

## Hypersensitive and forbidden transitions of trivalent europium ion in $\text{Tb}_{1.8}\text{Eu}_{0.2}(\text{MoO}_4)_3$ single crystal

S SHEIK SALEEM\* and T K K SRINIVASAN

Regional Sophisticated Instrumentation Centre, Indian Institute of Technology,  
Madras 600036, India

\*Present address: Department of Physics, Pondicherry Engineering College,  
Pondicherry University, Pondicherry 605 104, India

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**Abstract.** The fluorescent transitions  ${}^5D_{0,1} \rightarrow {}^7F_J$  ( $J=0-4$ ) of the europium ion in the  $\text{Tb}_{1.8}\text{Eu}_{0.2}(\text{MoO}_4)_3$  single crystal were recorded at 300 and 20 K. The forbidden and the hypersensitive transitions were observed in this system. The intensity ratio between  ${}^5D_0 \rightarrow {}^7F_1$  and  ${}^5D_0 \rightarrow {}^7F_2$  which is 1:5 is discussed in the light of covalency between the  $\text{Eu}^{3+}$  ion and  $\text{MoO}_4$  tetrahedra.

**Keywords.** Hypersensitive transition; europium ion; Raman spectra; forbidden transition;  $\text{Tb}_{1.8}\text{Eu}_{0.2}(\text{MoO}_4)_3$  crystal.

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### 1. Introduction

Trivalent europium ions in solids are often used as a structural probe since the absorption and emission spectra show marked dependence on its site symmetry in the host material. Extensive spectroscopic studies (Huber *et al* 1978; Faucher and Dexpert-Ghys 1981; Holsa and Porcher 1982; Ouwerkerk and Blasse 1980) have been made to characterize the energy distributions of  ${}^7F_J$  and  ${}^5D_J$  levels of  $\text{Eu}^{3+}$  ions doped in different host materials. This is possible due to the relatively high fluorescence intensity of ( ${}^5D_{0,1} \rightarrow {}^7F_J$ ) transitions even at 300 K.

It is known that the bands of  $\text{Eu}^{3+}$  in optical spectra due to  $J=2 \leftrightarrow 0$  transitions are sensitive to the environment in which  $\text{Eu}^{3+}$  is embedded. Such transitions are termed hypersensitive by Jorgensen (1962). Recently we have reported the vibrational (Saleem *et al* 1983a,b) and electronic (Saleem *et al* 1983c, 1984) spectra of  $\text{Tb}_{1.8}\text{Eu}_{0.2}(\text{MoO}_4)_3$  (hereafter denoted as TEMO). In this paper we report the fluorescent measurement of  ${}^5D_0 \rightarrow {}^7F_J$  transition of the  $\text{Eu}^{3+}$  ion in TEMO crystal at 300 and 20 K to understand the nature of the hypersensitive ( ${}^5D_0 \rightarrow {}^7F_2$ ) and forbidden ( ${}^5D_0 \rightarrow {}^7F_0$ ) transitions of  $\text{Eu}^{3+}$  ion in TEMO crystal.

### 2. Experimental

Optically good quality single crystal grown by Czochralski technique in the form of a disc (radius 4 mm, thickness 0.75 mm) is used for the present investigation. A laser

Raman spectrometer (Cary 82) equipped with a Ar<sup>+</sup> laser (Spectra Physics model 165) was used to obtain the spectra. The fluorescent transitions  ${}^5D_{0,1} \rightarrow {}^7F_J$  are excited with the 514.5 nm emission line of the Ar<sup>+</sup> laser. For investigations at 20 K, a cryodyne cryocooler was used. The sample was held at the tip of the copper rod connected to the cold head of the cryodyne. The temperature at the sample was measured with a gold-copper thermocouple.

### 3. Results and discussion

#### 3.1 Selection rules

The structure of TEMO is isotypic with Tb<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (Svensson *et al* 1979). Electric dipole transitions within the 4f shell of a rare-earth ion are allowed if the surroundings of the ion are such that its nucleus is not situated at the centre of inversion (Judd 1962). The theory of electric dipole transitions occurring between 4f ground state configurations was developed by Judd (1962) and Ofelt (1962). When there is no *J*-mixing, the selection rules for electric dipole transitions are:

$$\Delta S = 0, \quad L \leq 6, \quad J \leq 6$$

and if the initial state has a *J* value of zero then  $\Delta J = 2, 4, 6$  (Porcher and Caro 1980). The appropriate selection rule for magnetic dipole transitions  $\Delta J = 0, \pm 1; 0 \leftrightarrow 0$  is forbidden (Holsa and Porcher 1981). By this rule, for the europium ion the  ${}^5D_0 \rightarrow {}^7F_0$  and  ${}^5D_1 \rightarrow {}^7F_3$  transitions are prohibited. For the low symmetry cases corresponding to *C<sub>s</sub>*, *C<sub>n</sub>* and *C<sub>nv</sub>* point groups, the above transitions are allowed by group theory and are often observed (Blasse and Brill 1966). In particular, the  ${}^5D_0 \rightarrow {}^7F_0$  transition which has a pure electric dipole character is very interesting because of the strong dependence of its intensity on the nature of the crystalline matrix.

The hypersensitive transition can occur only in symmetries such as *C<sub>s</sub>*, *C<sub>1</sub>*, *C<sub>2</sub>*, *C<sub>2v</sub>*, *C<sub>3v</sub>*, *C<sub>4v</sub>*, *C<sub>6</sub>* (Judd 1966). The intensity ratio of  ${}^5D_0 \rightarrow {}^7F_1: {}^5D_0 \rightarrow {}^7F_2$  between forced ED transitions (*J* = 2) and magnetic dipole (*J* = 1) can be used as an indicator for the relative magnitude of hypersensitivity.

#### 3.2 Fluorescence spectra

The observed spectrum at room temperature and at 20 K in the region 2180–3300 cm<sup>-1</sup> is shown in figure 1. Table 1 describes the assignments of the fluorescence transitions at 300 and 20 K. Since the energy of the exciting line 514.5 nm (19436 cm<sup>-1</sup>) is well above the  ${}^5D_0$  and  ${}^5D_1$  energies of the Eu<sup>3+</sup> ion, fluorescence transitions from these levels to the ground  ${}^7F_J$  have been observed in the Raman spectra in the region 2000–3600 cm<sup>-1</sup>. The spectra recorded for the six different Raman tensors are the same except for slight differences in intensity. The very high intensity of the bands in this region compared to the normal modes of the molybdate ions (Saleem *et al* 1983a) in the region 10–2000 cm<sup>-1</sup> by a maximum factor of  $2 \times 10^2$  indicates that these bands are not due to multiphonon modes.

The strong and sharp line at 2202 cm<sup>-1</sup> is due to the  ${}^5D_0 \rightarrow {}^7F_0$  transition for which the equivalent energy is (19436–2202) 17234 cm<sup>-1</sup>. This transition which is parity-forbidden in the case of the free ion is allowed only through *J*-mixing effects (Blasse and

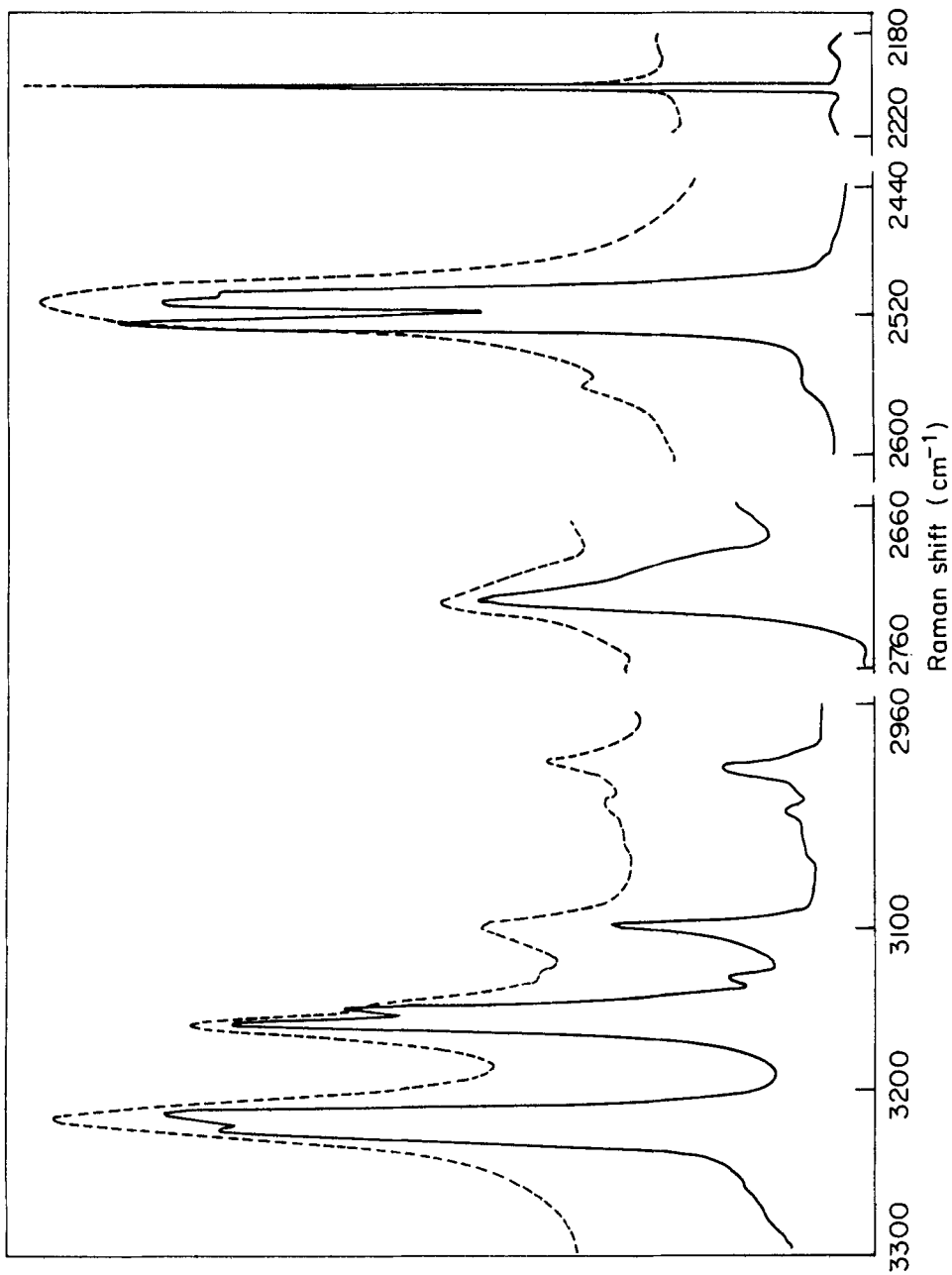


Figure 1. Fluorescence transitions observed in the Raman spectrum of TEMO in the region 2000–3500  $\text{cm}^{-1}$  at 300 K (—) and 20 K (---).

**Table 1.** Fluorescence transitions of TEMO in the region 2000–3500  $\text{cm}^{-1}$  at 300 and 20 K and their assignments.

Fluorescence lines		Equivalent energy* (in $\text{cm}^{-1}$ )	Assignments	
300 K	20 K			
2202	(45 × 2)†	2202	17234	$^5D_0 \rightarrow ^7F_0$
		2501	16935	$^5D_1 \rightarrow ^7F_3$
		2507	16929	$^5D_0 \rightarrow ^7F_1$
2508	(90 × 2 × 10 <sup>2</sup> )		16928	$^5D_0 \rightarrow ^7F_1$
		2520	16906	$^5D_1 \rightarrow ^7F_3$
		2558	16878	$^5D_0 \rightarrow ^7F_1$
2560	(18 × 2 × 10 <sup>2</sup> )		16876	$^5D_0 \rightarrow ^7F_1$
		2716	16720	$^5D_0 \rightarrow ^7F_1$
2720	(28 × 2)		16716	$^5D_0 \rightarrow ^7F_1$
3001	(12 × 10 <sup>3</sup> )	3001	16435	$^5D_0 \rightarrow ^7F_2$
3026	(5 × 10 <sup>3</sup> )		16410	$^5D_1 \rightarrow ^7F_4$
3044	(2 × 10 <sup>3</sup> )	3029	16407	$^5D_1 \rightarrow ^7F_4$
			16392	$^5D_1 \rightarrow ^7F_4$
		3048	16388	$^5D_1 \rightarrow ^7F_4$
		3100	16336	$^5D_0 \rightarrow ^7F_2$
3102	(12 × 10 <sup>3</sup> )		16334	$^5D_0 \rightarrow ^7F_2$
3150	Sh	3150	16286	$^5D_1 \rightarrow ^7F_4$
3161	(40 × 10 <sup>3</sup> )	3161	16275	$^5D_0 \rightarrow ^7F_2$
		3214	16222	$^5D_0 \rightarrow ^7F_2$
3217	(90 × 10 <sup>3</sup> )		16219	$^5D_0 \rightarrow ^7F_2$
		3228	16208	$^5D_1 \rightarrow ^7F_4$
3376	(4 × 10 <sup>3</sup> )		16060	$^5D_1 \rightarrow ^7F_4$
3440	(23 × 10 <sup>3</sup> )		15996	$^5D_0 \rightarrow ^7F_2$

\* Equivalent energy: Exciting energy – Raman shift; Exciting energy: 514.5 nm (19436  $\text{cm}^{-1}$ ); † Intensity values from peak heights; Sh = Shoulder.

Brill 1966). The observation of this transition in a way confirms the crystallographic data that the  $\text{Eu}^{3+}$  ion replaces the  $\text{Tb}^{3+}$  ion in the  $C_1$  site of  $\text{Tb}_2(\text{MoO}_4)_3$  structure (Borchardt and Bierstedt 1976). The most interesting feature of the spectra is the high intensity of the  $^5D_0 \rightarrow ^7F_0$  transition. A similar increase in intensity of this transition with increasing ionic radius of the host cation was observed earlier (Holsa and Porcher 1981). This can be applied in the present case since the ionic radius of  $\text{Eu}^{3+}$  is less than that of the host cation which is  $\text{Tb}^{3+}$ . Also, the high intensity can be correlated with interstate mixing as suggested by Kirby and Richardson (1983).

The half bandwidth of the  $^5D_0 \rightarrow ^7F_0$  at 20 K is  $\sim 4 \text{ cm}^{-1}$  as compared to  $2 \text{ cm}^{-1}$  in the case of  $\text{Eu}_2\text{O}_3$  (Rice and DeShazer 1969). We presume that in TEMO there are two slightly different sites of  $C_1$  symmetry causing the inhomogeneous broadening. The differences arise from the slightly different position of the  $\text{Eu}^{3+}$  ion and small variations in the crystal field parameters.

The intense line at  $2508 \text{ cm}^{-1}$  ( $16928 \text{ cm}^{-1}$ ) along with the others at 2560 and  $2720 \text{ cm}^{-1}$  is due to  $^5D_0 \rightarrow ^7F_1$  transitions. This assignment leads to a separation of  $306 \text{ cm}^{-1}$  between  $^7F_0$  and  $^7F_1$  and a splitting of  $212 \text{ cm}^{-1}$  for the  $^7F_1$  levels which are in good agreement with previous results (Koningstein and Grunberg 1971; Dieke 1963;

Bonnet *et al* 1978; Holsa and Porcher 1982). At 20 K the line at  $2508 \text{ cm}^{-1}$  splits into three lines having energies 2520, 2507 and  $2501 \text{ cm}^{-1}$ . Of these the intense line at  $2520 \text{ cm}^{-1}$  and the shoulder at  $2501 \text{ cm}^{-1}$  are assigned to the  ${}^5D_1 \rightarrow {}^7F_3$  transitions. This assignment is in agreement with the previous results (Holsa and Porcher 1982) and also reasonable since the split lines cannot be assigned to  ${}^5D_0 \rightarrow {}^7F_1$  because the three  ${}^5D_0 \rightarrow {}^7F_1$  transitions have already been assigned and no other  ${}^5D_{0,1} \rightarrow {}^7F_J$  transitions have their energies in this region.

Groups of lines in the region 2970–3300 ( $16466\text{--}16136 \text{ cm}^{-1}$ ) are due to  ${}^5D_0 \rightarrow {}^7F_2$  and  ${}^5D_1 \rightarrow {}^7F_4$  transitions. The strong lines at 3001 (16435), 3102 (16334), 3161 (16275), 3217 (16219) and 3440 (15970)  $\text{cm}^{-1}$  have been assigned to the  ${}^5D_0 \rightarrow {}^7F_2$  transitions. These transitions are the strongest among the observed  ${}^5D_0 \rightarrow {}^7F_J$  ( $J=0$  to 6) transitions. At 20 K all these lines gain intensity due to the increased Boltzmann population in the ground state and some new lines appear which are assigned to  ${}^5D_1 \rightarrow {}^7F_4$  transitions. The intensity ratio between  ${}^5D_0 \rightarrow {}^7F_1$  and  ${}^5D_0 \rightarrow {}^7F_2$  is found to be 1:5. The observed high intensity of the  ${}^5D_0 \rightarrow {}^7F_2$  transition provides another example for the influence of hypersensitivity. The ratio 1:5 is higher (1:3 for phosphate and 1:4.2 for silicate) than that observed for silicate and phosphate glasses and phosphate crystals (Reisfeld and Lieblisch 1973; Blanzat *et al* 1980) doped with  $\text{Eu}^{3+}$  ion. It can be said that the increase in the intensity of the hypersensitive bands in TEMO is due to the increased covalency between the  $\text{Eu}^{3+}$  ion and the oxygen atom of the Mo-O tetrahedra.

The increased covalency can also be established by calculating the optical electronegativity  $\chi$  for the  $\text{MoO}_4$  tetrahedra using the relation  $\sigma_{\text{obs}} = 30000 (\chi_{\text{opt}} - \chi_{\text{uncorr}})$  considering the values of  $\chi_{\text{uncorr}}$  (Eu) as 1.9 (Wybourne 1965) and  $\sigma_{\text{obs}}$  is the peak value of the charge transfer band. The lower the electronegativity of the tetrahedra the larger is the participation of the oxygen atom in the covalent bonding with the rare earth. The charge transfer band has been observed at 330 nm (Saleem *et al* 1983c) in TEMO which gives a value of 2.91 for  $\chi_{\text{opt}}$ . This is much lower than the values of 3.53 and 4.0 calculated respectively for P-O and Si-O tetrahedra. Hence the increase in the covalency between  $\text{Eu}^{3+}$  and oxygen of the  $\text{MoO}_4$  tetrahedra in TEMO, compared to  $\text{SiO}_4$  and  $\text{PO}_4$  tetrahedra.

#### 4. Conclusion

The observed high intensity of the forbidden  ${}^5D_0 \rightarrow {}^7F_0$  transitions confirm the diffraction data that the  $\text{Eu}^{3+}$  ion replaces the  $\text{Tb}^{3+}$  in  $C_1$  site in the  $\text{Tb}_2(\text{MoO}_4)_3$  structure (Borchardt and Bierstedt 1976). The higher ratio of 1:5 for the  ${}^5D_0 \rightarrow {}^7F_1 : {}^5D_0 \rightarrow {}^7F_2$  transition indicates increased covalency between the  $\text{Eu}^{3+}$  oxygen of the  $\text{MoO}_4$  tetrahedra.

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