalization [22] of Lofthus' method. The ion wavefunctions employed are those in [22] and [23]. The Eu^{3+} -ligand distances were taken from the literature [24–27]. In LnOX ($\text{Ln} = \text{La, Gd, or Y}$; $\text{X}=\text{Br}$ or Cl , space group P_4/nmm), the Eu^{3+} is coordinated to four O^{2-} and five halogen ions with C_{4v} site symmetry [24–26]. In LaOF (space group $R\bar{3}m$, rhombohedral structure), the Eu^{3+} is coordinated to four O^{2-} and four F^- ions with C_{3v} site symmetry [27]. The Eu^{3+} -ligand distances in these crystals are listed in table 3.

Table 3. The interatomic distances d (Å) between the rare-earth ions and the ligands in the crystals studied and the averaged value \bar{d} . X represents F, Cl, or Br, and X' represents Cl or Br on the fourfold symmetry axis.

d (Å)	LaOBr [24]	LaOF [27]	LaOCl [24]	GdOCl [26]	YOCl [25]
Ln-4O	2.40	2.58	2.40	2.28	2.28
Ln-4X	3.28	2.42	3.18	3.10	3.00
Ln-X'	3.47	—	3.14	3.04	3.04
\bar{d}	2.91	2.50	2.83	2.73	2.68

A local distortion probably exists, of course, around the Eu^{3+} ions in the crystals and the interionic distances may be different from the values given in table 3. However, the crystal-field calculations with C_{4v} and C_{3v} site symmetry for Eu^{3+} in LnOX ($\text{Ln} = \text{La, Gd, or Y}$; $\text{X} = \text{Cl}$ or Br) [16, 17] and in LaOF [14], respectively, have successfully reproduced the observed crystal-field splittings, so it would be reasonable to think that the local distortion does not change the coordination environment of Eu^{3+} significantly. It would be, in our opinion, a good approximation to neglect the local distortion and to use the values given by the x-ray works [24–27], listed in table 3, for the following discussions.

In figure 3(a) is shown the overlap integral (sum of the $\langle f|s\rangle$, $\langle f|p\sigma\rangle$ and $\langle f|p\pi\rangle$ overlap integral) for each kind of Eu^{3+} -ligand pair. Figure 3(b) and (c) shows the evolution of the

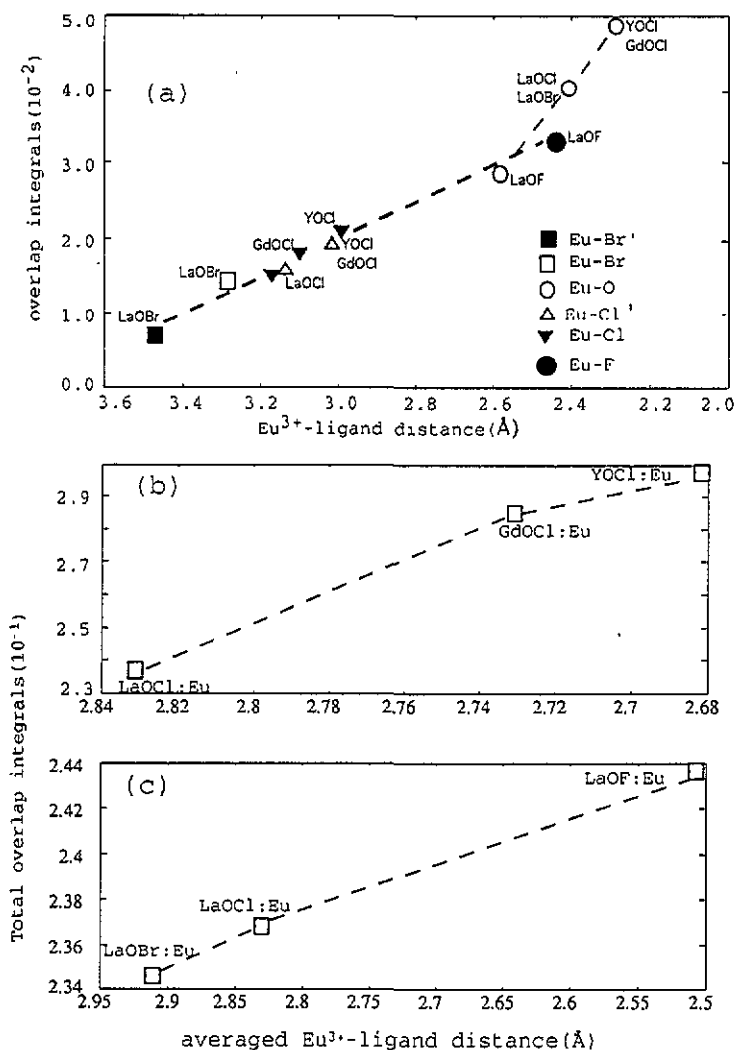


Figure 3. (a) Overlap integrals between f orbitals in Eu^{3+} and s and p orbitals in F^- , Cl^- , Br^- , and O^{2-} . Br' and Cl' represent the Br and Cl ions, respectively, on the fourfold axis. (b) variation of total overlap integral between Eu^{3+} and all the ligand ions with averaged Eu^{3+} -ligand distance along the LaOCl - GdOCl - YOCl series; (c) that along the LaOBr - LaOCl - LaOF series. The size of the triangles, circles, and squares represents the maximum error of each calculation. Broken lines are guides for the eye.

total overlap integral between Eu^{3+} and the ligands versus averaged Eu^{3+} -ligand distance along the LaOCl - GdOCl - YOCl series and the LaOBr - LaOCl - LaOF series, respectively.

The overlap integrals, as might be expected, increase with decreasing Eu^{3+} -ligand distance. It might be pointed out that the total overlap integral evolves (figure 3(b) and (c)) in a similar way as the free-ion parameters (figure 2), i.e., there is a diminution in the shift of the integral when the averaged Eu^{3+} -ligand distance decreases.

An interesting result is that the increase of the overlap integrals along the LaOBr - LaOCl - LaOF series (figure 3), which is in agreement with the experimental conclusion that

ionicity and covalency are positively correlated in ionic solids [28], is positively correlated to the reduction in F_2 , F_4 , and ζ along the same series (see figures 2 and 3). This result is in opposition to the anticorrelation between covalency and the 'nephelauxetic series' [2] unambiguously observed for transition-metal ions. According to the 'nephelauxetic series', the free-ion parameters should decrease along a series of ligands as

$$\text{free-ion value} > \text{F}^- > \text{O}_2^{2-} > \text{Cl}^- > \text{Br}^- > \text{I}^-$$

i.e. the heavier the halogen ligand, the larger the reduction. The anticorrelation between this series and covalency has been used to prove that the covalency does not play a significant role in the reduction of free-ion parameters in crystals [2,4]. So far, it seems that the 'anti-nephelauxetic series' for Eu^{3+} makes the situation more complex. This problem is discussed later.

In fact, the free-ion parameters decrease without exception under high pressure [4,5]. This fact, also observed in the present work (figure 1), is also in opposition to the anticorrelation between covalency and the 'nephelauxetic series', because the covalency of 4f electrons, or the overlap integral, will certainly increase with increasing pressure, as shown by the result of our calculation.

The facts mentioned above, in our opinion, are persuasive enough to remind us not to overlook the function of covalency in studying the reduction of free-ion parameters in crystal.

4. Discussion of the cloud-expanding models

There is no doubt that once a metal ion is embedded in a crystal, its electrons will, more or less, drift (expand) to the surrounding ions. This will have a strong influence upon the interaction in the metal ion. Actually, the important thing is not only the expansion itself, but also how the electron orbital expands, which has been shown by the very different results of the *ab initio* calculations of F_2 and ζ with different radial wavefunctions [29]. In this section, we will present a qualitative discussion of the two kinds of covalency model briefly mentioned in the first section of this paper.

4.1. Central-field covalency

In this mechanism, the reduction of free-ion parameters in crystals is attributed to a screening of the effective nuclear charge Z_{ef} due to the penetration of ligand electrons into the metal ion. Hence the variation of Z_{ef} , in this model, represents a spherically even expansion of the electron orbitals. It is well known [30] that, for lanthanides, $F_2 \propto Z_{\text{ef}}$ and $\zeta \propto Z_{\text{ef}}^3$. Assuming a small reduction ΔZ_{ef} , to a first approximation we have

$$\Delta\zeta/\zeta = 3\Delta Z_{\text{ef}}/Z_{\text{ef}} \quad (1)$$

and

$$\Delta F_2/F_2 = \Delta Z_{\text{ef}}/Z_{\text{ef}}. \quad (2)$$

The shift in ζ should be three times greater than the shift in F_2 . However, all the results of free-ion calculations, i.e. the intermediate-coupling calculation, for lanthanides [4,5,21,31] revealed that the shift in ζ was always weaker than the shift in F_2 . So the central-field

covalency mechanism does not seem to play the major role in the reduction of the free-ion parameters.

It should be mentioned that Huber *et al* [32] and Chi *et al* [16] have estimated the pressure influence on ζ and F_2 for Eu^{3+} and that their results showed that the pressure-induced shift in ζ (-15% Mbar^{-1} for Eu^{3+} in the LaOCl host [16] and -25% Mbar^{-1} for Eu^{3+} in the $\text{EuP}_5\text{O}_{14}$ host [32]) is much stronger than that in F_2 (-7% Mbar^{-1} for Eu^{3+} in the $\text{EuP}_5\text{O}_{14}$ host [32]); it is 2–10 times stronger than the shift in ζ given in the present paper (-9% Mbar^{-1} for Eu^{3+} in the LaOCl host) and in other works (-4% Mbar^{-1} for Pr^{3+} in the LaCl_3 host [4] and -2% Mbar^{-1} for Eu^{3+} in the $\text{La}_2\text{O}_2\text{S}$ host [5]). The authors [32] concluded therefore that the central-field covalency or the screening of the nuclear charge is the origin of the shift in F_2 and ζ . It should be noted, however, that they deduced the shift in ζ only from the ${}^7F_{1,2}$ [32] and ${}^7F_{0-4}$ multiplets [16] by using the Landé rule. In fact, the Landé rule is often a rough approximation. For example, for Eu^{3+} in LaOCl , $\{E({}^7F_3) - E({}^7F_2)\} / \{E({}^7F_2) - E({}^7F_1)\} = 1.2$ (see table 2), instead of 1.5 as predicted by the Landé rule. Moreover, from table 2, we can see that, up to 13 GPa, the shift in the interval $E({}^7F_1) - E({}^7F_0)$, $E({}^7F_2) - E({}^7F_1)$, $E({}^7F_3) - E({}^7F_2)$, $E({}^7F_4) - E({}^7F_3)$, $E({}^5D_1) - E({}^5D_0)$, and $E({}^5D_2) - E({}^5D_1)$ is -1.6% , -4.8% , 0.5% , -0.5% , -0.2% , and -0.7% , respectively (with an averaged value of about -1.2% , which is close to the shift in ζ of -1.18% in this work). It is therefore clear that if we use the Landé rule and only the spin-orbit splitting of 7F manifolds to deduce the shift in ζ , we will obtain a shift in ζ much stronger than that given by an intermediate-coupling calculation. The result of an intermediate-coupling calculation, in our opinion, is more reliable than the result given with the Landé rule.

4.2. Symmetry-restricted covalency

In this mechanism, the drift of the open-shell electrons in the metal ion to the ligands is treated to a first approximation as a simple loss of amplitude of the open-shell wavefunction, which can be compensated by the appearance of the ligand orbital in the open-shell wavefunctions [2]:

$$\varphi'_\Gamma = N_\Gamma \left(\varphi_\Gamma - \sum_\tau \lambda_{\Gamma\tau} \chi_\tau \right) \quad (3)$$

where Γ stands for the different atomic states, τ stands for the various ligands and φ'_Γ , φ_Γ , χ_τ , N_Γ and $\lambda_{\Gamma\tau}$ represent the mixed molecular orbital, atomic open-shell orbital, ligand orbital, normalization constant and mixing coefficient, respectively. The normalization constant is given by

$$N_\Gamma = \left(1 - 2 \sum_\tau \lambda_{\Gamma\tau} S_{\Gamma\tau} + \sum_\tau \lambda_{\Gamma\tau}^2 \right)^{-1/2} \quad (4)$$

where $S_{\Gamma\tau} = \langle \varphi_\Gamma | \chi_\tau \rangle$ is the overlap integral. $\lambda_{\Gamma\tau}$ can be approximately expressed as a sum of $S_{\Gamma\tau}$ and a covalency parameter $\gamma_{\Gamma\tau}$, which increases with $S_{\Gamma\tau}$ [33]. A reasonable argument has been put forward in [32] for neglecting the ligand part in (3) in calculating the Coulomb repulsion between the open-shell electrons. Then we have

$$\langle \varphi'_\Gamma | \varphi'_\Gamma | 1/r_{12} | \varphi'_\Gamma | \varphi'_\Gamma \rangle = N_\Gamma N_\Gamma N_\Gamma N_\Gamma \langle \varphi_\Gamma | \varphi_\Gamma | 1/r_{12} | \varphi_\Gamma | \varphi_\Gamma \rangle \quad (5)$$

and

$$\langle \varphi'_\Gamma | (1/r) dV(r)/dr | \varphi'_\Gamma \rangle = N_\Gamma N_\Gamma \langle \varphi_\Gamma | (1/r) dV(r)/dr | \varphi_\Gamma \rangle. \quad (6)$$

Since $N_{\Gamma} \simeq 1$ and since there is no large difference between the N_{Γ} values, the product $N_{\Gamma_1} N_{\Gamma_2} N_{\Gamma_3} N_{\Gamma_4}$ can be replaced by N^4 [3] so that (5) and (6) lead to $F'_k = N^4 F_k$ and $\zeta' = N^2 \zeta$, respectively; F'_k and ζ' represent the Slater and spin-orbit coupling parameters for a metal ion in a crystal. Assuming a small ΔN , one obtains to a first approximation

$$\Delta F_k / F_k = 4 \Delta N / N \quad (7)$$

and

$$\Delta \zeta / \zeta = 2 \Delta N / N. \quad (8)$$

The shift, weaker in ζ than in F_2 , agrees with the experimental results. However, if the reduction of F_k and ζ depends only on ΔN , it should always have a positive correlation with overlap integral and increase from 1^- to F^- along the $1-\text{Br}-\text{Cl}-\text{F}$ ligand series, which is in opposition with the experimental results for transition-metal ions (see section 3, 'nephelauxetic series') [2, 6, 31, 35].

4.3. A combined cloud-expanding model

The above two cloud-expanding mechanisms represent two different ways of expansion. In fact, there is no clear reason why we should treat the two mechanisms separately. The screening of effective nuclear charge due to ligand charge penetration and the admixture of the atomic orbitals exists, of course, simultaneously. Considering only one mechanism, the expansion must be underestimated and poorly described. Combining the two mechanisms and taking the same approximations as above, we obtain

$$\Delta F_2 / F_2 = \Delta Z_{\text{ef}} / Z_{\text{ef}} + 4 \Delta N / N \quad (9)$$

and

$$\Delta \zeta / \zeta = 3 \Delta Z_{\text{ef}} / Z_{\text{ef}} + 2 \Delta N / N. \quad (10)$$

Thus a 1.3% and 1.2% decrease in F_2 and ζ , respectively, from LaOCl:Eu to YOCl:Eu or from 1 bar to 13 GPa, would correspond to a decrease of 0.3% and 0.2% in N and Z_{ef} . If we assume a reasonable ratio $\lambda_{\Gamma_x} = 2.2 S_{\Gamma_x}$ [2] for $\langle f|p\pi \rangle$ overlap [6], then a 0.3% decrease in N_{Γ_x} leads to $\Delta S_{\Gamma_x} / S_{\Gamma_x} \simeq 50\%$, comparable to the 37% decrease in S_{Γ_x} in our calculated overlap from LaOCl:Eu to YOCl:Eu .

Considering the 'nephelauxetic series', it could be explained qualitatively as follows. The ΔZ_{ef} in the central-covalency model is in fact, a reflection of the spherical (even) expansion of the open-shell orbital. It might not be a 'real' change of the effective nuclear charge, because the spherical expansion, or ΔZ_{ef} , depends not only on the 'real' change, or the screening of Z_{ef} , but also on the repulsion between the open-shell orbital and the ligand orbital due either to electrostatic interaction or to the repulsive effect of the overlap. Generally speaking, the larger the overlap is, the stronger the repulsive effect will be [2]. For 4f electrons, this repulsion might be greatly reduced because of the 'shielding' of the 5s and 5p closed shells. So ΔZ_{ef} , as well as ΔN , might be simply and positively correlated to overlap, as is the reduction of F_k and ζ for lanthanides, as has been observed in this work for Eu^{3+} along the $\text{LaOBr}-\text{LaOCl}-\text{LaOF}$ host series. For the d orbital, however, there is no 'shielding' against the ligands, so the repulsion between the d orbital and the ligand orbital must be much stronger and it must increase more strongly along the $1-\text{Br}-\text{Cl}-\text{F}$ ligand series because of the increasing overlap (see figure 3 and [28]), increasing ionicity, increasing electronegativity, and especially because of the shortening of the metal-ligand distance. So it is possible, from equations (9) and (10), that $\Delta N / N$ increases while $\Delta Z_{\text{ef}} / Z_{\text{ef}}$, or the spherical cloud expansion, decreases along the sequence $1-\text{Br}-\text{Cl}-\text{F}$ in such a way that $\Delta \zeta / \zeta$ and $\Delta F_k / F_k$ diminish in the same order, as happens in the so-called 'nephelauxetic series'.

5. Conclusion

The reduction of the phenomenological free-ion parameters for Eu^{3+} in crystals with increasing pressure and along the host series $\text{LaOCl}-\text{GdOCl}-\text{YOCl}$ and $\text{LaOBr}-\text{LaOCl}-\text{LaOF}$, especially the 'anti-nephelauxetic series' (cf section 2) demonstrated by the reduction along the latter series, and the positive correlation and the similarity between the shift of the free-ion parameters and the shift of the overlap integral (see figures 1, 2 and 3), remind us that it is not reasonable or cautious to rule out the covalency effect and the cloud-expanding effect on the reduction of free-ion parameters in crystals. Further work, experimental or theoretical, will have to be done to verify the role of covalency in this problem. The difficulty in performing the theoretical calculation, however, originates from two factors. Firstly, as far as we are aware, we still lack a wavefunction that can strictly reflect the radial expansion of the atomic orbital in crystals. A pure free-ion wavefunction, as calculated by some authors [22, 23], will certainly underestimate the covalency effect when used in calculating the overlap integral and the normalization constant N_{Γ} (cf section 4.2). Secondly, an accurate determination of the variation of the effective nuclear charge in crystals is still difficult because of the lack of a detailed explanation for the complex nature of ΔZ_{ef} , as discussed in section 4.3 in the present paper. At present, therefore, a theoretical determination of the contribution of covalency to the reduction of free-ion parameters in crystals would be premature.

As shown in section 4.3, a combined cloud-expanding model, proposed in this work to avoid the weaknesses of the two former cloud-expanding models, agrees well with the experimental results. Further work in this direction could be done, in our opinion, by using a semi-empirical ion wavefunction to calculate the phenomenological free-ion parameters, as has been done by some authors for the transition-metal ions [3, 35, 36]. In view of the above-mentioned difficulties, this would be a good choice.

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