Influence of Pressure on Free-Ion and Crystal Field Parameters of Eu^{3+} in $\text{Y}_2\text{O}_3\text{S:Eu}$

Shenkin Liu*, Yuanbin Chi, Chunxiao Gao, Lizhong Wang, and Guangtian Zou

*Changchun Institute of Physics, Academia Sinica, Changchun 130021, China

National Laboratory of Superhard Materials, Jilin University, Changchun 130023, China

In this paper the pressure dependence of crystal field (CF) parameters and free-ion parameters of the Eu^{3+} ion in $\text{Y}_2\text{O}_3\text{S:Eu}$ is studied experimentally in the pressure range from 0 to 13 GPa. Pressure strengthens the interionic interaction in the crystal. The CF strength parameter S increases by a factor of 11%. The Slater parameter F_2 and the spin-orbit parameter show about 0.4 % and 0.2 % decrease, respectively.

[pressure, crystal field, free-ion parameter, energy level, $\text{Y}_2\text{O}_3\text{S:Eu}$]

1. Introduction

$\text{Y}_2\text{O}_3\text{S:Eu}$ is one of the most important phosphors. The study of its physical and chemical properties has both theoretical and technological interest. In order to understand deeply and improve this material, a lot of researches have been made in recent thirty years. High pressure can continuously reduce the interionic distance and change the interaction between ions in crystals. The luminescence spectra of the Eu^{3+} ion are familiar to us because of its characteristic energy levels. This feature makes it easy to interpret the spectra. The luminescence of Eu^{3+} is an useful probe for studying the ion interaction in crystals.

We studied the pressure dependence of CF parameters of the Eu^{3+} ion in $\text{Y}_2\text{O}_3\text{S:Eu}$ on a strongly reduced 7F_1 ($J=0-6$) level basis ten years ago [1]. In this work we studied the changes in the Stark levels and the barycenters of the multiplets ^{25+1}L , with pressure again and examined the pressure dependence of CF parameters and free-ion parameters on an extended level basis.

2. Experimental

A sample of polycrystalline $\text{Y}_2\text{O}_3\text{S:Eu}$ was used in this work. It was prepared by a solid reaction at high temperature. The concentration of Eu is 4 mol.%. The high-pressure luminescence measurements were carried out with a gasketed diamond-anvil cell. The sample, ruby chips and pressure-transmitting medium were placed in the hole in the gasket. The ruby chips were used to determine the pressure in the hole. The well-known 4:1 methanol-ethanol mixture was used as the medium.

The luminescence of the sample was excited by the 457.9 nm line of an argon-ion laser and recorded with a Spex-1403 monochromator at room temperature. About 50 spectral lines ranging from 11500cm^{-1} to 21500cm^{-1} were received at ambient pressure and at high pressure up to 16 GPa.

3. Results and discussion

3.1. Pressure effect on the luminescence and energy levels

The spectral lines measured in this work originate from the electron transitions between $^3D_{0,2}$ and $^7F_{0,5}$ multiplets. Their assignment was made according to the articles published by Sovers et al [2] and by Alves et al [3]. All lines shifted to the red and their intensities decreased with increasing pressure. When the pressure was higher than 13 GPa, some of them were too weak to record. The red-shift rates observed were not larger than $9\text{cm}^{-1}/\text{GPa}$. On the basis of the peak positions of the spectral lines measured at various pressures, the positions of the 22 levels were

determined at pressures up to 13 GPa. These levels belong to the $^7F_{0,4}$ and $^5D_{0,2}$ multiplets. The ground state 7F_0 was taken as the energy reference. The result was given in Table 1.

From the table we can see that all the levels lower with pressure except $^7F_1(E)$. The levels of $^5D_{0,2}$ lower faster than that of $^7F_{1,4}$ do. The both levels of 7F_1 close to each other with pressure. And so do the both levels of the 5D_1 multiplet.

Making use of these Stark levels the barycenters of the $^7F_{0,4}$ and $^5D_{0,2}$ multiplets can be obtained at various pressures. The values of the barycenters of the multiplets were listed in Table 2.

Because the level $^7F_3(A)$ could not be obtained from the spectral lines, in the calculation of the 7F_3 multiplet barycenter the calculated value of the $^7F_3(A)$ level was used to take the place of its observed value. From the table it is obvious that the 7F_1 multiplets change slowly and the 5D_1 multiplets descend more fast with increasing pressure. This phenomenon shows that in the same term ^{25+1}L the multiplet barycenters change with pressure in much the same way.

3.2. Effect on the crystal field

When a rare earth ion is incorporated in a crystal its energy levels are shifted and split into so-called CF levels because of the effect of the crystal environment. This effect is embodied in the CF. In a crystal the Hamiltonian H of a rare earth ion can be written as

$$H = H_F + H_C \quad (1)$$

H_F is the free ion Hamiltonian describing the interaction within the 4f electrons. H_C is the CF Hamiltonian representing the interaction between the rare earth ion and its crystalline environment.

In $\text{Y}_2\text{O}_3\text{S}$ the point symmetry of the Y^{3+} ion site is C_{3v} . For the Eu^{3+} ion in $\text{Y}_2\text{O}_3\text{S:Eu}$ the CF Hamiltonian H_C can be represented by six nonzero crystal field parameters B_q^k as follows[2].

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

The tensor operators C_q^k are related to the spherical harmonics Y_q^k by

$$C_q^k = [4\pi/(2k+1)]^{1/2} \sum_i Y_q^k(\theta_i, \varphi_i) \quad (3)$$

In the summation the i runs over all 4f electrons in the Eu^{3+} ion. In calculation of the matrix elements the intermediate coupling wavefunctions were used. We calculated the matrix elements of H_C between 7F , 5D and 5G terms. The J-mixing caused by CF was taken into account by involving the off-diagonal elements between states with different J values. For the sake of time saving we had the off-diagonal elements between 7F and 5D or 5G states equal to 0 because different spin values make the elements extremely small. Thus the resulting matrix is a 119×119 square-matrix, the direct sum of a 49×49 square matrix and a 70×70 one. A set of parameters selected gave a matrix and by diagonalizing it the calculated Stark levels were obtained. Then we adjusted the CF parameters to fit the calculated levels into the observed ones, so that an optimal set of CF parameters was achieved at the end.

The best values of B_q^k sets for the Eu^{3+} ion in $\text{Y}_2\text{O}_3\text{S:Eu}$ are given in Table 3 and the calculated Stark levels are listed in Table 1. The rms deviations of the calculation are also given in Table 3. In comparison to the values reported previously [1] it can be seen that the σ values did not increase due to considering the ${}^5D_{0,2}$ multiplets in the calculation.

In order to describe the CF strength quantitatively, a CF strength parameter S has been introduced. It can be evaluated from the B_q^k parameters according to the formula [4]

$$S = \left\{ \frac{1}{3} \sum_k \frac{1}{2k+1} \left[(B_0^k)^2 + 2 \sum_{q>0} (B_q^k)^2 \right] \right\}^{1/2} \quad (4)$$

The values of S obtained are listed in Table 3. The CF strengthens with increasing pressure because of the enhancement of the interaction between the central ion and its crystalline environment.

3.3. Effect of pressure on the free-ion energies

From Table 2, we can see that 5D term lowers obviously with pressure. These changes show that the pressure influences the interaction inside the Eu^{3+} ion.

In the 4f configuration the Hamiltonian H_F can be written as [5]

$$H_F = \sum_k f^k F_k + \sum_i \zeta \bar{S}_i \cdot \bar{L}_i + [\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7)] \quad (5)$$

The first term represents the interelectronic repulsion. F_k are the Slater parameters and f^k the corresponding coefficients. The second is the spin-orbit interaction and ζ the spin-orbit coupling parameter. The last term is the so-called configuration interaction.

And α , β , γ are the configuration interaction parameters, $G(G_2)$ and $G(R_7)$ the eigenvalues of Casimir's operators for Lie groups G_2 and R_7 . In order to minimize the number of free 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 calculation. They are 20, -640, 1750, 0.1484 and 0.0161 respectively. After constructing the matrix of H_F , free-ion energies can be obtained by diagonalizing it. In the least-squares refining calculation the best-fit values of F_2 and ζ for Eu^{3+} in $\text{Y}_2\text{O}_3\text{S:Eu}$ at pressures were obtained and listed in Table 4. The rms deviations were also listed in the same table. The free-ion

Table 1. The observed and calculated values [in cm^{-1}] of the Stark levels of the Eu^{3+} ion in $\text{Y}_2\text{O}_3\text{S:Eu}$ at pressures.

		0.0 GPa		2.5 GPa		5.0 GPa		7.5 GPa		10.0 GPa		13.0 GPa	
		exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.
7F_1	E	351	351	352	352	352	352	354	353	356	354	357	359
	A	387	387	383	384	378	380	374	377	370	373	365	361
7F_2	E	917	920	914	918	910	914	907	912	904	909	900	902
	A	946	945	941	944	935	938	930	933	924	927	918	926
7F_3	E	1192	1189	1195	1190	1199	1194	1202	1196	1206	1200	1208	1202
	A	1867	1868	1867	1869	1866	1869	1866	1869	1865	1868	1865	1868
7F_4	E	1882	1880	1880	1878	1878	1877	1876	1875	1874	1873	1872	1871
	A	1921	1921	1924	1919	1926	1920	1928	1920	1930	1921	1934	1928
7F_4	E	1929	1930	1929	1931	1929	1932	1929	1932	1929	1932	1930	1931
	A		2026		2028		2032		2033		2036		2039
7F_4	A	2596	2586	2591	2584	2585	2576	2580	2572	2574	2564	2570	2559
	E	2803	2809	2801	2803	2799	2801	2797	2799	2794	2797	2792	2794
7F_4	A	2858	2854	2858	2856	2858	2857	2859	2858	2859	2859	2860	2859
	E	2969	2963	2971	2968	2874	2971	2976	2972	2978	2974	2981	2977
7F_4	A	3003	3011	3006	3018	3009	3022	3012	3025	3015	3030	3017	3025
	E	3023	3023	3026	3026	3029	3029	3032	3032	3035	3034	3038	3041
5D_0	A	17155	17156	17141	17141	17127	17127	17113	17113	17098	17098	17082	17082
5D_1	E	18907	18908	18893	18893	18879	18879	18867	18868	18851	18853	18832	18832
	A	18915	18912	18899	18899	18883	18883	18867	18868	18851	18853	18832	18832
5D_2	E	21330	21331	21313	21314	21295	21296	21278	21279	21260	21262	21240	21242
	A	21395	21391	21379	21375	21363	21359	21346	21344	21329	21329	21310	21304
5D_2	E	21408	21409	21392	21393	21376	21376	21360	21360	21344	21343	21330	21331

Table 2. Experimental and calculated multiplet barycenters (cm^{-1}) of the Eu^{3+} ion in $\text{Y}_2\text{O}_3\text{S:Eu}$ at different pressures.

	0.0 GPa		2.5 GPa		5.0 GPa		7.5 GPa		10.0 GPa		13.0 GPa	
	exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.
$^7\text{F}_1$	363	382	362	383	361	383	361	382	361	382	360	382
$^7\text{F}_2$	1039	1052	1037	1053	1036	1053	1034	1052	1033	1052	1030	1052
$^7\text{F}_3$	1919	1915	1920	1915	1920	1915	1020	1915	1920	1914	1920	1914
$^7\text{F}_4$	2892	2902	2893	2901	2893	2901	2893	2900	2894	2900	2894	2899
$^5\text{D}_0$	17155	17173	17127	17143	17127	17143	17113	17128	17098	17113	17082	17096
$^5\text{D}_1$	18910	18901	18880	18871	18880	18871	18865	18856	18850	18840	18832	18823
$^5\text{D}_2$	21372	21363	21338	21332	21388	21332	21322	21316	21304	21299	21286	21281

Table 3. CF parameter set B_q^k (cm^{-1}), CF strength parameter S (cm^{-1}) and rms deviation (cm^{-1}) for $\text{Y}_2\text{O}_3\text{S:Eu}^{3+}$ at different pressures (GPa).

P	B_0^2	B_0^4	B_2^4	B_0^6	B_2^6	B_4^6	σ	S
0.0	118	798	1121	576	-276	414	6	373
2.5	110	767	1145	526	-274	494	5	378
5.0	97	801	1165	534	-282	518	6	387
7.5	86	820	1183	528	-286	532	6	394
10.0	70	843	1208	529	-300	547	7	402
13.0	16	716	1292	616	-251	546	6	414

Table 4. Values of Slater Parameter F_2 and spin-orbit coupling parameter (cm^{-1}) for Eu^{3+} in $\text{Y}_2\text{O}_3\text{S}$ at different pressures

Pressure(GPa)	F_2	ζ	rms deviation
0.0	349.85	1329.78	14.2
2.5	349.57	1329.58	14.1
5.0	349.28	1329.08	14.1
7.5	349.00	1328.53	14.3
10.0	348.69	1328.04	14.2
13.0	348.37	1327.36	14.9

energies calculated by using these values of F_2 and ζ were given in Table 2.

From Table 4 it can be seen that F_2 and ζ decrease with increasing pressure. At 13 GPa the relative reductions in F_2 and ζ nearly equal to 0.4 % and 0.2 %, respectively. This result shows that the reductions are mainly due to so-called symmetry-restricted covalency mechanism[6]. In this model the decrease of free-ion parameters is ascribed to the admixture of the electron state of the ligands into the states of the open shells in the RE ions and the relative reduction in F_k is about twice as large as the one in ζ .

Acknowledgement

This work is supported by the National Natural Science Foundation of China.

References

- [1] Liu Shenxin, Chi Yuanbin, and Wang Lizhong, *J.Lumin.*, **40&41** 395 (1988).
- [2] O. J. Sovers, and T. Yoshioka, *J. Chem. Phys.*, **49**,4954(1968).
- [3] R. V. Alver, J.J.Pearson, K.A.Wickersheim, and R.A.Buchanan, *Proc. 8th Rare Earth Research Conf. Reno, VN*, 703(1970).
- [4]N.C.Chang, J.B.Gruber, R.P.Leavitt, C.A.Morrison, *J.Chem. Phys.*, **76**, 3877(1982).
- [5]B.G.Wybourne, *Spectroscopic Properties of Rare Earths*, Wiley, New York, 1965.
- [6]Qiuping Wang and A.Bulou, *J.Phys.: Condens.Matter*, **5**, 7657(1993).