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Influence of hydrostatic pressure upon the energy level scheme of Eu^{3+} in an $\text{La}_2\text{O}_2\text{S}$ crystal

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Abstract. The fluorescence spectra of Eu^{3+} in an $\text{La}_2\text{O}_2\text{S}$ crystal have been measured at room temperature and under hydrostatic pressures up to 13 GPa. The pressure dependence of the energy levels of Eu^{3+} in $\text{La}_2\text{O}_2\text{S}$ has been determined. The observed crystal-field levels shift upwards or downwards with increasing pressure and undergo a distinct change in shift rates at about 10 GPa. The relative shift rates of the observed centroids of ${}^5\text{D}_{0-2}$ multiplets are about the same. Simulations of the observed energy levels of Eu^{3+} in $\text{Y}_2\text{O}_2\text{S}$ crystals have also been carried out in order to make a comparison between the results for $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and those for $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. Of the six crystal-field parameters, only B_0^2 shows a somewhat puzzling change with increasing pressure and decreasing internuclear distances due to different isomorphous hosts. In the pressure range up to 13 GPa, the Slater parameters F_2 , F_4 and F_6 show a decrease of 0.38(9)%, 0.38(0)% and 0.38(3)%, respectively; the spin-orbit coupling parameter ζ decreases by 0.20%. In order to understand the regular decrease in the ${}^5\text{D}_{0-2}$ multiplets with increasing pressure, we have inspected the calculated free-ion energy levels under different pressures and found that the energy E of any excited level can be related to pressure P by $E = E_0(1 - cP)$, in which $c = 2.90(\pm 0.15) \times 10^{-4} \text{ GPa}^{-1}$.

1. Introduction

There are two powerful experimental methods used to understand quantitatively the splitting and shift of the energy levels of lanthanide ions embedded in crystal. The first is to measure the energy levels of a given lanthanide ion in various isostructural host lattices and to study the change in the crystal field caused by different interatomic distances [1]. In this method, however, the presence of different ligands and local distortions around the lanthanide ion in each host and the limited number of isostructural crystals available for spectroscopic studies restrict the information observed. The second is to apply a high pressure to the lanthanide-ion-doped crystals and thereby to study the pressure and internuclear distance dependence of the crystal field directly. In this research field, much work has been carried out in recent years and valuable results obtained [2–8].

The spectra of Eu^{3+} in an $\text{La}_2\text{O}_2\text{S}$ crystal have been studied previously [9, 10]. The space group of the $\text{La}_2\text{O}_2\text{S}$ crystal lattice is D_{3d}^3 [11] and, under normal pressure, the interatomic distances are as follows: La–S, 3.07 Å; La–O, 2.38 Å; La–O', 2.41 Å (the distance to the O atom on the threefold symmetry axis). The Eu^{3+} impurities

in $\text{La}_2\text{O}_2\text{S}$ will replace La^{3+} ions, be coordinated to three sulphur and four oxygen ions and have C_{3v} site symmetry.

In this work, we measured the fluorescence spectra of $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at room temperature and high hydrostatic pressures up to 13 GPa. On the basis of the observed Stark levels and the multiplet centroids at different pressures, we carried out crystal-field and centroid calculations and obtained the pressure dependence of the crystal-field and free-ion parameters. The pressure effects on the energy levels for Eu^{3+} in $\text{La}_2\text{O}_2\text{S}$ and on the crystal-field and free-ion parameters are discussed in this paper.

2. Theory and fitting procedure

When a free ion is embedded in a crystal, the crystal-field potential, represented by a Hamiltonian H_{cf} , will contribute to the Hamiltonian of the ion. Then the Hamiltonian of the ion can be written as [12]

$$H = H_{\text{fi}} + H_{\text{cf}} \quad (1)$$

in which H_{fi} is the free-ion Hamiltonian expressed in terms of the Slater parameters F_k , the spin-orbit interaction parameter ζ and the configuration interaction parameters α , β and γ ; H_{cf} is the crystal-field Hamiltonian expressed in terms of the crystal-field parameters B_q^k . To determine these empirical parameters, we performed the calculations in two steps. First, the free-ion parameters are adjusted to fit the experimental multiplet centroids and then the crystal-field parameters are adjusted to fit the experimental crystal-field levels.

2.1. Centroid calculations

In the centroid calculations the Coulomb and the spin-orbit interactions were taken into account but the configuration interaction was neglected [7] by setting $\alpha = \beta = \gamma = 0$. Wybourne [13] has calculated the matrix elements of the Coulomb interaction which can be expressed in terms of the Slater parameters F_2 , F_4 and F_6 . The matrix elements of the spin-orbit interaction were calculated with the help of the relationship given in [12]. Intermediate coupling was considered in our calculations.

2.2. Crystal-field calculations

For Eu^{3+} in C_{3v} site symmetry, the crystal-field Hamiltonian can be expressed as

$$H_{\text{cf}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_{-3}^4 - C_3^4) + B_0^6 C_0^6 + B_3^6 (C_{-3}^6 - C_3^6) + B_6^6 (C_{-6}^6 + C_6^6). \quad (2)$$

H_{fi} in equation (1) was treated as a variable intermediate parameter (one for each multiplet) in the crystal-field calculations.

In view of the poor simulations in the past for excited ${}^5\text{D}$ levels and the conclusion [1] that, for strongly mixed levels (e.g. ${}^5\text{D}$ and ${}^5\text{G}$), poor simulation should be anticipated, we carried out the crystal-field calculations on the 49 ${}^7\text{F}_J$ bases, 25 ${}^5\text{D}_J$ bases and 45 ${}^5\text{G}_J$ bases. The ${}^5\text{G}$ term was involved because its energy levels are very close to, and strongly mixed with, the energy levels of the lowest ${}^5\text{D}_J$ levels. In the calculations, the five intermediate parameters for ${}^5\text{G}_J$ multiplets were fixed to reasonable

values. In calculating the matrix elements of H_{cf} , we used the intermediate-coupling wavefunctions of Eu^{3+} which included all the compositions of septet and quintet states and some compositions of the triplet states that mix strongly with the ${}^5\text{D}_J$ states. The J -mixing caused by the crystal field was also taken into account by including the non-diagonal matrix elements between the states with different J -values, but the non-diagonal matrix elements between the ${}^7\text{F}_J$ states and the excited states (of ${}^5\text{D}_J$ and ${}^5\text{G}_J$) were omitted. Our work showed that this omission had almost no influence on the results of the calculations. Then the resulting 119×119 matrix appears as the direct sum of a 49×49 matrix and a 70×70 matrix.

3. Experiments and results

The sample of polycrystalline $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (4.7 mol%) was provided by the Changchun Institute of Physics, Academia Sinica. An x-ray diffraction experiment showed that the space group of the sample is D_{3d}^3 .

The fluorescence spectra of the sample were recorded at room temperature and different pressures. The hydrostatic pressure was generated by a gasketed diamond-anvil cell [14] in combination with the ruby luminescence method for pressure determination [15]. A methanol-ethanol-water mixture (methanol:ethanol:water=16:3:1) was used as the pressure medium which assures a truly hydrostatic pressure up to about 14 GPa. The 4579 Å line of an argon ion laser was used to excite the sample. The fluorescence spectra were recorded with a Spex-1403 Ramalog instrument.

107 fluorescence lines in the range 11 500–21 500 cm^{-1} have been assigned to transitions between the crystal-field components of ${}^5\text{D}_{0-2}$ and ${}^7\text{F}_{0-6}$ multiplets with the help of the previous results [9, 16]. At room temperature, the number of the fluorescence lines recorded at a high pressure is larger than the number of the lines recorded at ambient pressure. Some ${}^5\text{D}_2$ - ${}^7\text{F}_{5,6}$ lines present at 77 K and absent at room temperature and ambient pressure appeared again at about 1 GPa and room temperature. These 'high-pressure lines', in our opinion, are due to the upward shift of the charge-transfer states with increasing pressure [10]. This shift makes it difficult for 4f electrons to migrate from ${}^5\text{D}_2$ to ${}^5\text{D}_1$ and ${}^5\text{D}_0$ and strengthens the ${}^5\text{D}_2$ - ${}^7\text{F}_J$ transitions. All the fluorescence lines shifted to the red and became increasingly weaker with increasing pressure. Above 13 GPa, some lines were so weak that their peak positions could not be determined. The pressure dependences of some lines are shown in figure 1.

4. Pressure effect on the crystal-field interaction

4.1. Energy levels

The pressure dependences of the 26 crystal-field levels were deduced from the fluorescence lines observed at different pressures and are shown in figure 2. Under high pressures, the crystal-field components of ${}^7\text{F}_{0-5}$ multiplets shifted upwards or downwards and all the crystal-field components of ${}^5\text{D}_{0-2}$ multiplets moved downwards at about the same rate. The shifts in the ${}^5\text{D}$ levels with pressure are much more rapid than those in the ${}^7\text{F}$ levels. It should be noted that most of the observed levels show special changes in shifts at about 10 GPa and the splittings of the ${}^7\text{F}_1$ and ${}^5\text{D}_1$ multiplets decrease with increasing pressure below 10 GPa and increase thereafter.

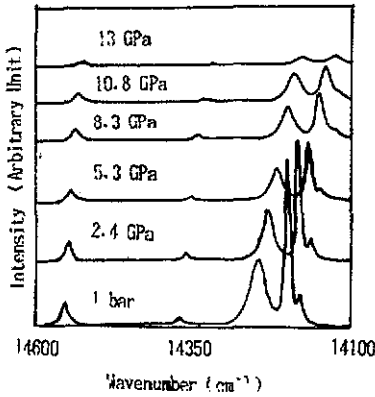


Figure 1. The pressure effect on the ${}^5D_0-{}^7F_4$ transition lines of $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$.

These changes in the shifts of the levels, in our opinion, are caused by a sudden distortion of the crystal lattice of the $\text{La}_2\text{O}_2\text{S}$ host at about 10 GPa. In view of the fact that no fluorescence anomalies happened in the experiments, we believe that the lattice distortion did not disturb the site symmetry of the Eu^{3+} , although it changed the pressure dependence of the crystal field. This lattice distortion should be checked by x-ray diffraction experiments at high pressures.

4.2. Crystal-field parameters

The pressure effect on B_q^k for Eu^{3+} in $\text{La}_2\text{O}_2\text{S}$ was studied by fitting B_q^k to the crystal-field components of the ${}^7F_{0-4}$ and ${}^5D_{0-2}$ multiplets observed at various pressures. The best-fit values of B_q^k at different pressures are listed in table 1. These B_q^k sets reproduce the experimental crystal-field levels quite well. The deviation between the calculated and the observed Stark levels of the 5D multiplets is not larger than that of the 7F multiplets. The RMS deviations of the calculations are about 6 cm^{-1} and no major discrepancies occur. The comparison between the calculated and the observed Stark levels is shown in figure 3.

In order to make a comparison between the isomorphous $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, we also carried out crystal-field calculations for Eu^{3+} in a $\text{Y}_2\text{O}_2\text{S}$ host with the help of the previously observed crystal-field levels under hydrostatic pressures up to 10 GPa [6]. The best-fit B_q^k sets are listed in table 2.

Table 1. The best-fit B_q^k sets, the crystal-field strength parameter S and the RMS deviation σ of the calculations for $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at various pressures.

	$P = 1\text{ atm}$	$P = 3\text{ GPa}$	$P = 6\text{ GPa}$	$P = 9\text{ GPa}$	$P = 13\text{ GPa}$
$B_0^2\text{ (cm}^{-1}\text{)}$	58	54	40	29	39
$B_2^4\text{ (cm}^{-1}\text{)}$	762	776	718	696	727
$B_4^4\text{ (cm}^{-1}\text{)}$	922	962	1028	1078	1118
$B_0^6\text{ (cm}^{-1}\text{)}$	452	459	504	531	556
$B_2^6\text{ (cm}^{-1}\text{)}$	-182	-202	-192	-201	-215
$B_4^6\text{ (cm}^{-1}\text{)}$	369	398	412	404	431
$S\text{ (cm}^{-1}\text{)}$	314	326	338	349	363
$\sigma\text{ (cm}^{-1}\text{)}$	5.9	6.1	5.8	6.2	6.3

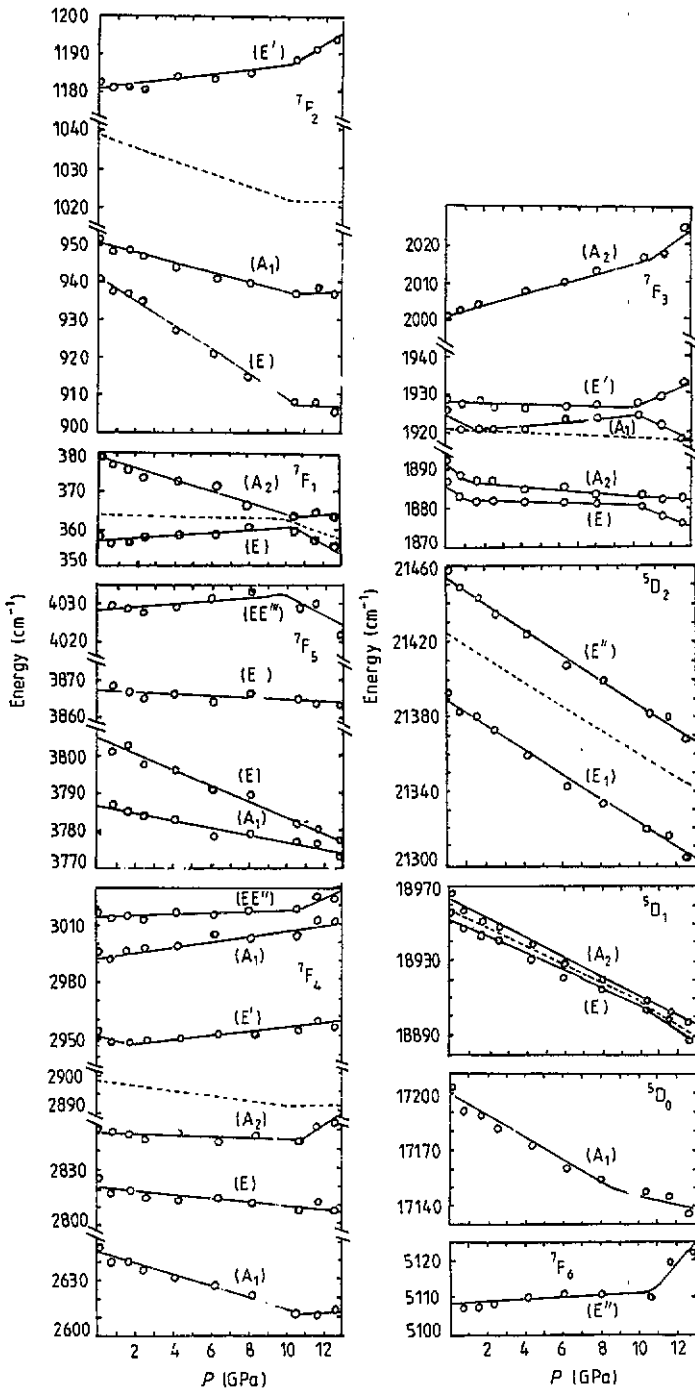


Figure 2. The pressure dependence of the 26 crystal-field levels of ${}^7\text{F}_{0-6}$ and ${}^5\text{D}_{0-2}$ multiplets for Eu^{3+} in $\text{La}_2\text{O}_2\text{S}$. The broken curves represent the pressure dependence of the multiplet centroids. The letters in parentheses correspond to the irreducible representations of the C_{3v} point group to which the levels were assigned.

The values of B_q^k in table 2 are quite different from the previous results reported in [6]. For example, in [6], $B_0^2 = 83$, $B_0^4 = 1100$, $B_3^4 = 882$, $B_0^6 = 325$, $B_3^6 = -378$ and $B_6^6 = 524$ at ambient pressure. The difference between these two results is

Table 2. The best-fit B_q^k sets, the crystal-field strength parameter S and the RMS deviation σ of the calculations for $Y_2O_2S:Eu^{3+}$ at various pressures.

	$P = 1 \text{ atm}$	$P = 2.5 \text{ GPa}$	$P = 5 \text{ GPa}$	$P = 7.5 \text{ GPa}$	$P = 10 \text{ GPa}$
$B_0^2 \text{ (cm}^{-1}\text{)}$	117	99	77	62	43
$B_0^4 \text{ (cm}^{-1}\text{)}$	692	690	691	702	710
$B_3^4 \text{ (cm}^{-1}\text{)}$	1107	1136	1170	1190	1222
$B_0^6 \text{ (cm}^{-1}\text{)}$	491	501	521	526	534
$B_3^6 \text{ (cm}^{-1}\text{)}$	-335	-337	-343	-345	-349
$B_6^6 \text{ (cm}^{-1}\text{)}$	461	469	480	495	510
$S \text{ (cm}^{-1}\text{)}$	364	370	380	386	395
$\sigma \text{ (cm}^{-1}\text{)}$	5.7	5.8	6.1	6.0	6.2

significant although the pressure dependences of B_q^k in these two results are similar. In our opinion, this difference is due to the addition of 5D levels in the present crystal-field calculations and means that in determining the crystal-field parameters the crystal-field splittings of highly excited states are not negligible.

The B_q^k for $La_2O_2S:Eu^{3+}$ and $Y_2O_2S:Eu^{3+}$ all undergo similar changes under pressure; if a particular B_q^k is larger (or smaller) for $Y_2O_2S:Eu^{3+}$ than for $La_2O_2S:Eu^{3+}$, then it will increase (or decrease) with increasing pressure. This seems reasonable in view of the facts that La_2O_2S and Y_2O_2S have the same crystalline structure and that the internuclear distances are larger in the La_2O_2S crystal than in the Y_2O_2S crystal [16]. However, there is evidently a different situation for B_0^2 .

B_0^2 is larger for $Y_2O_2S:Eu^{3+}$ than for $La_2O_2S:Eu^{3+}$ at room temperature and ambient pressure, which means that we expect B_0^2 to increase with increasing pressure. However, in fact, B_0^2 decreases greatly with increasing pressure below 10 GPa for both $La_2O_2S:Eu^{3+}$ and $Y_2O_2S:Eu^{3+}$. This kind of evolution of B_0^2 is difficult to understand when we consider the previous results for Eu^{3+} -doped $LnOX$ ($X = Cl, Br, I$) [1, 2, 4]. For this series, B_0^2 did not show any particular behaviour and decreased with decreasing internuclear distance [1] and increasing pressure [2, 4]. The puzzling behaviour of B_0^2 for the La_2O_2S and Y_2O_2S hosts indicates that the influence of the decrease in internuclear distances due to different isomorphous hosts upon the crystal field is not always equivalent to the decrease in internuclear distances due to a high pressure. At present, we are not able to explain this complex nature of B_0^2 for the La_2O_2S and Y_2O_2S hosts.

4.3. Crystal-field strength

Now we shall study the influence of pressure on the crystal field in $La_2O_2S:Eu^{3+}$ and $Y_2O_2S:Eu^{3+}$ in more detail. To do this, we consider B_q^k as the components of a generalized vector B^k and utilize the length of B_q^k to weight the crystal-field strength [17]. The crystal-field strength parameter S is derived from the B_q^k set according to [18]

$$S = \left[\frac{1}{3} \sum_k \frac{1}{2k+1} \left((B_0^k)^2 + 2 \sum_{q>0} [(Re B_q^k)^2 + (Im B_q^k)^2] \right) \right]^{1/2}. \quad (3)$$

This parameter reflects the averaged (or total) effect of the crystal-field interaction. The values of S for $La_2O_2S:Eu^{3+}$ and $Y_2O_2S:Eu^{3+}$ at different pressures are listed in

Table 3. The values of R_k and A_k at ambient pressure and 13 GPa. R is the ratio of the crystal-field strength in $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at ambient pressure and 13 GPa to the crystal-field strength in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at ambient pressure.

P	R_2 (deg)	R_4 (deg)	R_6 (deg)	A_2 (deg)	A_4 (deg)	A_6 (deg)	R (deg)
1 atm	1.98	1.13	1.28	0	6.49	10.29	1.16
13 GPa	3.00	0.98	1.07	0	1.10	10.56	1.00

tables 1 and 2, respectively. S is always larger for $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ than for $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and increases with increasing pressure for both of them. This means that the increase in pressure and the decrease in internuclear distances have strengthened the crystal field in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. However, it is not always the case. The effect of the pressure or the decrease in internuclear distances on the crystal field, according to other researchers, seems to depend on the crystalline structure of the host lattice. For example, the crystal fields in Eu^{3+} -doped rare-earth oxyhalides LnOX ($X = \text{Cl}, \text{Br}, \text{I}$) were weakened by decreasing internuclear distances [1] and increasing pressure [4].

It should be noted that the value of S for $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at 13 GPa approaches the value of S for $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at ambient pressure. This result seems reasonable and indicates that, with increasing pressure, the crystal field in $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ becomes close to the crystal field in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at ambient pressure. The similarity between these two crystal fields can be described in more detail by a scale factor

$$R_k = |B_Y^k|/|B_{\text{La}}^k| \quad (4)$$

and the angle between the two generalized vectors B_Y^k and B_{La}^k

$$A_k = \cos^{-1}(B_{\text{La}}^k \cdot B_Y^k/|B_{\text{La}}^k||B_Y^k|) \quad (5)$$

where B_{La}^k is the B^k vector for $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at various pressures and B_Y^k is the B^k -vector for $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at ambient pressure. Identity of the two crystal fields would correspond to $R_k = 1$ and $A_k = 0$. From table 3 we can see that R_4 , R_6 and R become close to unity and that A_4 is reduced to 1.10° at 13 GPa. The similarity between the crystal field in $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at 13 GPa and the crystal field in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ at ambient pressure is obvious, although R_2 and A_6 are still large at 13 GPa. We think that the increases in R_2 and A_6 with increasing pressure are mainly due to the lattice distortion of the $\text{La}_2\text{O}_2\text{S}$ crystal at high pressures and imply that the difference between the local environments of Eu^{3+} in the $\text{La}_2\text{O}_2\text{S}$ and $\text{Y}_2\text{O}_2\text{S}$ hosts became greater in some aspects as the pressure increased.

5. Pressure effect on free ions

5.1. Free-ion energy levels

The pressure dependence of the eight centroids of the ${}^7\text{F}_{0-4}$ and ${}^5\text{D}_{0-2}$ multiplets was deduced from the observed crystal-field levels of Eu^{3+} in $\text{La}_2\text{O}_2\text{S}$ in the pressure range up to 13 GPa and is shown in figure 2 by broken curves. All the centroids decrease linearly with increasing pressure. It should be noted that the shifts of the ${}^5\text{D}$ multiplets are much larger than those of the ${}^7\text{F}$ multiplets and that the relative

shifts of the three ${}^5\text{D}$ multiplets are about the same. Up to 13 GPa, the ${}^5\text{D}_0$, ${}^5\text{D}_1$ and ${}^5\text{D}_2$ centroids shift by $-0.40(7)\%$, $-0.39(1)\%$ and $-0.39(6)\%$, respectively. The ${}^7\text{F}$ centroids show no regular decrease as the ${}^5\text{D}$ centroids do. The large regular decrease in the ${}^5\text{D}$ centroids is obviously caused by the decreases in the Coulomb and spin-orbit interactions with increasing pressure. For ${}^7\text{F}$ multiplets, J -mixing is much stronger and tends to shift the free-ion energy levels irregularly. So there is no regularity in the shifts of the ${}^7\text{F}$ centroids.

5.2. Free-ion parameters

The pressure dependence of the best-fit F_k and ζ for Eu^{3+} in the $\text{La}_2\text{O}_2\text{S}$ host is shown in figure 4. The RMS deviation between the calculated and the observed multiplet centroids is about 60 cm^{-1} and shows a slight increase with increasing pressure. At ambient pressure, $F_2 = 395.6\text{ cm}^{-1}$, $F_4 = 54.6\text{ cm}^{-1}$, $F_6 = 5.9\text{ cm}^{-1}$ and $\zeta = 1333.1\text{ cm}^{-1}$. Compared with $F_2 = 395.8\text{ cm}^{-1}$ and $\zeta = 1326\text{ cm}^{-1}$ reported in [16], only ζ shows a notable increase which, in our opinion, was mainly caused by the lack of ${}^7\text{F}_5$, ${}^7\text{F}_6$ and ${}^5\text{D}_3$ multiplets in our calculation. Up to 13 GPa, the relative shifts in F_k and ζ are about 0.38% and 0.20% , respectively. The shifts in F_k are twice the shift in ζ . The reason for the decreases in F_k and ζ is the redistribution of the $4f$ electron clouds under pressure and, as a result, the decreases in the Coulomb and spin-orbit interaction energies.

According to the nephelauxetic model [19], if a lanthanide ion is embedded in a crystal, the $4f$ electron clouds expand, and F_k and ζ decrease. Up to now, the mechanism of this cloud expansion has not been beyond dispute [7]. Every proposed mechanism has its strong and weak points. In our opinion, the symmetry-restricted covalency mechanism is the most reasonable. According to this mechanism, the cloud expansion is caused by the symmetry-restricted covalency of the $4f$ electrons. In general, this covalency increases, and F_k and ζ decrease, when the internuclear distances decrease with increasing pressure, which is in accordance with our observed result for Eu^{3+} (figure 4). In an averaged version of this model [20, 21], the relative decrease in ζ should be half that in F_k , which is in fair agreement with our observed decreases of 0.39% and 0.20% in F_k and ζ , respectively, from ambient pressure to 13 GPa.

5.3. The regularity in the shift of the excited energy levels with increasing pressure

From figure 2, we found that the relative shifts of the ${}^5\text{D}_{0-2}$ multiplet centroids are about the same, i.e. the higher a level the larger is its rate of decrease. This regularity can also be noted in the shifts in the ${}^3\text{D}_2$, ${}^3\text{P}_0$ and ${}^3\text{P}_1$ multiplets of the Pr^{3+} ion with increasing pressure [7].

We can also study this regularity by inspection of the calculated energy levels at different pressures because the RMS deviation between the calculated and the observed levels remains about the same at high pressures, and, as a result, the pressure dependence of the calculated levels should be the same as that of the observed levels. We have inspected the calculated free-ion energy levels for Eu^{3+} in the $\text{La}_2\text{O}_2\text{S}$ host in the pressure range up to 13 GPa and found that the energy E of any level can be related to the hydrostatic pressure P by

$$E = E_0(1 - cP) \quad (6)$$

where E_0 is the energy of the level at ambient pressure and c is the relative shift rate of the level, which is the same for all the calculated levels. For Eu^{3+} in the $\text{La}_2\text{O}_2\text{S}$ host, $c = 2.90(\pm 0.15) \times 10^{-4}\text{ GPa}^{-1}$.

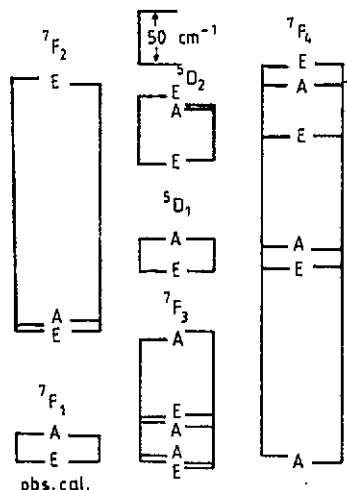


Figure 3. The comparison of observed and calculated CF splittings of ${}^7F_{1-4}$ and ${}^5D_{1-2}$ for $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$.

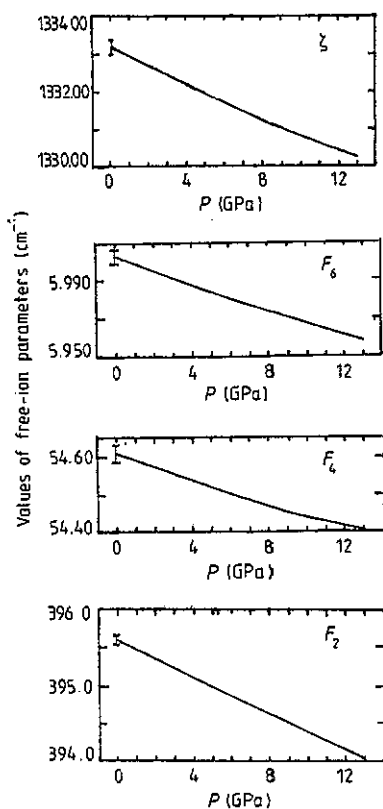


Figure 4. The pressure dependence of the Slater parameters F_k and the spin-orbit parameter ζ for Eu^{3+} in $\text{La}_2\text{O}_2\text{S}$.

6. Discussion and conclusion

In the crystal-field calculations, we considered the levels of 7F_J and the lowest 5D_J and 5G_J multiplets as the basis set; we used the intermediate-coupling wavefunctions, including all the compositions of septet and quintet states and some compositions of triplet states having strong coupling to the 5D_J states, to calculate the matrix elements of H_{cf} . In this way, the simulations for the 5D_J levels were greatly improved. The agreement between the calculated and the observed crystal-field components of the ${}^5D_{0-2}$ multiplets was unexpectedly satisfactory. This result implies that the J -mixing between the 5D states and the 5G states may have a strong influence upon the positions of the 5D levels.

The crystal-field parameter B_0^2 showed an increase along the $\text{La}_2\text{O}_2\text{S}$, $\text{Gd}_2\text{O}_2\text{S}$, $\text{Y}_2\text{O}_2\text{S}$ series [22] which demonstrates a decrease in the internuclear distances. However, B_0^2 decreases with increasing pressure (tables 1 and 2). Therefore, we conclude that the decrease in the internuclear distance due to pressure, in some cases, has a different influence upon the crystal field from the decrease in internuclear distance due to different isomorphous hosts. This result indicates that a high-pressure study of the crystal field is essential.

However, as for the crystal-field strength and the nephelauxetic effect, the pressure

seems to have the same effect as the interatomic distance decrease due to different isomorphous hosts. For example, according to our calculations, $F_2 = 395.60 \text{ cm}^{-1}$ and 394.52 cm^{-1} for Eu^{3+} in the $\text{La}_2\text{O}_2\text{S}$ host at ambient pressure and at 9 GPa, respectively; $F_2 = 394.58 \text{ cm}^{-1}$ for Eu^{3+} in the $\text{Y}_2\text{O}_2\text{S}$ host at ambient pressure. The reason for this, in our opinion, is that the crystal-field strength and nephelauxetic effect are predominantly determined by ligands. For B_0^2 , according to the superposition model [7], the influence from the more distant ions cannot always be neglected. Therefore, the pressure dependence of B_0^2 should be more complex than the pressure dependences of the higher-order crystal-field parameters, the crystal-field strength and the nephelauxetic effect.

The crystal-field strength and the nephelauxetic effect in $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ were strengthened by increasing pressure and decreasing internuclear distances, which is in accordance with the result [7] that the crystal field is to a large extent dominated by overlap and covalency effects and the assumption that the nephelauxetic effect is caused by the covalency of 4f electrons. The result of our calculation also verified the prediction of the covalency model that the nephelauxetic decrease in ζ should be half the decrease in F_k but, in view of the weak points of the covalency model [7], much work should be carried out to improve the model.

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