Effect of pressure on electron state of Eu^{3+} in Gd_2O_2S

Chi Yuanbin[a],*, Liu Shenxin[b], Wang Qiuping[c], Wang Lizhong[a]

[a] *National Laboratory of Superhard Materials, Jilin University, Changchun 130023, People's Republic of China*
[b] *Changchun Institute of Physics, Academia Sinica, Changchun 130021, People's Republic of China*
[c] *Physics Department of Harbin Normal University, Harbin 150080, People's Republic of China*

Abstract

The fluorescence spectra of Eu^{3+} in Gd_2O_2S have been measured at room temperature and under pressures within the range of 0–14.8 GPa. The crystal-field levels of the $^7F_{0-6}$ and $^5D_{0-2}$ multiplets of the Eu^{3+} ion have been determined at different pressures. With increasing pressure the crystal-field splittings of the $^7F_{2-5}$ and $^5D_2$ multiplets increase; however, the splittings of $^7F_1$ and $^5D_1$ decrease. The crystal-field parameters B_q^k and the crystal-field strength parameter S_t versus B_q^k were also determined at different pressures. In the pressure range up to 14.8 GPa, S_t increases by 11%. Under pressure, the barycenters of the $^7F_{1-2}$ and $^5D_{0-2}$ multiplets descend, the Slater parameter F_2 and the spin-orbit coupling parameter ζ reduce. The symmetry-restricted covalency mechanism plays a main role in the reduction of F_2 and ζ. © 1998 Elsevier Science B.V. All rights reserved.

PACS: 71.70.Ch; 81.40.Vw; 71.55. − i; 78.55. − m

Keywords: Fluorescence spectra; Eu^{3+}; Gd_2O_2S

1. Introduction

When a rare earth (RE) ion is embedded in a crystal, its level scheme is changed, the multiplet barycenters are shifted, the energy levels split into so-called crystal-field (CF) levels. These phenomena show that the electron state of an RE ion in a crystal differs from that of a free RE ion obviously, owing to the influence of the crystal environment.

Pressure can continuously reduce the interatomic distance in condensed matter, thus it is a powerful experimental tool used to study the electron state of an RE ion (as a center of luminescence) in a crystal and the interaction between the RE ion and its ligands.

In recent years, a lot of work concerned with high-pressure study of electron behavior had been carried out and some valuable results were obtained [1–10].

In this work the spectra of $Gd_2O_2S : Eu^{3+}$ were measured under pressures up to 14.8 GPa. From the experimental data the pressure dependences of

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* Corresponding author.

the energy levels for the Eu^{3+} ion were determined. The CF parameters B_q^k, the Slater parameter F_2 and the spin-orbit coupling parameter ζ were obtained at different pressures. The related calculation of these parameters and the discussion about their changes with pressure are given in this paper.

2. Experiments and results

The sample used in this work is polycrystalline $Gd_2O_2S : Eu^{3+}$ powder prepared by a solid reaction at high temperature. The concentration of Eu^{3+} in the sample is nominally 4.7 mol%. The 488 nm line and the 457.9 nm line of an argon ion laser were used to excite the sample. The fluorescence spectra were recorded with a Spex-1403 Raman Spectrometer. A gasketed diamond anvil cell was used for generating high pressure. A methanol–ethanol–water mixture (methanol : ethanol : water $= 16 : 3 : 1$) was used as the pressure transmitting medium which can give hydrostatic pressure environment up to 14 GPa. The pressure experienced by the sample was determined by the shift of the ruby R_1-line. All the measurements were performed at room temperature.

About 120 fluorescence lines in the range of $11\,500$–$21\,500$ cm^{-1} were measured and assigned to the electron transitions between the $^5D_{0-2}$ and $^7F_{0-6}$ multiplets of the Eu^{3+} ion with the help of Refs. [11,12]. Because the volume of the sample in the diamond anvil cell is very small and the fluorescence intensity descends with increasing pressure, the number of spectral lines observed at high pressure is much smaller than that at ambient pressure, and the higher the pressure, the smaller the number is. For example, 83 lines were observed at 1.2 GPa and only 33 lines at 14.8 GPa. A part of the fluorescence spectra from $Gd_2O_2S : Eu^{3+}$ at different pressures are presented in Fig. 1. The peak positions of the 33 stronger lines at ambient pressure and their average pressure coefficients in the pressure range of the experiments are given in Table 1. From the table it can be seen that all spectral lines shift to the red at various rates between 2 cm^{-1} GPa^{-1} and 9 cm^{-1} GPa^{-1}. On the basis of the peak positions of the spectral lines measured at
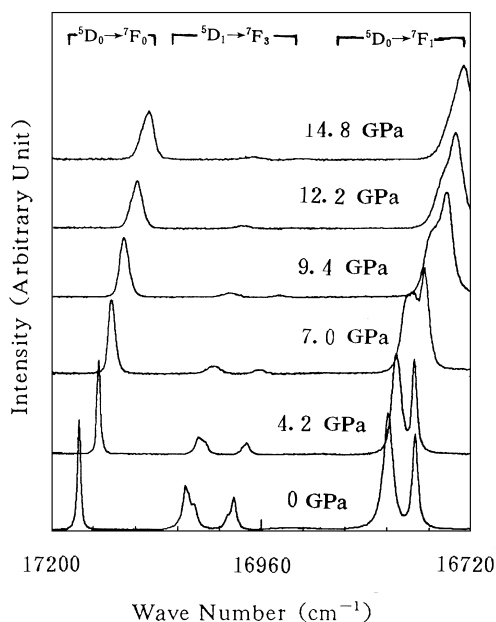

Fig. 1. Part of fluorescence spectra of Eu^{3+} in Gd_2O_2S at different pressures.

various pressures, the CF levels belonging to the multiplets $^7F_{1-6}$ and $^5D_{0-2}$ have been determined at corresponding pressures and are plotted in Fig. 2. In Fig. 2 the dashed lines represent the multiplet barycenters and the $^7F_0$ singlet was taken as the energy zero-point. Some CF levels of the $^7F_{1-6}$ multiplets shift upwards and others downwards, but all of the CF levels of the $^5D_{0-2}$ multiplets move downwards with increasing pressure. Furthermore, the CF levels of the $^5D_{0-2}$ multiplets shift much faster than that of the $^7F_{1-6}$, which is the reason why all fluorescence lines shift to the red. From Fig. 2 it can be seen that with pressurization the splittings of all multiplets observed in this work increase except that of $^7F_1$ and $^5D_1$, which decrease. Under pressure the change of the multiplet-splittings of Eu^{3+} in Gd_2O_2S is similar to that of Eu^{3+} in Y_2O_2S [7] and La_2O_2S [9], but is in contrast with that in REOX : $Eu^{3+}(X = Cl, Br)$. For REOX : Eu^{3+} [4,10,13] the CF splittings of the ^7F_J and ^5D_J multiplets tend to decrease under pressure.

The values of the barycenters of the $^7F_{0-4}$ and $^5D_{0-2}$ multiplets at different pressures are given in

Table 1
Positions (in cm^{-1}) of the 33 stronger fluorescence lines at ambient pressure and their average pressure coefficients (in cm^{-1} GPa^{-1}) for Eu^{3+} in Gd$_2$O$_2$S

Transition	Assignment	Position	Pressure coefficient
$^5D_0 \rightarrow {}^7F_0$	$A_1 \rightarrow A_1$	17168	− 5.3
$^5D_0 \rightarrow {}^7F_1$	$A_1 \rightarrow E$	16815	− 5.1
	$A_1 \rightarrow A_2$	16784	− 3.7
$^5D_0 \rightarrow {}^7F_2$	$A_1 \rightarrow A_1$	16221	− 3.1
	$A_1 \rightarrow E$	15976	− 6.0
$^5D_0 \rightarrow {}^7F_3$	$A_1 \rightarrow E$	15284	− 5.2
	$A_1 \rightarrow A_1$	15247	− 5.8
$^5D_0 \rightarrow {}^7F_4$	$A_1 \rightarrow A_1$	14560	− 2.9
	$A_1 \rightarrow E$	14206	− 6.2
	$A_1 \rightarrow E$	14167	− 6.3
	$A_1 \rightarrow A_1$	14147	− 6.5
$^5D_0 \rightarrow {}^7F_5$	$A_1 \rightarrow A_1$	13397	− 3.6
	$A_1 \rightarrow E$	13112	− 5.8
$^5D_0 \rightarrow {}^7F_6$	$A_1 \rightarrow E$	12045	− 6.1
$^5D_1 \rightarrow {}^7F_0$	$E \rightarrow A_1$	18921	− 5.3
$^5D_1 \rightarrow {}^7F_1$	$A_2 \rightarrow A_2$	18544	− 4.6
$^5D_1 \rightarrow {}^7F_2$	$E \rightarrow E$	17994	− 3.9
$^5D_1 \rightarrow {}^7F_3$	$E \rightarrow A_2$	17047	− 5.3
	$E \rightarrow A_1$	16998	− 6.0
$^5D_1 \rightarrow {}^7F_4$	$E \rightarrow E$	16113	− 4.6
	$E \rightarrow A_2$	16064	− 5.6
$^5D_2 \rightarrow {}^7F_0$	$E \rightarrow A_1$	21411	− 6.2
	$E \rightarrow A_1$	21347	− 6.6
$^5D_2 \rightarrow {}^7F_1$	$E \rightarrow A_2$	20963	− 5.4
$^5D_2 \rightarrow {}^7F_2$	$E \rightarrow E$	20156	− 7.8
$^5D_2 \rightarrow {}^7F_3$	$A_1 \rightarrow E$	19536	− 5.0
	$A_1 \rightarrow E$	19490	− 5.9
	$E \rightarrow E$	19461	− 5.6
	$E \rightarrow E$	19418	− 7.5
$^5D_2 \rightarrow {}^7F_4$	$E \rightarrow A_1$	18800	− 3.8
	$E \rightarrow E$	18383	− 7.6
$^5D_2 \rightarrow {}^7F_5$	$A_1 \rightarrow A_2$	17535	− 7.1
	$E \rightarrow A_2$	17458	− 8.2

Table 2. The multiplet barycenters of $^7F_{1-2}$ and $^5D_{0-2}$ descend by degrees with pressure. Up to 14.8 Gpa the descents of multiplet barycenters are about 10 cm^{-1} for $^7F_1$ and $^7F_2$, however, they are more than 80 cm^{-1} for $^5D_{0-2}$. The barycenter of $^7F_4$ multiplet keeps invariant bascially throughout the pressure range. With pressurization the barycenter of the $^7F_3$ multiplet first descends and then ($p > 6$ GPa) rises slowly.

3. Energy level simulation and discussion

The Hamiltonian of an RE ion embedded in a crystal can be written as

$$H = H_F + H_C. \qquad (1)$$

H_F is the free-ion Hamiltonian, it respresents the interactions inside the RE ion, such as the Coulomb repulsion between 4f electrons, the spin-orbit coupling, the configuration interaction etc. H_C is the CF Hamiltonian describing the interaction between the RE ion and its crystal environment, it was treated as a perturbation to H_F. These interactions are expressed with the help of some phenomenological parameters. To determine these parameters, the calculations were performed in two steps. First, the CF parameters were adjusted to fit the experimental CF levels, secondly the free-ion parameters were adjusted to fit the experimental multiplet-barycenters.

3.1. CF calculation and effect of pressure on the CF strength

The Eu^{3+} ion in Gd$_2$O$_2$S has C$_{3v}$ site symmetry, its CF Hamiltonian can be expressed as

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

in which the tensor operators C_q^k are related to the spherical harmonics Y_q^k by the equation

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

the coefficients B_q^k are the CF parameters to be determined. In the calculation a 119×119 matrix which concludes the matrix elements between ^7F, ^5D and ^5G terms was constructed. The ^5G term was involved because its energy levels are very close to and strongly mixed with the energy levels of the ^5D_J multiplets. In calculating the matrix elements of H_C the intermediate-coupling wave functions of Eu^{3+} were used; they included all the compositions of septet and quintet states. The J-mixing caused by the CF was also taken into account by including the off-diagonal matrix elements between the states
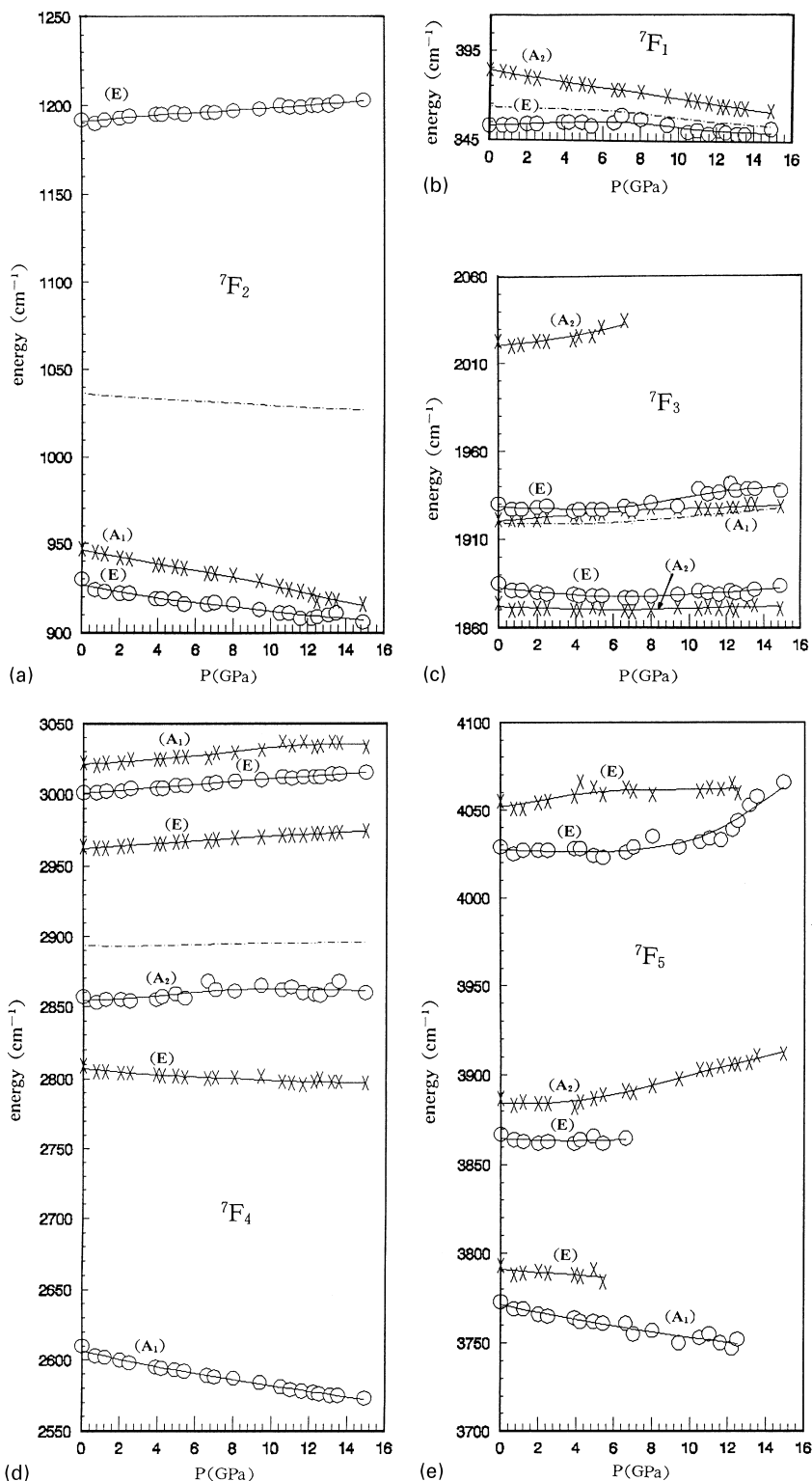
Fig. 2. Pressure dependences of CF levels of the $^7F_{1-6}$ and $^5D_{0-2}$ multiplets for Eu^{3+} in Gd_2O_2S. The dashed lines represent the barycenters of the multiplets.

Fig. 2. Continued.

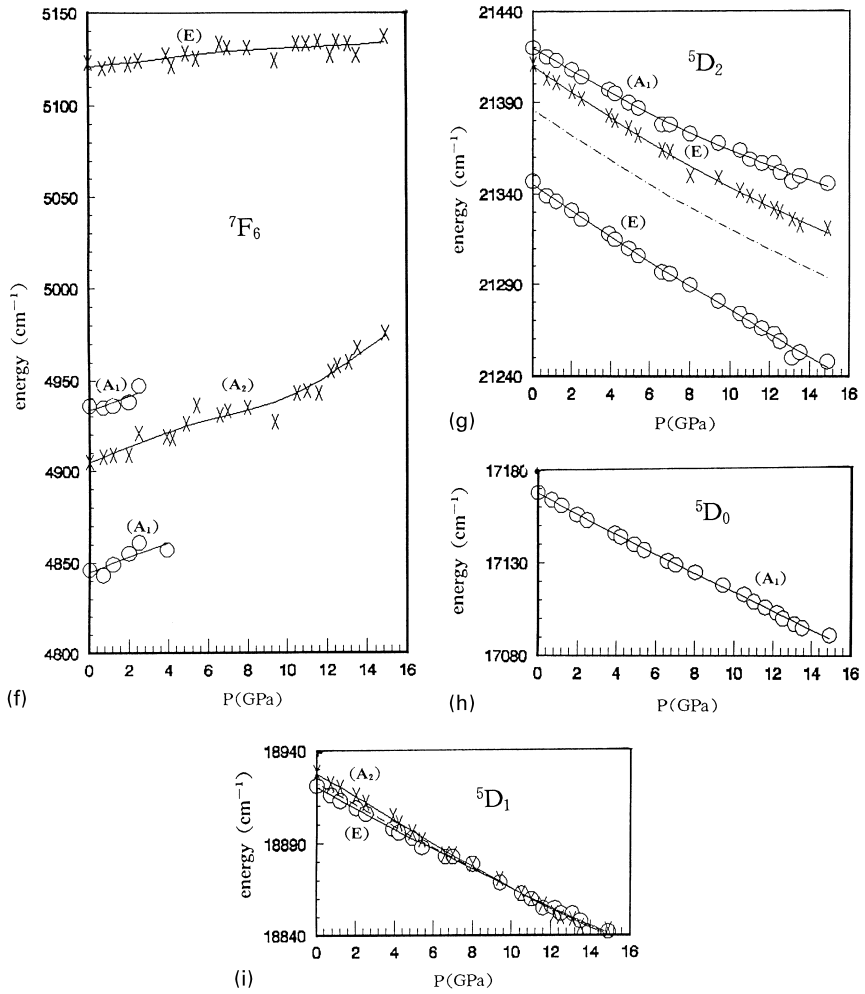Table 2
Experimental and calculated multiplet-barycenters (in cm^{-1}) for Eu^{3+} in Gd$_2$O$_2$S at different pressures

	0.0 GPa		4.0 GPa		8.0 GPa		12.0 GPa		14.8 GPa	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
$^7F_0$	0	0	0	0	0	0	0	0	0	0
$^7F_1$	363	383	362	382	360	382	355	382	354	383
$^7F_2$	1038	1054	1033	1052	1031	1052	1027	1052	1028	1053
$^7F_3$	1921	1917	1918	1915	1921	1914	1925	1915	1928	1916
$^7F_4$	2895	2905	2893	2901	2895	2900	2895	2900	2895	2901
$^5D_0$	17168	17185	17145	17162	17125	17140	17104	17118	17088	17103
$^5D_1$	18923	18915	18899	18889	18879	18868	18855	18846	18842	18832
$^5D_2$	21387	21379	21359	21351	21331	21328	21310	21305	21297	21293

Table 3
CF parameter set B_q^k, CF strength parameter S_t and rms deviation σ for $Gd_2O_2S : Eu^{3+}$ at various pressures (cm^{-1})

P (GPa)	B_0^2	B_0^4	B_3^4	B_0^6	B_3^6	B_6^6	σ	S_t
0.0	166	869	1048	368	− 376	448	15	364
2.0	144	891	1065	373	− 379	471	13	370
4.0	138	897	1084	378	− 392	479	12	376
6.0	135	906	1093	385	− 397	503	12	381
8.0	115	934	1105	390	− 388	530	11	387
10.0	101	951	1111	398	− 385	556	11	391
12.0	80	982	1112	415	− 376	581	10	396
14.8	43	1029	1114	439	− 361	625	13	404

with the same S-values but different J-values, the off-diagonal matrix elements between the ^7F_J states and the excited states (^5D_J and ^5G_J) were omitted. Our calculations showed that this omission had almost no influence on the results of the calculations. Thus the resulting 119×119 matrix is a direct sum of a 49×49 matrix and a 70×70 matrix. The free-ion energies of the diagonal elements were treated as adjustable intermediate parameters, one for each $^{2S+1}L_J$.

By adjusting the CF parameters and the intermediate parameters to make the eigenvalues of Hamiltonian H fit to the values of the 28 CF levels observed, the best-fit values of the CF parameters B_q^k at different pressures are listed in Table 3. The deviations between the calculated and observed CF levels of the ^5D_J multiplets are not larger than that of the ^7F_J multiplets. The rms deviations of the calculations are not larger than $15\ cm^{-1}$.

In order to study the dependence of the CF on pressure, the values of CF strength parameter S_t at different pressures were evaluated using the values of B_q^k in Table 3 according to Chang's definition [14]

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

S_t is an invariant under arbitrary rotation of the crystal lattice and is also a quantitative measure of the CF strength. The values of S_t at various pressures up to 14.8 GPa are also shown in Table 3. For $Gd_2O_2S : Eu^{3+}$ the CF strength parameter

S_t increases with pressure. This reveals that the increase in pressure leading to decrease of nuclear separation has strengthened the crystal field acting on Eu^{3+}. At pressure of 14.8 GPa the value of S_t increases by 11%. The wave functions extracted from the CF calculation show that the increase in CF strength brings about a corresponding increase of J-mixing for Eu^{3+} in Gd_2O_2S.

3.2. Simulation of free-ion levels

In the free-ion calculation the observed value of a multiplet barycenter was considered as the free-ion energy of the multiplet, ignoring the second-order effect caused by the CF. Neglecting some weak interactions, the Hamiltonian H_F can be written as

$$H_F = \sum_k f^k F_k + \zeta \sum_i s_i \cdot l_i + [\alpha L(L+1)$$

$$+ \beta G(G_2) + \gamma G(R_7)]. \quad (5)$$

The first term represents the Coulomb repulsion of 4f electrons, F_k are the Slater parameters; the second term stands for the spin–orbit coupling interaction interaction and ζ is the spin–orbit coupling parameter; the last term expresses the configuration interaction, α, β and γ are the configuration interaction parameters.

In this work the experimental data available are limited. 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 the reasonable values 20, − 640, 1750, 0.1484 and 0.0161 [3,15] in the whole pressure range of this work, respectively. The set of basis functions used in the calculation of the free-ion levels includes all the septets, quintets and triplets and some singlets. These singlets are all the ^1S, ^1P, ^1D, ^1F and ^1G terms. By using the set of basis functions a 272×272 matrix of H_F was constructed and it can be resolved into several sub-matrices according to their J-values. In the fitting calculation seven experimental multiplet barycenters ($^5D_{0-2}$ and $^7F_{0-4}$) were used to determine the values of F_2 and ζ.

3.3. Pressure effect on free-ion parameters

Using above-mentioned procedure the pressure dependence of the parameters F_2 and ζ was derived from the high-pressure data of $Gd_2O_2S:Eu^{3+}$ up to 14.8 GPa. The variations of F_2 and ζ under pressure are illustrated in Figs. 3 and 4, respectively. The calculated values of the free-ion levels for Eu^{3+} in Gd_2O_2S are given in Table 2. The rms deviation σ increases from 13.9 cm^{-1} at ambient pressure to 18.0 cm^{-1} at 14.8 GPa.

The slater parameter F_2 and the spin-orbit coupling parameter ζ reduce with increasing pressure, which results in the shifts of the multiplet barycenters of Eu^{3+} in Gd_2O_2S. At 14.8 GPa the relative reductions in F_2 and ζ amount to about 0.4% and 0.2%, respectively. Because the fluorescence from Eu^{3+} in Gd_2O_2S weakens obviously with increasing pressure, at pressures higher than 6 GPa, the experimental errors of some CF levels are greater. Thus the calculated data of ζ in Fig. 4 are not regular in 8–14.8 GPa.

The pressure compels the nuclear separation between the Eu^{3+} ion and its ligands to decrease, which makes the 4f electron of Eu^{3+} in Gd_2O_2S delocalize, as a result the free-ion parameters reduce. In other words, the reductions of the Slater parameter F_2 and the spin-orbit coupling parameter ζ can be ascribed to the 4f electron cloud expansion of the Eu^{3+} ion in Gd_2O_2S. This expansion is modeled by two different covalency mechanisms [16]: the central-field covalency mechanism (CFCM) and the symmetry-restricted covalency mechanism (SRCM). According to the models, the open-shell 4f orbitals expand when a RE ion is incorporated in a crystal. The CFCM relates the reductions of the Slater parameter F_2 and the spin-orbit coupling parameter ζ in a crystal to an isotropic expansion of the 4f electrons. This expansion is caused by screening the effective nuclear charge Z_{ef} of the RE ion. Because $F_2 \propto (Z_{ef})$ and $\zeta \propto (Z_{ef})^3$ for the lanthanides, the following relations nearly hold [16]:

$$\Delta F_2/F_2 = \Delta Z_{ef}/Z_{ef}, \qquad (6)$$

and

$$\Delta\zeta/\zeta = 3\Delta Z_{ef}/Z_{ef}. \qquad (7)$$

This implies that the relative reduction in ζ should be about three times as large as that in F_2, which is not consistent with our result. So the CFCM does not play a main role in the reductions of F_2 and ζ.

The SRCM relates the changes of F_2 and ζ in a 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 orbitals φ_Γ by $N_\Gamma\varphi_\Gamma$, where N_Γ is the

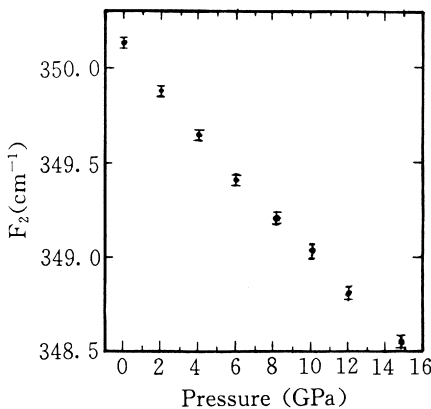
Fig. 3. Variation of the Slater parameter F_2 for $Gd_2O_2S:Eu^{3+}$ under pressure.

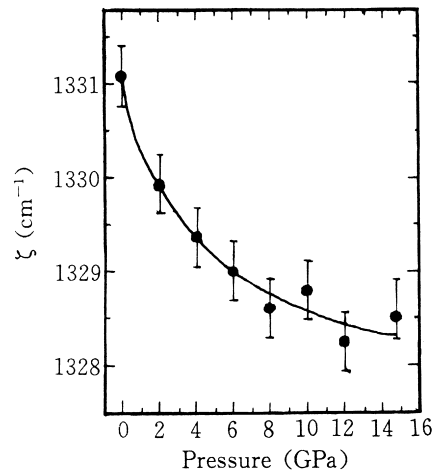Fig. 4. Variation of the spin-orbit coupling parameter ζ for $Gd_2O_2S:Eu^{3+}$ under pressure.

renormalization constant and Γ labels the symmetry. If small differences in N_Γ are neglected, then the relations

$$\Delta F_2/F_2 = 4\Delta N/N, \tag{8}$$

and

$$\Delta\zeta/\zeta = 2\Delta N/N, \tag{9}$$

are approximately tenable [16], where N represents the average value of N_Γ. These expressions show that the relative reduction in F_2 is nearly twice as that in ζ.

Combining the two mechanisms, the reductions in F_2 and ζ are given by the expressions

$$\Delta F_2/F_2 = \Delta Z_{ef}/Z_{ef} + 4\Delta N/N, \tag{10}$$

$$\Delta\zeta/\zeta = 3\Delta Z_{ef}/Z_{ef} + 2\Delta N/N. \tag{11}$$

By using these relations and the relative reductions of the free-ion parameters at 14.8 GPa it can be found that $\Delta Z_{ef}/Z_{ef} \doteq 0$ and $\Delta N/N \doteq -0.1\%$, which means the SRCM plays a main part in the reductions of F_2 and ζ.

The situation $Gd_2O_2S : Eu^{3+}$ is quite different from that in $GdOBr : Eu^{3+}$. For Eu^{3+} in GdOBr the relative reduction in ζ is always larger than that in F_2 and the central-field covalency mechanism is mainly responsible for the reductions in F_2 and ζ [13].

Acknowledgements

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