Structural and Optical Investigations of Sodium Europium Carbonate Na₃Eu(CO₃)₃

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The crystal structure and the luminescence properties of a new carbonate, $Na_3Eu(CO_3)_3$, are presented. $Na_3Eu(CO_3)_3$ is orthorhombic, acentric, *Ama*2, $Z = 4$; $a = 9.942(2)$ Å, $b = 11.024(3)$ Å, $c = 7.147(2)$ Å; $R = 0.019$, $R_W = 0.051$, 2374 unique reflections. The anionic subnetwork is built up from the stacking of "standing on edge" and "flat lying" carbonate layers into which Na^+ and Eu^{3+} ions are inserted. The symmetry of the EuO_9 polyhedra is C_s. The Eu^{3+} luminescence technique confirms the presence of a unique low symmetry site for the rare earth atom. The electrostatic crystal field (cf) effects on the ^7F multiplet are evaluated on the basis of the phenomenological cf theory. The simulation using C_{2v} symmetry for the rare earth atom gives good agreement between the calculated and experimental $^7F_{0-6}$ energy level schemes (r.m.s. standard deviation 8.9 cm⁻¹). Out of 49 theoretical $^7F_{JM}$ Stark components, 39 observed components are deduced from the absorption and emission spectra. © 1997 Academic Press

INTRODUCTION

In the search for new rare-earth-based phosphors, we started to explore mixed systems containing fluoride and carbonate entities. The static luminescence properties of $KGd(CO_3)F_2 : Eu^{3+}$ (1), $Na_3La_2(CO_3)_4F : Eu^{3+}$ (2), $BaEu(CO_3)_2F$ (2), and $Ba_3Eu(CO_3)_2F_3$ (3) were studied.

These compounds were obtained at high temperature (740°C) and high pressure (200 MPa) under hydrothermal conditions from alkaline or alkaline earth carbonates and rare earth fluorides (4, 5, and references therein). At variance from these results, however, an anionic exchange between the starting materials Na_2CO_3 and EuF_3 occurs in aqueous solution at low temperature (220°C) and autogenous pressure (2 MPa) and leads to $Na_3Eu(CO_3)_3$.

In the first part of this paper we report on the crystal structure of this new carbonate, $Na_3Eu(CO_3)_3$, and in the second part on its luminescence properties.

EXPERIMENTAL

$Na_3Eu(CO_3)_3$ is obtained in Teflon-lined PARR autoclaves (internal volume 25 cm³). The experimental conditions are as follows: 2.59 g Na_2CO_3, 1.02 g EuF_3, 5 cm³ H_2O, 220°C, 3 days.

Single crystals were selected by optical examination and X-ray diffraction data were collected on a Siemens AED2 four-circle diffractometer. The crystal cell of $Na_3Eu(CO_3)_3$ was obtained from long exposure rotation photographs. The conditions of the intensity measurement are reported in Table 1, with crystal data. The scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-Ray Crystallography (6). Absorption effects were corrected by the Gauss method.

The optical absorption measurements of $Na_3Eu(CO_3)_3$ were performed on a powder sample at room temperature and at 9 K. A Cryodyne Refrigeration System Model 22C was used for low temperature measurements. It consists of a compressor and a cold head. The temperature is regulated by an autotuning temperature controller Lake Shore Model 330. The spectra were recorded on a Cary 2400 spectrophotometer in the UV, the visible, and the IR wavelength regions from 300 to 2500 nm (33,000 to 4000 cm⁻¹).

The luminescence of $Na_3Eu(CO_3)_3$ was obtained from a powder sample under the 457.9 nm excitation of a Spectra Physics 164 Ar-ion laser. A Spectra Physics 375/376 continuous wave dye laser (with rhodamine 6G as the dye) pumped by an argon-ion laser was also used to excite selectively the lowest excited ^5D level, $^5D_0$ at 580 nm. For the narrowing of the line transitions at lower temperatures

TABLE 1
Crystallographic Data and Conditions of Data Collection for $Na_3Eu(CO_3)_3$

Crystal dimensions (mm³)	$0.12 \times 0.13 \times 0.03$
Absorption (cm⁻¹)	$\mu = 82.1$
Space group	$Ama2$
Z	4
Parameters	
a (Å)	9.942(2)
b (Å)	11.024(3)
c (Å)	7.147(2)
Volume (Å³)	783.4(3)
Calculated density	3.400
Secondary extinction factor	$1.3(9) \times 10^{-8}$
Weighting scheme $w = 1/(\sigma^2(F_0) + (aP)^2 + bP)$ where $P = (\max(F_0^2 \text{ or } 0) + 2F_c^2)/3$	$\begin{cases} a = 0.0341 \\ b = 7.36 \end{cases}$
Number of refined parameters	85
Max Δ/σ	0.05
Reliability factors R; wR_2	0.0195; 0.051
Max, min heights in the final difference fourier map (e Å⁻³)	+2.36, −2.35
Centering reflections ($2\Theta \approx 30°$)	40
Reflections for refined cell parameters	40 (scans at $\pm \Theta$)
Scan mode ω-2Θ in N steps of $\Delta\omega = 0.035°$	$37 \leq N \leq 45$
Data collection range	$2\Theta \leq 80°$
Aperture (mm)	4.5×4.5
Measured reflections	2770
Two measured centrosymmetric sets in mmm symmetry	$|h| < 12, |k| < 19, |l| < 17$
Standard reflections	0 4 4; 2 4 0; −2 4 0
Maximum standard intensity variation	2%
Independent reflections ($I > 2\sigma(I)$)	2374

the luminescence was studied at liquid nitrogen temperature. The liquid nitrogen temperature was attained by immersing the sample in liquid nitrogen in a quartz sample holder. The emission was dispersed by a 1-m Jarrell–Ash monochromator and detected by a Hamamatsu R 374 photomultiplier. The luminescence spectra were recorded in the visible wavelength region between 400 and 750 nm.

CRYSTAL STRUCTURE OF $Na_3Eu(CO_3)_3$

The starting solution for the structure determination of $Na_3Eu(CO_3)_3$ was obtained in the centric $Cmcm$ space group by using SHELS-86 and SHELXL-93 programs (7, 8). The Patterson map analysis gave Eu atom positions. After refinement, analysis of the Fourier difference map allowed us to locate Na, C, and O atoms. At this stage, several mirror symmetry related sites with 50% occupancy were observed, leading to incoherent interatomic distances and $R = 0.10$. This last factor dropped to $R = 0.03$ when the $C2cm$ acentric space group was tested. Finally, refinements of atomic coordinates, anisotropic thermal motion, and the secondary extinction factor in the standard $Ama2$ space group converged to $R = 0.019$ and $wR = 0.051$. Note that, as in the $KCu(CO_3)F$ structure (9), the identical orientation of carbonate groups in parallel layers ("flat lying" layers, see structure description) unambiguously confirms the acentric character of the structure.

The final results are reported in Tables 2a and 2b; selected interatomic distances and angles are listed in Table 3.

C(1) and C(2) atoms occupy $8c$ ($x \approx 0$ and $\frac{1}{2}$) and $4b$ ($x = \frac{1}{4}$ and $\frac{3}{4}$) positions, respectively. Consequently, the carbonate anion subnetwork is built up from the stacking of alternating $C(1)O_3$ and $C(2)O_3$ layers, separated by $a/4$ (Fig. 1). According to the notation introduced by Grice et $al.$ (10), these $C(1)O_3$ and $C(2)O_3$ layers are respectively "standing-on-edge" and "flat-lying." Their formulation, which takes into account the presence of europium and sodium atoms in the layer planes, is $[Na(2)]_2[C(1)O_3]_4$ and $[Na(1)]_2[Na(3)]_2Eu_2[C(2)O_3]_2$ or $Na_2(CO_3)_4$ and $Na_4Eu_2(CO_3)_2$. It must be noted that the flat-lying $C(2)O_3$ layers present a pseudohexagonal symmetry with

TABLE 2a
Atomic Coordinates, Isotropic Temperature Factors (Å²), and Valence Bond in $Na_3Eu(CO_3)_3$

	x	y	z	B_{iso}(Å²)	$\sum s^a$	$\sum s_{exp}$
Na(1)	1/4	−0.2074(1)	0.0019(8)	0.55(3)	1.02	1
Na(2)	0	0	0.0667(3)	1.32(3)	1.12	1
Na(3)	1/4	0.0180(2)	0.3874(3)	1.08(2)	1.40	1
Eu	1/4	0.72838(1)	1/2	0.547(3)	3.18	3
C(1)	−0.0011(3)	0.2039(2)	0.3259(4)	0.74(3)	3.99	4
C(2)	1/4	0.0122(3)	−0.2286(5)	0.93(4)	3.95	4
O(1)	1/4	0.1158(3)	0.6924(4)	1.31(4)	2.05	2
O(2)	0.1131(2)	0.1648(2)	0.2662(3)	0.99(3)	2.20	2
O(3)	0.1093(2)	−0.1414(2)	0.2991(3)	1.14(3)	2.14	2
O(4)	1/4	0.4133(3)	0.1790(5)	1.41(4)	2.07	2
O(5)	0.0101(2)	0.1969(2)	−0.0830(4)	1.39(3)	1.98	2
O(6)	1/4	0.0096(3)	−0.0444(4)	1.10(4)	2.00	2

^{a} Valence bond $s = \exp[(R_0 - d)/0.37]$ calculated with values R_0 from Ref. (14).

TABLE 2b
Anisotropic Temperature Factors in Na₃Eu(CO₃)₃

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	0.0118(5)	0.0067(4)	0.0094(5)	0.0024(20)	0	0
Na(2)	0.0166(8)	0.0124(6)	0.0209(8)	0	0	−0.0012(6)
Na(3)	0.0137(7)	0.0102(6)	0.0170(7)	0.0022(6)	0	0
Eu	0.0070(5)	0.0061(5)	0.0077(5)	0.00045(9)	0	0
C(1)	0.0093(8)	0.0104(8)	0.0086(7)	0.0000(6)	0.0016(7)	−0.0007(7)
C(2)	0.0137(13)	0.0070(10)	0.0125(13)	−0.0022(9)	0	0
O(1)	0.0285(15)	0.0094(10)	0.0118(10)	0.0020(8)	0	0
O(2)	0.0075(6)	0.0158(7)	0.0142(7)	0.0015(6)	0.0028(5)	0.0024(6)
O(3)	0.0095(7)	0.0119(7)	0.0217(9)	0.0046(6)	−0.0034(6)	−0.0029(6)
O(4)	0.0276(15)	0.0111(10)	0.0148(11)	−0.0040(9)	0	0
O(5)	0.0140(8)	0.0164(8)	0.0222(9)	0.0108(7)	−0.0046(7)	−0.0034(7)
O(6)	0.0206(13)	0.0114(9)	0.0097(8)	0.0019(7)	0	0

$a_{\rm H} = b_{\rm H} = 0.5(b^2 + c^2)^{1/2} = 6.57$ Å and $\gamma_{\rm H} = 114.1°$ (Fig. 2); in these layers, as mentioned before, the orientation of all carbonate groups is identical. Figure 2 shows EuO₉ europium polyhedra, separated by carbonate groups. The europium atom is surrounded by three oxygen atoms in the layer plane and six others on both sides of the plane (Fig. 3). Sodium atoms occupy three crystallographic sites: Na(1) and Na(3) are sixfold coordinated while Na(2) is surrounded by eight oxygen atoms (Table 3).

ANALYSIS OF THE ABSORPTION SPECTRA

At 9 K, the absorption spectrum of Na₃Eu(CO₃)₃ consists of electronic transitions originating from the $^7F_0$ ground level alone. At 300 K all components of the $^7F_1$ level are populated, giving some $^7F_1 \rightarrow {}^{2S+1}L_J$ transitions. In fact, the spectra are not much different between the two temperatures. The energy of the peaks of the whole spectrum is reported in Table 4. The $^7F_0 \rightarrow {}^5L_6$ is the most intense transition in the spectrum. For $^7F_0 \rightarrow {}^5D_{0-2}$ elec-

tronic transitions, 1, 3, and 2 lines are observed respectively and for the $^7F_0 \rightarrow {}^7F_6$ transition (Fig. 4), almost all sublevels have been assigned. The vibronics at 430 cm^{-1} are observed for two components of the $^7F_6$ level (Fig. 4, Table 4). No vibronics for the hypersensitive $^7F_0 \rightarrow {}^5D_2$ transition are detected.

The $^5D_3$ level is not observed in the 9 K spectrum. At room temperature, several weak lines are observed at 415–420 nm (24,038, 23,938, and 23,869 cm^{-1}), corresponding certainly to the $^7F_1 \rightarrow {}^5D_3$ transition. The very weak lines situated at 31,620 and 31,377 cm^{-1} are the highest $^7F_0 \rightarrow {}^5H_{3-4}$ transitions observed in the UV region.

From absorption data it is evident that the europium ion occupies only one site in Na₃Eu(CO₃)₃. Moreover, the $^5D_1$ splitting (45 cm^{-1}) is small and indicates relatively weak two-rank crystal field (cf) parameters. The observation

TABLE 3
Selected Interatomic Distances (Å) in Na₃Eu(CO₃)₃

C(1)–O(5)	1.275(3)	C(2)–O(1)	1.274(4)	Eu–O(4)	2.407(3)
C(1)–O(2)	1.287(3)	C(2)–O(4)	1.274(5)	Eu–O(6)	2.433(3)
C(1)–O(3)	1.291(3)	C(2)–O(6)	1.317(5)	2 × Eu–O(2)	2.442(2)
				2 × Eu–O(3)	2.465(2)
				2 × Eu–O(5)	2.482(2)
				Eu–O(1)	2.525(3)
Na(1)–O(1)	2.378(4)	2 × Na(2)–O(5)	2.422(2)	2 × Na(3)–O(2)	2.285(2)
Na(1)–O(6)	2.415(3)	2 × Na(2)–O(3)	2.524(2)	2 × Na(3)–O(3)	2.333(2)
Na(1)–O(2)	2.584(4)	2 × Na(2)–O(2)	2.569(2)	Na(3)–O(4)	2.383(4)
Na(1)–O(3)	2.645(5)	2 × Na(2)–O(6)	2.611(1)	Na(3)–O(1)	2.432(4)
Na(1)–O(5)	2.659(3)				
Na(1)–O(4)	2.664(6)				
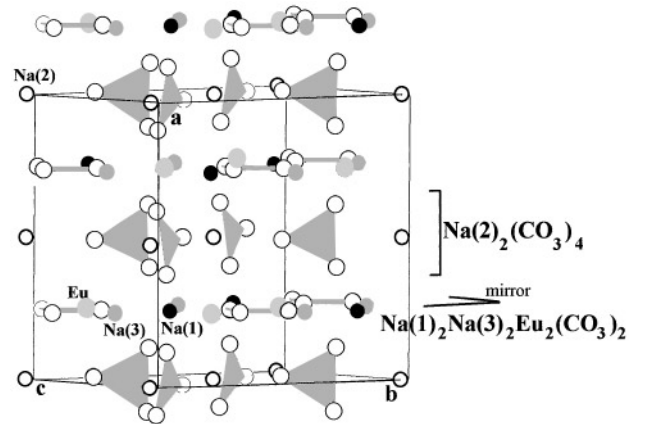
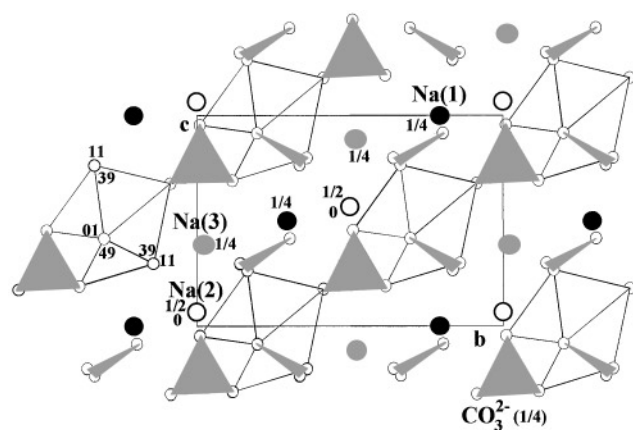**FIG. 1.** Perspective view of Na₃Eu(CO₃)₃ structure showing "flat lying" and "standing on edge" carbonate layers.

FIG. 2. Europium polyhedra (at $x = \frac{1}{4}$) connected by carbonate groups in $Na_3Eu(CO_3)_3$ (heights of the oxygen atoms in general positions are in hundreds).
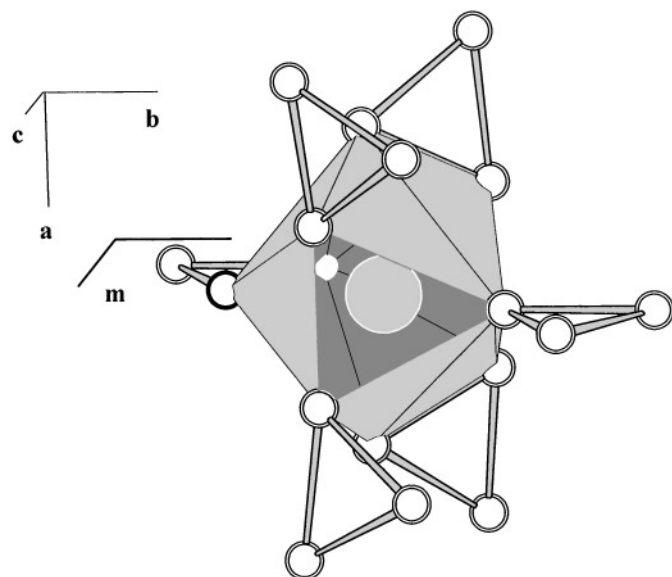
of the $^5D_0 \rightarrow {}^7F_6$ transition is of great interest for the cf simulation, especially for six-rank cf parameters (calculated energies are given in Table 4). Evidence for the presence of vibronics is shown also.

FIG. 3. Europium polyhedron and the six neighboring carbonate groups in $Na_3Eu(CO_3)_3$.

TABLE 4
Electronic Transitions of the Europium Absorption Spectrum in $Na_3Eu(CO_3)_3$ at 9 K

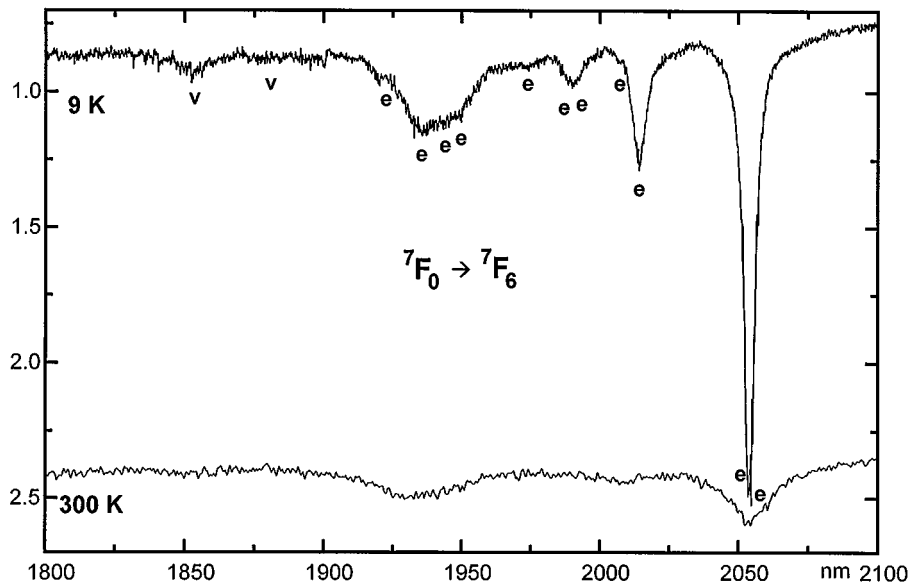| Transition	Energy (cm^{-1})	Transition	Energy (cm^{-1})			E_{calc}
$^7F_0 \rightarrow {}^5H_{3-4}$	31,620					
	31,377	$^7F_0 \rightarrow {}^5D_3$	Not observed			
$^7F_0 \rightarrow {}^5D_4$	27,762					
+	27,609	$^7F_0 \rightarrow {}^5D_2$	21,487			
$^7F_0 \rightarrow {}^5L_8$	27,465		21,453			
	27,371	$^7F_0 \rightarrow {}^5D_1$	19,011			
	27,222		18,997			
			18,966			
$^7F_0 \rightarrow {}^5G_{2-6}$	26,645					
	26,728	$^7F_0 \rightarrow {}^5D_0$	17,234			
	26,624	$^7F_0 \rightarrow {}^7F_6$		5396	C + 432	
	26,533			5305	B + 435	
	26,465				M	5216
	26,423		5208		L	5212
	26,319		5165		K	5165
$^7F_0 \rightarrow {}^5L_7$	26,189		5147		J	5159
	26,161		5130		I	5127
	26,025		5065		H	5064
	25,934				G	5054
					F	5033
$^7F_0 \rightarrow {}^5L_6$	25,358		5036		E	5021
	25,196		5024		D	4969
	25,176		4982		C	4967
	25,117		4964		B	4871
	25,044		4870		A	4867
	24,960		4869			
	24,941					
	24,885					

FIG. 4. Part of absorption spectra of Eu^{3+} ions in $Na_3Eu(CO_3)_3$ at 9 and 300 K.

ANALYSIS OF THE LUMINESCENCE SPECTRA

The emission spectrum of $Na_3Eu(CO_3)_3$ ($\lambda_{exc} = 457.9$ nm) consists of a great number of narrow lines attributed to $^5D_0 \rightarrow {^7F_{0-5}}$ electronic transitions (Fig. 5). Several extra lines, due to vibronics and to a very small amount of impurity, were detected too. The luminescence arises practically alone from the $^5D_0$ level to the ground ^7F_J multiplet. This fact is due to the high concentration of europium ions and probably to multiphonon de-excitation: all transitions from higher ^5D_J ($J = 1$–2) levels are then quenched to $^5D_0$.
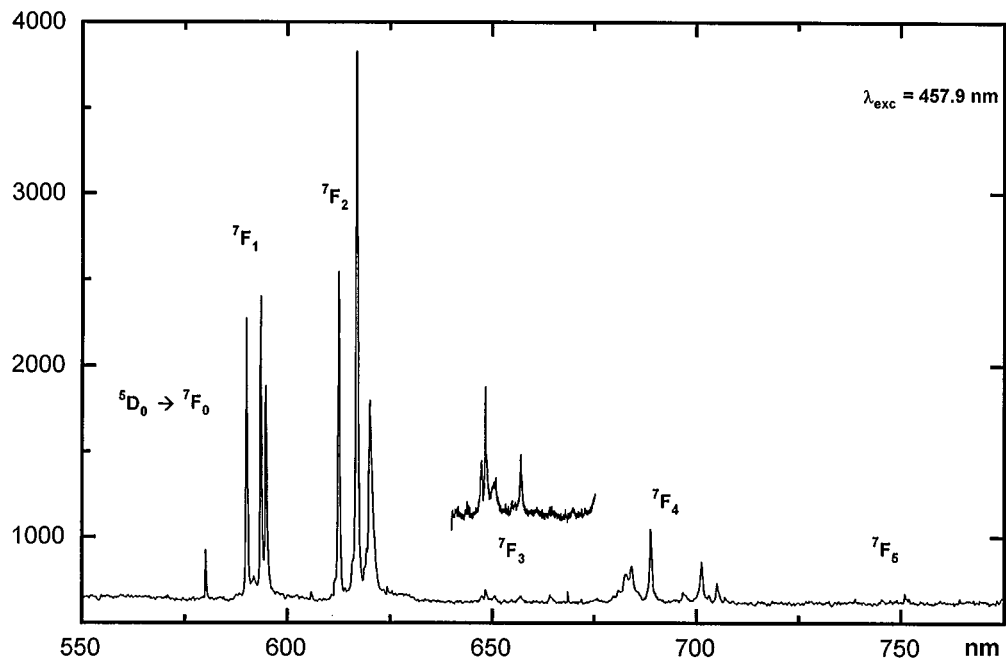

FIG. 5. Luminescence spectrum of Eu^{3+} in $Na_3Eu(CO_3)_3$ ($\lambda_{exc} = 457.9$ nm) at 77 K.

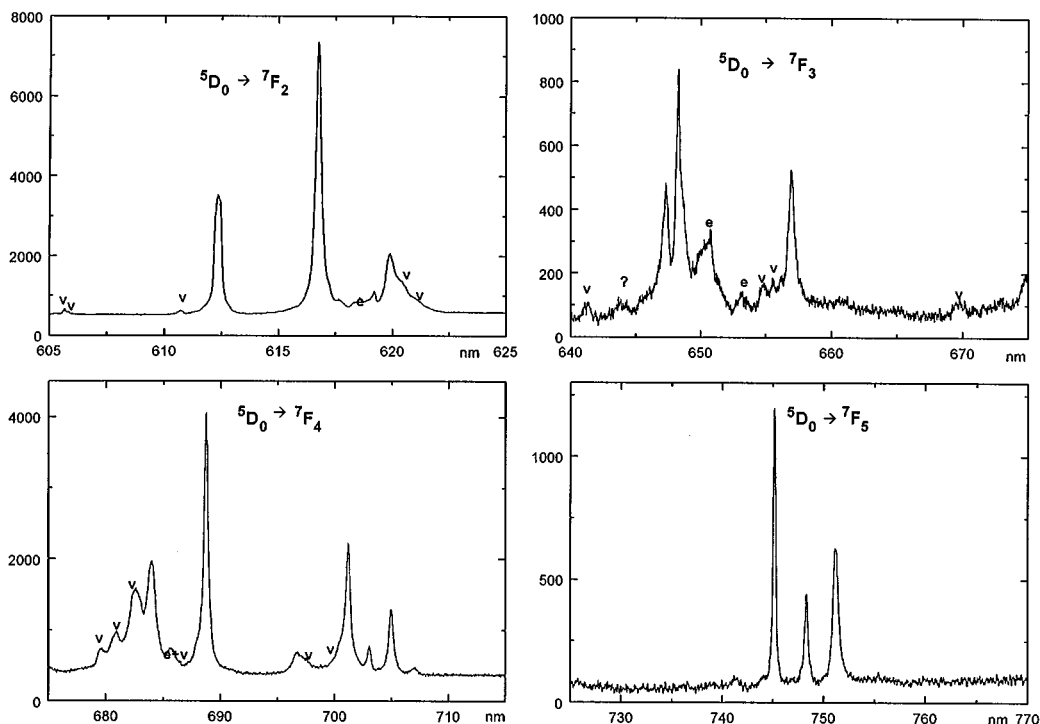**FIG. 6.** Parts of luminescence spectrum under dye excitation ($\lambda_{exc} = 580$ nm) of Eu^{3+} in $Na_3Eu(CO_3)_3$.

A sharp single peak situated at 580 nm with relatively high intensity is found (Fig. 5). This line corresponds to the $^5D_0 \rightarrow {}^7F_0$ transition and shows unambiguously that the europium ion occupies a single crystallographic site. Moreover, the great number of electronic lines indicates a low point symmetry for the rare earth atom, which is in accordance with the structural data. A dye laser excitation ($\lambda_{exc} = 580$ nm) also confirms that all observed lines belong to a single site (Fig. 6).

The C_s site symmetry generates no selection rules between different Stark levels. Therefore, the degeneracy of the ^7F_J levels is completely lifted and the number of observed lines for each $^5D_0 \rightarrow {}^7F_J$ transition is $2J + 1$. Effectively, three narrow lines are detected for the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition ($J = 1$) and five for the hypersensitive electric dipole $^5D_0 \rightarrow {}^7F_2$ transition ($J = 2$) in the emission spectrum. These two transitions have practically equal strength (Fig. 5).

The presence of the $^5D_0 \rightarrow {}^7F_3$ transition in the spectrum is due to the ^7F_J wavefunction mixing by the cf effect, giving it a magnetic/electric dipole character. This transition is weak and several broad lines rend difficult the identification of the electronic sublevels (Fig. 5). Relatively intense lines are observed for the $^5D_0 \rightarrow {}^7F_4$ transition and only four lines for the $^5D_0 \rightarrow {}^7F_5$ transition. Many vibronic lines are also detected in the vicinity of the electronic transitions. These lines are indicated by the v symbol in Figs. 4 and 6. They

correspond to the C–O stretching frequencies at about 430, 620, and 730 cm^{-1} and are associated with $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$) transitions. This phenomenon is often observed in carbonate or borate compounds (11). The energy level scheme is reported in Table 5.

CRYSTAL FIELD SIMULATION

The ground configuration of the trivalent europium ion (Eu^{3+}) is $4f^6$. It possesses a total of 3003 $|SLMJ\rangle$ Stark sublevels. The treatment of the $4f^6$ configuration as a whole is a very hard task. Usually, the phenomenological crystal field simulation of the Eu^{3+} energy level scheme can be performed taking into account only the 49 components of the ^7F_J ground multiplet. The cf calculation was realized with the matrix diagonalization program GROMINET (12) considering the J mixing between wavefunctions with different J and M_J values.

According to Wybourne's formalism (13), the crystal field Hamiltonian can be expressed as

$$H_{cf} = \sum_{kq}[B_q^k(C_q^k + C_{-q}^k) + iS_q^k(C_q^k - C_{-q}^k)].$$

B_q^k and S_q^k are the real and imaginary cf parameters and C_q^k are the spherical harmonics.

TABLE 5
Electronic and Vibronic Transitions in the Emission Spectrum of Europium in $Na_3Eu(CO_3)_3$ ($\lambda_{exc} = 580$ nm).
Experimental and Calculated Crystal Field Energy Levels

Transition	Energy (cm^{-1}) (vibronics)	$^{2S+1}L_J$ levels	Energys (exp)		Energy (cm^{-1}) (calc)
$^5D_0 \rightarrow {}^7F_0$	17,236 = 580 nm	$^7F_0$	A0	0	
$^5D_0 \rightarrow {}^7F_1$	16,947	$^7F_1$	A1	289	283
	16,847		B1	389	388
	16,813		C1	423	429
$^5D_0 \rightarrow {}^7F_2$	(16,505)	$^7F_2$	A0 + 731		
	(16,501)		A0 + 735		
	(16,369)		C1 + 444		
	16,328		A2	908	925
	16,210		B2	1026	1010
	16,161		C2	1075	1065
	16,145		D2	1091	1098
	16,127		E2	1109	1113
	(16,113)		B1 + 734		
	(16,096)		C1 + 717		
$^5D_0 \rightarrow {}^7F_3$	(15,592)	$^7F_3$	A2 + 736		
	(15,530)		?		
	15,444		A3	1792	1800
	15,422		B3	1814	1822
	15,377		C3	1859	1851
	15,363		D3	1873	1886
			E3		1894
	15,305		F3	1931	1920
	(15,269)		?		
	(15,251)		A2 + 1077		
	15,220		G3	2016	2007
	(14,930)		D3 + 433		
$^5D_0 \rightarrow {}^7F_4$	(14,716)	$^7F_4$	A3 + 728		
	(14,684)		B3 + 738		
	(14,651)		C3 + 726		
	14,619		A4	2617	2615
	14,583		B4	2653	2663
	14,522		C4	2714	2718
	14,356		D4	2880	2869
	14,333		E4	2903	2895
	14,264		F4	2972	2968
	14,226		G4	3010	3002
	14,187		H4	3049	3050
	14,145		I4	3091	3106
$^5D_0 \rightarrow {}^7F_5$	13,491	$^7F_5$	A5	3745	3751
	13,423		B5	3813	3817
			C5		3830
	13,370		D5	3866	3869
	13,320		E5	3916	3910
			F5-G5-H5		4046-4035-3947
			I5-J5-K5		4152-4119-4118

TABLE 6
Crystal Field Parameters (cm^{-1}) of Eu^{3+} in $Na_3Eu(CO_3)_3$, Residue (cm^{-2}), and r.m.s. Standard Deviation

B_0^2	B_2^2	B_0^4	B_2^4	B_4^4	B_0^6	B_2^6	B_4^6	B_6^6	Levels	Residue	σ
351	164	15	-182	740	-218	391	-1316	388	39	2377	8.9

In $Na_3Eu(CO_3)_3$ the europium ion occupies the C_s point symmetry. In that case the cf Hamiltonian contains 15 crystal field parameters, 9 real and 6 imaginary. For simplification we started with the Hamiltonian corresponding to a higher C_{2v} symmetry, reducing the number of cf parameters to nine real ones:

$$H_{cf}(C_{2v}) = B_0^2 + B_0^4 + B_0^6 + B_2^2(C_2^2 + C_{-2}^2)$$
$$+ B_2^4(C_2^4 + C_{-2}^4) + B_2^6(C_2^6 + C_{-2}^6)$$
$$+ B_4^4(C_4^4 + C_{-4}^4) + B_4^6(C_4^6 + C_{-4}^6)$$
$$+ B_6^6(C_6^6 + C_{-6}^6).$$

The least-squares fitted parameter set (Table 6) in approaching C_{2v} symmetry reproduces the experimental scheme well (Tables 4 and 5).

CONCLUSION

The crystal structure of $Na_3Eu(CO_3)_3$ is established by single X-ray diffraction. It is built up from carbonate layers separated by $a/4 \approx 2.5$ Å. Eu^{3+} cations occupy C_s symmetry sites and form EuO_9 polyhedra. The crystal field is weak in $Na_3Eu(CO_3)_3$, as already encountered in other carbonates or fluoride carbonates.

A sodium rare earth carbonate was evidenced recently by Grice *et al.* (10), $Na_4(Ln)_2(CO_3)_5$ petersenite, which presents also mixed type carbonate layers. However, this mineral differs from $Na_3Eu(CO_3)_3$. The succession and the nature of the layers are two $[Na_3(CO_3)_3]$ lying flat and two $[NaLn_2(CO_3)_4]$ lying flat and standing on base in petersenite. In $Na_3Eu(CO_3)_3$, $Na(CO_3)_2$ flat lying layers alternate with $Na_2Eu(CO_3)$ layers standing on edge. This arrangement, in turn, is very similar to that found in $Na_2Ca_2(CO_3)_3$ shortite (15); in this phase, the layer composition is $Na(CO_3)_2$ and $NaCa_2(CO_3)$.

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