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Effect of pressure on the electron state of Eu³⁺ in GdOBr

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Abstract

The fluorescence spectra of the Eu^{1,*} ion in GdOBr:Eu^{1,*} were measured under pressures up to 12.4 GPa at room temperature. The dependence of the CF levels of the ${}^{1}D_{n,-3}$ and ${}^{2}F_{n,-4}$ multiplets for the Eu^{1,*} ion on pressure was obtained from the spectra. Below 8 GPa with increasing pressure, the splittings of the multiplets studied do not increase and that of the ${}^{7}F_{1,}$, ${}^{7}F_{2}$, and ${}^{5}D_{1}$ multiplets decrease obviously. At higher pressure, the splittings of the ${}^{7}F_{1,}$, ${}^{7}F_{2}$, and ${}^{5}D_{1}$ multiplets increase slowly. On the basis of the experimental data, the free-ion parameters F_{2} and ζ , the crystal-field parameters B_{2}^{i} and the crystal-field strength parameters S were determined at different pressures. The values of F_{2} and ζ always reduce with pressure. The central-field covalency mechanism is dominant for the reduction of F_{2} and ζ . © 1997 Elsevier Science S.A.

Keywords: Fluorescence spectra; Trivalent europium; GdOBr; Effect of pressure

1. Introduction

When a rare earth (RE) ion is incorporated in a crystal, its energy levels are shifted and split into so-called crystalfield (CF) levels because of the effect of the crystal environment. The number of CF levels only depends on the site symmetry of the RE ion and can be determined exactly with the help of group theory method, but the quantitative relationship between the level scheme of the central RE ion and its crystal environment is a very complicated problem. Although several theoretical models describing this relationship have been proposed, a lot of experimental and theoretical researches are still needed in order to solve this problem better.

The Eu^{3+} ion is convenient to study the CF effect on electron state because of the particular features of its energy level scheme. The RE oxyhalides (REOX) can form several isostructural host lattices by varying the host anion or the cation, so REOX doped with Eu^{3+} were paid attention to [1,2]. On the other hand, high pressure can decrease the interatomic distance in a crystal continuously to form a continuous isomorphous series, it becomes a powerful tool for the direct study of the dependence of energy levels on the crystal environment and for extracting some information about the electron and the environment. For this reason a lot of work on EROX:Eu³⁺ have been carried out both at ambient and at high pressure [3-7].

In the present work, the fluorescence spectra of Eu^{3+} in GdOBr:Eu³⁺ were measured at pressures ranging from 0 to 12.4 GPa. The pressure dependence of the CF levels of the Eu³⁺ in was obtained on the basis of the peak positions of the spectral lines at various pressures. The CF parameters and the free-ion parameters at different pressures were also obtained by fitting the experimental data. The pressure effect on the electron states for Eu³⁺ is discussed in this paper.

2. Experimental

The polycrystalline powder GdOBr:Eu³⁺ used in this work was prepared by a solid-state reaction between gadolinium oxide and ammonium bromide. The nominal concentration of Eu in the sample is 4 mol%. The high pressure was generated by a gasketed diamond anvil cell (DAC). The well-known 4:1 methanol-ethanol mixture was used as pressure transmitting medium and the pressure was determined by the shift of the R_1 line of the ruby.

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The fluorescence was excited by the 457.9 nm line from an argon ion laser and recorded with a Spex-1403 Raman spectrometer. All the high pressure fluorescence experiments were carried out at room temperature.

3. Results and discession

3.1. Pressure effects on the fluorescence and levels

The spectral range studied is between 21 500 and 13 000 cm⁻¹. More than 70 fluorescence lines were measured at ambient pressure. These spectral lines were assigned to transitions from the CF levels of the ${}^{5}D_{0-2}$ multiplets to that of the ${}^{7}F_{0-5}$ multiplets according to the work published by Hölsä and Porcher [2]. Because the amount of Gd0Br:Eu³⁺ in the sample chamber of DAC is very small and the fluorescence from Eu³⁺ in Gd0Br:Eu³⁺ weakens obviously with increasing pressure, the number of the fluorescence lines measured at high pressure is less than that at ambient pressure. At low pressures about 56 lines were recorded, some of them became ambiguous and hard to be recognized under pressures above 6 GPa. At pressure of 12 GPa only the 26 stronger spectral lines could be

Table 1

The positions (cm⁻¹) of the 26 stronger luminescence lines for GdOBr:Eu¹⁺ at normal pressure and their average redshift rates (cm⁻¹/ GPa)

Transition	Assignment	Position	redshift rate
$D_0 \rightarrow F_0$	A, →A,	17 232	5.0
'D _o →'F	$A_1 \rightarrow A_2$	17 020	5.6
	A,→E	16 767	4.3
$D_0 \rightarrow F_2$	A,→E	16 257	6.0
	A,→A,	16 103	1.9
[°] D ₀ → ⁷ F,	A,→E	15 337	3.0
	A,→E	15 265	4.3
`D _u →'F,	$A_1 \rightarrow A_1$	14 564	4.8
	A,→E	14 341	0.4
	A, -→A,	14 285	2.7
	A,→E	14 213	0.0
[•] D ₀ → ⁷ F,	A,→A,	13 218	6.9
`D,→ ⁷ F,	$A, \rightarrow A,$	18 734	5.3
⁵ D, → ⁷ F,	E→E	18 029	6.1
$D \rightarrow F$	A,→A,	17 091	5.8
	E→B′	16 935	2.0
$D_2 \rightarrow F_0$	A,→A,	21 419	4.3
'D, → 'F	E→E	21 005	5.6
`D,→'F,	E→B″	20 479	5.9
	B'-→E	20 429	6.8
	E→B'	20 168	5.8
⁵ D,→ ⁷ F,	B″→E	19 590	3.9
`D,→'F,	E→B″	18 401	5.5
	B'→B'	18 343	4.9
$D_2 \rightarrow F_1$	B″-→E	17 761	7.2
	E→E	17 566	2.0

observed, they are all electric dipole transitions, except the ${}^5D_0(A_1) \rightarrow {}^7F_1(A_2)$ line which is a magnetic dipole transition. The peak positions of the 26 lines at normal pressure and their average redshift rates in the pressure range studied were given in Table 1. A part of the fluorescence spectra at various pressures was given in Fig. 1.

The obvious features of the fluorescence spectra for Eu³⁺ in GdOBr:Eu³⁺ are the intense ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions. The former is strongly forbidden by the free-ion selection rules, but allowed by the rules derived from group theory for C4v site symmetry. The experiments show the fluorescence of the sample is getting weaker and weaker with increasing pressure. The intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ line descends more rapidly than that of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ lines and the intensity ratio ${}^{5}D_{0} \rightarrow {}^{7}F_{0}/$ ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, obviously decreases with increasing pressure. The separation of the two lines of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition reduces under pressures below 8 GPa, which reflects that the separation of the two CF levels of the ⁷F₁ multiplet lessens with pressure up to 8 GPa. These phenomena are mainly related to the decrease in the absolute value of the CF parameter B_0^2 with pressurization below 8 GPa. According to the CF theory, the parameter B_0^2 is principally responsible for the separation of the CF levels of the 'F₁ multiplet. The smaller the $|B_0^2|$, the smaller the separation. The descent of the $|B_0^2|$ also causes a decrease of the amount of the ${}^{7}F_{20}$ component in the $|{}^{7}F_{00},A_{1} > mixed$ state. The ${}^{7}F_{20}$ component in the $|{}^{7}F_{00},A_{1}>$ mixed state is mainly responsible for the intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition.

From the experiments it was found that most of the fluorescence lines observed slowly shift to the red with pressurization, a few of the lines, such as ${}^{5}D_{0}(A_{1}) \rightarrow {}^{7}F_{2}(A_{1})$, ${}^{5}D_{0}(A_{1}) \rightarrow {}^{7}F_{4}(E)$ and ${}^{5}D_{1}(E) \rightarrow {}^{7}F_{3}(B')$ transitions, first shift to the blue and th n to the red. Only one line, ${}^{5}D_{1}(A_{2}) \rightarrow {}^{7}F_{4}(E)$, shifts to the blue at a very small rate throughout the experiments.

On the basis of the peak positions of the spectral lines measured at various pressures, the dependence of 26 CF levels, belonging to the ${}^{5}D_{0-2}$ and ${}^{7}F_{0-5}$ multiplets, on pressure was determined and plotted in Fig. 2, where the ⁷F₀ level was taken as the energy null point. The dashed lines in the figure represent the multiplet barycenters. Because some CF levels have not been determined from the experiments, these missing values of the CF levels were replaced by their calculated values in evaluating the barycenters. The calculated values of the CF levels were found out with the CF parameters B_a^k which were obtained by fitting the experimental data. The fitting details will be described below. It can be seen from Fig. 2 that some CF levels of the ${}^{7}F_{1-5}$ multiplets shift upwards and others downwards, but all of the CF levels of the ⁵D₀₋₂ multiplets move downwards under pressure. In general, the CF energy levels of the ${}^{5}D_{0-2}$ multiplets descend faster than that of the ${}^{7}F_{1-5}$ multiplets, which is the reason why most of the fluorescence lines shift to the red. From the pressure



Fig. 1. The fluorescence spectra from the ${}^{5}D_{0} \rightarrow {}^{2}F_{0,1}$ and ${}^{5}D_{2} \rightarrow {}^{2}F_{1,2}$ transitions of Eu^{**} doped in GdOBr at various pressures. (1) ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, (2) ${}^{5}D_{0} \rightarrow {}^{2}F_{1}$, (3) ${}^{5}D_{2} \rightarrow {}^{2}F_{1}$, and (4) ${}^{5}D_{2} \rightarrow {}^{2}F_{2}$.

dependence of the CF levels it was also found that below 8 GPa all the multiplet splittings studied do not increase with increasing pressure, as was usually expected. Both the CF levels of the ⁷F₁ multiplet at first come close to each other with pressure below 8 GPa and then separate from each other slowly. The splitting behaviour of the ⁷F₁ and ⁵D₁ multiplets is similar to that of the ⁷F₁ multiplet, but the decrease of the ⁷F₃ multiplet splitting with increasing pressure is much faster than that of the ⁷F₁ and ⁵D₁ multiplet splittings. For the ⁵D₂, ⁷F₄ and ⁷F₂ multiplets, the splittings do not change obviously. Under pressure, the CF level change of Eu³⁺ in GdOBr:Eu³⁺ is similar to that of Eu³⁺ in LaOBr:Eu³⁺ [3] and LaOCI:Eu³⁺ [6], but obviously different from that of Eu³⁺ in Ln₂O₂S:Eu³⁺, the CF level splittings of the ⁷F₂₋₄ and ⁵D₂ multiplets obviously increase with pressure.

The values of the barycenters of the ${}^{7}F_{0.4}$ and ${}^{5}D_{0-2}$ multiplets at different pressures were given in Table 2. In the range of the experiment pressures the multiplet

barycenters all descend by degrees with pressure. The descent of multiplet barycenters is only a few cm⁻¹ for the ${}^{7}F_{1}$ and ${}^{7}F_{2}$ multiplets, however, it is more than 60 cm⁻¹ for the ${}^{5}D_{0-2}$ multiplets.

3.2. Free-ion calculation

In calculating energy levels of a RE ion with 4f^N configuration in crystals it is convenient to consider the total Hamiltonian H as a sum of H_F and H_C . H_C is the CF Hamiltonian describing the interaction of 4f electrons with the crystal environment and is treated as a perturbation to H_F . H_F is the free-ion Hamiltonian representing the interactions inside the RE ion. It can be expressed as

$$H_{\rm F} = \sum_{k} f^{k} F_{k} + \zeta \sum_{i} s_{i} \cdot l_{i} + \alpha L(L+1) + \beta G(G_{2}) + \gamma G(R_{7}), \qquad (1)$$



Fig. 2. The pressure dependence of CF levels of the ${}^{3}F_{1}$, and ${}^{3}D_{0}$; multiplets for Eu * doped in GdOBr. The solid and hollow circles represent experimental data and the dashed lines represent the multiplet barycenters. The letters correspond to the irreducible representations of the C₄, point group to which the level were assigned.

where the first term stands for the 4f electron Coulomb repulsion, the second represents the spin-orbit coupling interaction and the others express the configuration interaction. F_i is the Slater parameters, f^A is the corresponding coefficient. ζ is the spin-orbit coupling parameter, s_i and l_i are the spin angular momentum and orbital angular momentum of the *i*th 4f electron, respectively. α , β and γ are the configuration interaction parameters, L is the total orbital angular momentum, $G(G_2)$ and $G(R_2)$ are the eigenvalues of Casimir's operators for the Lie groups G_2 and R_7 .

In the work, the experimental data available are considerably smaller. In order to minimize the number of the free-ion parameters, the parameters α , β , γ and the ratios F_4/F_2 and F_6/F_2 were fixed to reasonable values in the whole pressure range of this work, they are 20, -640, 1750, 0.1484 and 0.0161, respectively. The basis set used in the calculating of the free-ion levels includes all of the



septets, quintets and triplets and a part of the singlets. These singlets are all the ${}^{1}S$, ${}^{1}P$, ${}^{1}D$, ${}^{1}F$ and ${}^{1}G$ terms. The barycenters of the ${}^{2S+1}L_{J}$ multiplets were considered as the experimental values of the free-ion levels of ${}^{2S+1}L_{J}$, neglecting the second order effect caused by the CF. In constructing the matrix of H_{F} , the basis set mentioned above was used. In a least-squares refining calculation we started with the parameters F_{2} and ζ given by Shen [7], and the most suitable values of F_{2} and ζ were obtained by fitting to the experimental multiplet barycenters.

3.3. Pressure effect on the free-ion parameters

The best-fit values of F_2 and ζ for Eu³⁺ in GdOBr:Eu³⁺

at different pressures up to 12 GPa are listed in Table 3. The calculated values of the barycenters by using the parameters were given in Table 2. The r.m.s. deviation σ is not larger than 11 cm⁻¹ and is defined as

$$\sigma = \left[\sum_{i} \sigma_{i}^{2} / (N - M)\right]^{1/2}, \qquad (2)$$

where σ_i is the difference between the calculated and observed energies of the ith multiplet, N is the number of barycenters included and M is the number of parameters used.

From Table 3 it can be seen that the Slater parameters F_2 and the spin-orbit coupling parameter ζ decrease with

Pressure	(GPa)												
00		2.5		5.2		7.0		8.2		10.0		12.0	
Exp	Cal.	Exp.	Cal.										
	6		6	c	0	•	0	0	0	0	0	0	0
0		192	787	180	386	378	385	378	385	379	385	377	385
380	301	107.	1064	1070	1061	1067	6501	1069	1059	1070	1058	1069	1058
5/0	2001	0701	1934	1944	0261	1938	1927	1938	1926	1937	1925	1937	1925
0661	1661	SCOL	0.00	9100	2923	2910	2918	2907	2917	2902	2916	2902	2915
2933	7667	266 21	066 21	202 21	17 207	17 194	17 197	17 189	17 192	17 177	17 182	17 172	17 177
0 17 252	977 /1	10 075	18 966	18 959	18 950	18 946	18 937	18 939	18 931	18 929	18 920	18 925	18914
C86.81 .0	0/6 9/	11 438	21 449	21 419	21 428	21 406	21411	21400	21405	21 388	21 392	21 381	21 386

increasing pressure. This phenomenon can be explained by a combined covalency model [10]. The model contains two parts: the central-field covalency model and the symmetryrestricted covalency model. According to the covalency model, the open-shell 4f orbitals expand when a lanthanide ion is incorporated in a crystal.

The central-field covalency mechanism relates the decreases of the Slater parameter and the spin-orbit coupling parameter in the crystal to an isotropic expansion of the 4f electrons. This expansion is caused by screening the effective nuclear charge Z^* of the RE ion due to a spherically symmetric penetration of ligand orbitals into the RE ion. Because $F_2 \times Z^*$ and, $\zeta \propto (Z^*)^3$ for the lanthanides, the following relations nearly hold [5]

$$\Delta F_{\gamma}/F_{\gamma} = \Delta Z^{*}/Z^{*}, \tag{3}$$

and

$$\Delta \zeta / \zeta = 3 \Delta Z^* / Z^*. \tag{4}$$

This implies that the relative change in ζ is about 3 times as large as that in F_2 .

The symmetry-restricted covalency mcchanism relates the change in the free-ion parameters in the crystal to the symmetry-dependent admixture of 4f orbitals and ligand orbitals. The admixture causes the renormalization of the 4f orbitals, and its effect on F_2 and ζ is approximated by simply replacing the 4f radial wavefunctions φ_{Γ} by $N_{\Gamma}\varphi_{\Gamma}$, where N_{Γ} is the renormalization constants and Γ labels the symmetry. If the small differences in N_{Γ} are neglected, then the relations

$$\Delta F_{2}/F_{2} = 4\Delta N/N, \tag{5}$$

and

$$\Delta \zeta / \zeta = 2\Delta N / N, \tag{6}$$

are approximately tenable [5], where N represents the average value of N_I . These expressions show that the relative change in F_2 is nearly twice that in ζ .

Combining the two mechanisms, the relative decreases in F_2 and ζ can be written as

$$\Delta F_{2}/F_{2} = \Delta Z^{*}/Z^{*} + 4\Delta N/N, \tag{7}$$

and

$$\Delta \zeta / \zeta = 3\Delta Z^* / Z^* + 2\Delta N / N. \tag{8}$$

From the data given in Table 3 one finds that the variations in F_2 and ζ under pressure up to 12 GPa amount to 0.35 and 0.54%, respectively. The relative decrease of ζ/ζ with respect to $\Delta F_2/F_2$ is about 1.6 times. The direct use of Eq. (7) and Eq. (8) gives for this case $\Delta Z^*/Z^* = -0.15\%$ and $\Delta N/N = -0.05\%$. This result indicates that the contribution from the central-field covalency model to the decrease of F_2 and ζ is mainly in the case of Eu³⁺.

Parameter	Pressure (GPa)								
	0	2.5	5.2	7.0	8.2	10.0	12.0		
<i>F</i> ,	351.36	351.17	350.83	350.58	350.46	350.25	350.14		
Ċ	1341.79	1340.54	1338.05	1336.29	1335.82	1334.97	1334.59		
σ	9.8	10.0	9.3	8.5	9.1	10.2	10.5		

Table 3 Slater parameters (cm $^{-1}$) and spin-orbit coupling parameters (cm $^{-1}$) of Eu $^{+}$ in GdOBr:Eu $^{+}$ under different pressures

3.4. Pressure effect on the crystal field

When a crystal is in compression, its interatomic distance contracts, which brings about a change in the interaction between the central ion and its crystal environment. This change is embodied by the variation of the CF parameters. For the C_{4v} site symmetry of the Eu³⁺ ion in GdOBr:Eu³⁺ the CF Hamiltonian H_C is described by five nonzero CF parameters B_a^{4}

$$H_{\rm C} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4 (C_{-4}^4 + C_4^4) + B_0^6 C_0^6 + B_4^6 (C_{-4}^6 + C_4^6),$$
(9)

where C_q^k is the tensor operator associated with the spherical harmonics by

$$C_{q}^{k} = [4\pi/(2k+1)]^{1/2} \sum_{i} Y_{q}^{k}(\theta_{i}, \varphi_{i}).$$
(10)

To derive these parameters the 26 experimental energy levels available at various pressures were used. In the calculation, the ⁷F and ⁵D manifolds have been considered. In the constructing of the matrix of H_c the intermediate coupling wavefunction was used and J-mixing caused by H_c was taken into account. The free-ion energies of the diagonal elements of H_F were treated as adjustable parameters, one for each $^{2s+1}L_J$. The eigenvalues and eigenfunctions of the CF levels in ⁷F_J and ⁵D_J were obtained by diagonalizing the matrix of H. By adjusting the related param ⁴ers to fit the CF levels observed, the best fitting values of B_q^k were found out from the refining calculation. These values at different pressures are listed in Table 4.

These parameters B_q^k reproduce the level scheme of the Eu³⁺ ion in GdOBr quite well. It can be seen from Table 4

Table 4 CF parameter set B_q^i (cm⁻¹), CF strength parameter S (cm⁻¹) for GdOBr:Eu¹ at different pressures

Pressure	B_0^2	B ⁴ ₀	B ⁴	B ⁶	Β'₁	S
0.0 GPa	- 1091	- 984	860	890	387	445
2.5 GPa	- 1078	- 901	848	925	367	436
5.2 GPa	- 1021	- 846	864	1009	358	429
7.0 GPa	- 988	-828	867	1070	343	426
8.2 GPa	- 966	-814	866	1090	360	424
10.0 GPa	- 962	-767	879	1104	314	421
12.0 GPa	-973	- 776	879	1119	314	424

that the values of B_q^4 at ambient pressure are consistent with that reported by Hölsä and Porcher [2] well. The r.m.s. deviation between the calculated and observed CF levels is not greater than 10 cm⁻¹. With increasing pressure the values of $|B_0^2|$, $|B_0^4|$ and B_0^4 tend to decrease, but that of B_4^4 and B_0^6 have an increasing tendency. Except for B_0^4 , they change with pressure in a similar way to LaOBrEu³⁺ [3].

In order to study the dependence of the CF strength on pressure, the CF strength parameter S at different pressures was evaluated using the values of B_{q}^{k} in Table 4 according to [2]:

$$S = \left\{\frac{1}{3}\sum_{k}\frac{1}{2k+1}\left[(B_{0}^{k})^{2} + 2\sum_{q>0}|B_{q}^{k}|^{2}\right]\right\}^{1/2}.$$
 (11)

S is an invariant under arbitrary rotation of the crystal lattice and also a quantitative measure of the CF strength. The values of S at various pressures up to 12 GPa for GdOBr:Eu³⁺ are also shown in Table 4. The value of S decreases by 5.4% in the pressure range of this work. This situation bears a resemblance to that in LaOBr:Eu³⁺ [3] and LaOCI:Eu³⁺ [6], but is contrary to that in Ln₂O₂S:Eu³⁺ [8,9].

It is known that J-mixing is caused by the CF. In the CF calculation the eigenfunctions of the CF energy levels were extracted. The results showed that the change regularity of the J-mixing effect with pressure is in agreement with that of the CF, i.e. under pressure the descent of the J-mixing effect is closely correlated to the weakening of the CF strength.

Acknowledgments

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