

## Optical Luminescence of Electronic and Vibronic Transitions in $Gd_{2-x}Y_x(SO_4)_3 \cdot 8H_2O$

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X-ray and ultraviolet-excited emission spectra of  $Gd_2(SO_4)_3 \cdot 8H_2O$  show the electronic  ${}^6P_{3/2,5/2,7/2} \rightarrow {}^8S_{7/2}$  lines of  $Gd^{3+}$  accompanied by vibronics involving the water and sulfate vibrations. Removal of the water of hydration by heating eliminates the water vibronics, while the spectrum of  $Gd_2(SO_4)_3 \cdot 8D_2O$  exhibits the expected shift toward the electronic origin of vibronics attributed to the water of hydration. In a dilute system of composition  $Gd_{0.8}Y_{1.2}(SO_4)_3 \cdot 8H_2O$  we also see the  ${}^6D_J, {}^6I_J \rightarrow {}^8S_{7/2}$  level transitions. © 1990 Academic Press, Inc.

### 1. Introduction

Although nonselective, X-ray excitation is a powerful means with which to study luminescence of ions and defects emitting in the ultraviolet (1, 2). In the case of  $Gd^{3+}$  the emission is located at energies above  $32,000\text{ cm}^{-1}$  and arises from the transitions  ${}^6G_J, {}^6D_J, {}^6I_J$ , and  ${}^6P_J \rightarrow {}^8S_{7/2}$  (all within the  $4f^7$  electronic configuration). In the present paper we report the X-ray- and UV-excited emission of  $Gd_2(SO_4)_3 \cdot 8H_2O$  and  $(Gd_{1-x}Y_x)_2(SO_4)_3 \cdot 8H_2O$ . Vibronic coupling between the electronic transitions of  $Gd^{3+}$  and vibrational transitions of the water and sulfate ligands is observed.

### 2. Experimental

Samples were prepared by dissolving either pure  $Gd_2O_3$  (99.999% Research Chemi-

cals) or mixtures with  $Y_2O_3$  (99.999% Research Chemicals) in nitric acid and precipitating the sulfate with dilute sulfuric acid. To reduce the solubility of the sulfate, an equal volume of methanol was added. After filtering and washing with methanol and acetone, the product was dried at  $150^\circ\text{C}$  and a TGA analysis was carried out with a DuPont 1090B thermal analyzer. Theoretical weight loss for the pure Gd compound is 19.29% assuming eight waters of hydration; 19.32% was found, confirming the material to be the octahydrate. The X-ray pattern was in excellent agreement with ASTM File Card 31-535. The X-ray-excited emission spectra were measured as described previously (2, 3). The X-ray source was a Mo target. Tube current and voltage were 45 mA and 45 kv, respectively. UV data were obtained using a SPEX Fluorolog II spectrophotometer.

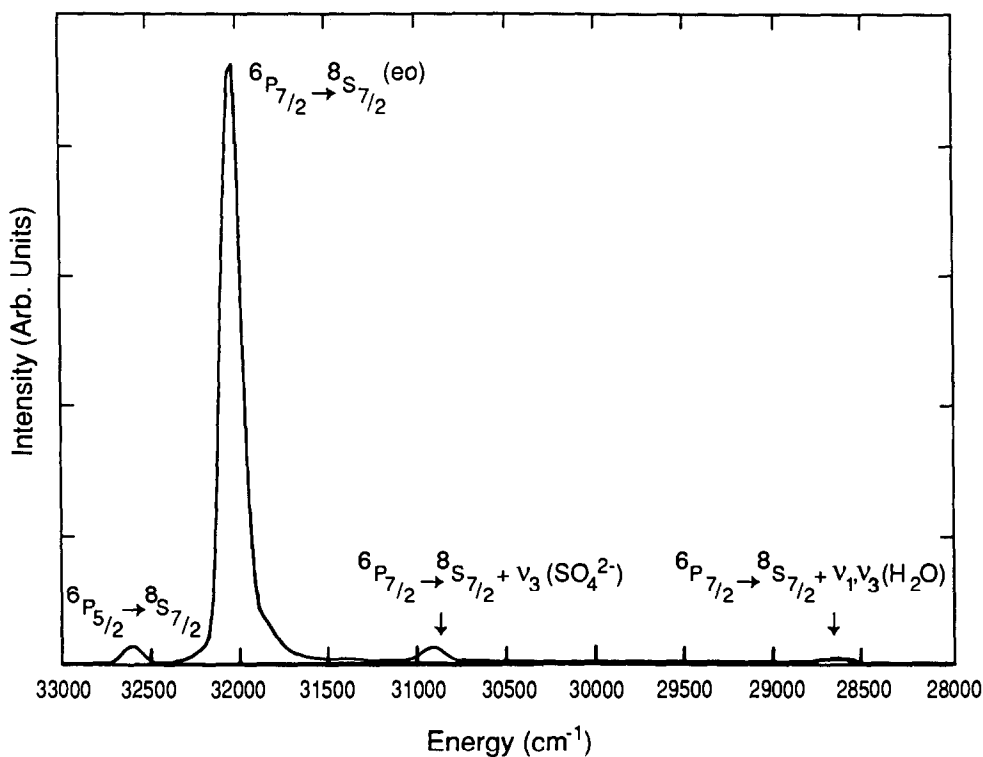


FIG. 1. X-ray-excited emission spectrum of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  at room temperature.

### 3. Results

In Fig. 1 we show the X-ray-excited emission spectrum of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , where the  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  transition dominates the spectrum. The  ${}^6\text{P}_{5/2} \rightarrow {}^8\text{S}_{7/2}$  transition at  $32,625 \text{ cm}^{-1}$ , as well as the vibronic  $\text{SO}_4$  ( $\nu_3$ ) emission at  $30,910 \text{ cm}^{-1}$ , are each about 5% as intense as the  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  transition. The OH vibronic transition at  $28,695 \text{ cm}^{-1}$  is barely visible. In  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  transitions originating from the  ${}^6\text{D}_J$  and  ${}^6\text{I}_J$  levels are absent. This is not the case in solid solutions having lower  $\text{Gd}^{3+}$  concentrations, such as  $\text{Y}_{1.2}\text{Gd}_{8.8}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ . The emission from this compound under X-ray excitation is shown in Fig. 2.

We have also measured the emission spectrum at 5 K using UV excitation of the  ${}^6\text{I}_J$  levels of  $\text{Gd}^{3+}$  (269 nm). At low temperature the OH vibronics appear far more com-

plex than at room temperature, as can be seen in Fig. 3. To conclusively demonstrate that our assignment of the water vibronics is correct, we dehydrated  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  at  $400^\circ\text{C}$ , yielding the anhydrous compound  $\text{Gd}_2(\text{SO}_4)_3$ , which is stable from  $186$  to  $801^\circ\text{C}$  according to our thermogravimetric data. The spectrum of anhydrous  $\text{Gd}_2(\text{SO}_4)_3$  is compared to that of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  in Fig. 4 and, as expected, the water vibronics are absent. Finally, we also prepared  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{D}_2\text{O}$  by hydrating  $\text{Gd}_2(\text{SO}_4)_3$  with  $\text{D}_2\text{O}$  and observed the expected shift of the water vibronics toward the electronic origin (Table I).

### 4. Discussion

The structure of the rare earth octahydrates has been the subject of several in-

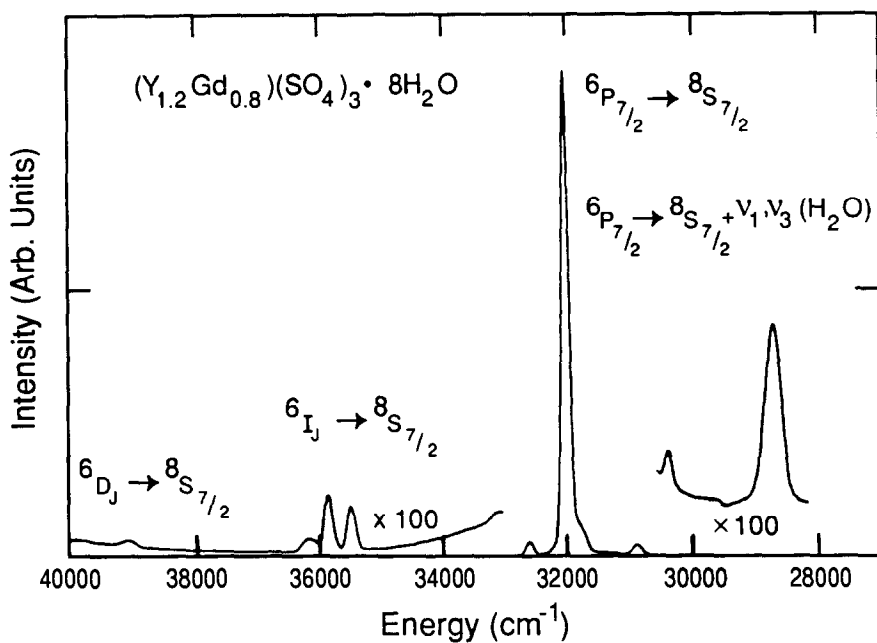


FIG. 2. X-ray-excited emission spectrum of  $Gd_{0.8}Y_{1.2}(SO_4)_3 \cdot 8H_2O$  at room temperature. The  ${}^6D_J, {}^6I_J \rightarrow {}^8S_{7/2}$  transitions can clearly be seen, as can the water and sulfate vibronics.

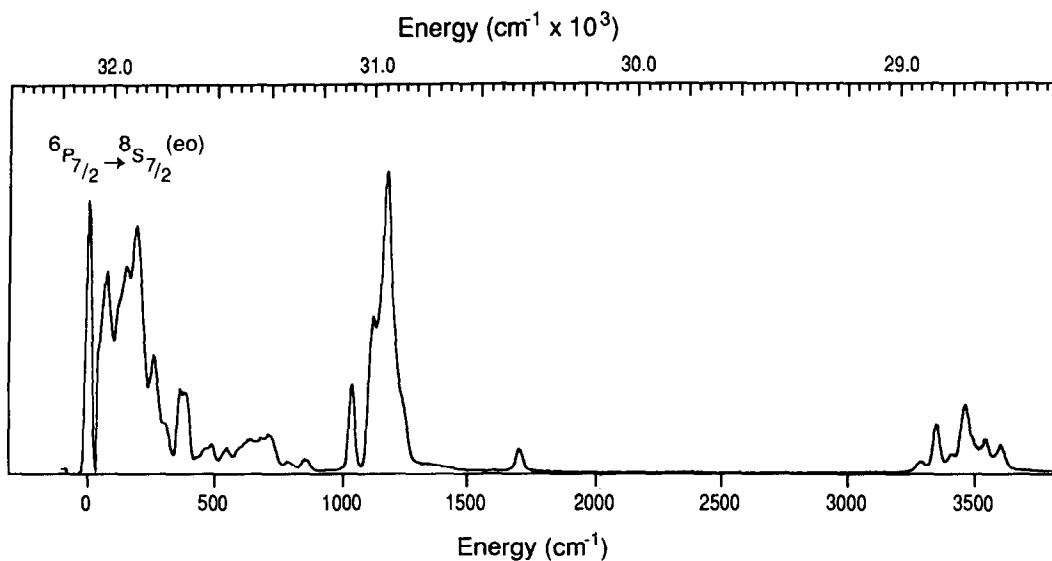


FIG. 3. UV-excited ( $37,175\text{ cm}^{-1}$ ) emission spectrum of  $Gd_2(SO_4)_3 \cdot 8H_2O$  at 5 K. The  ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$  transition has been reduced in intensity in order to provide a reference point for the vibronic transitions.

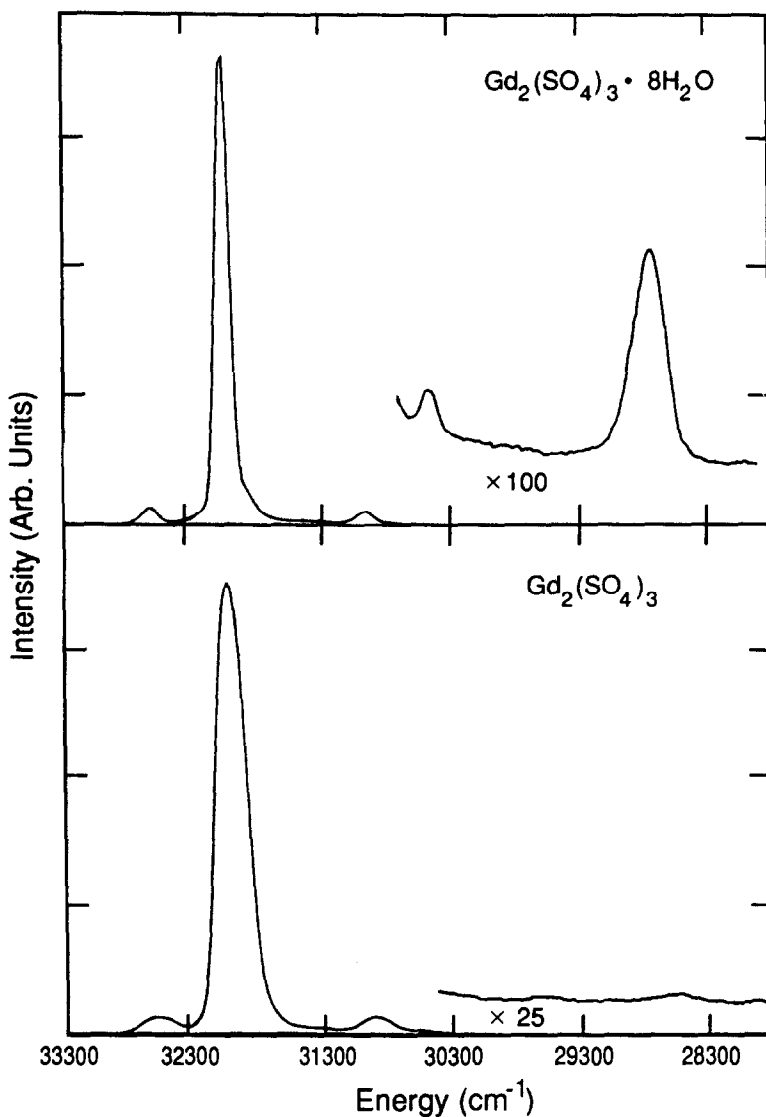


FIG. 4. Comparison of the X-ray-excited emission spectra of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and  $\text{Gd}_2(\text{SO}_4)_3$ . Despite the smaller amplification factor in the lower frame, it is clear that the water vibronics are nearly absent in  $\text{Gd}_2(\text{SO}_4)_3$ , as expected.

vestigations. Fitzwater and Rundle (4) first reported that  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  crystallizes in the centric space group  $C2/c$  ( $C_{2h}^6$ ). Gebert-Sherry (5) later came to the conclusion, based on a piezoelectric test, that  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is acentric with space group  $Cc$  ( $C^4$ ). This structure would have

two different  $\text{Gd}^{3+}$  sites, whereas the  $C2/c$  structure would have one site. More recent structure determinations by Farag *et al.* (6), as well as a neutron diffraction study by Bartl and Rodek (7) of the Nd compound, support the centric space group  $C2/c$ . Based upon an optical second harmonic

TABLE I  
X-RAY-EXCITED EMISSION LINES OF  $\text{Gd}_{2-x}\text{Y}_x(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  AT ROOM TEMPERATURE

Energy (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
39,100 <sup>c</sup>	vvw	<sup>6</sup> D <sub>J</sub> → <sup>8</sup> S <sub>7/2</sub>
39,024 <sup>c</sup>	vvw	<sup>6</sup> D <sub>J</sub> → <sup>8</sup> S <sub>7/2</sub>
36,166 <sup>c</sup>	vvw	<sup>6</sup> I <sub>J</sub> → <sup>8</sup> S <sub>7/2</sub>
36,101 <sup>c</sup>	vvw	<sup>6</sup> I <sub>J</sub> → <sup>8</sup> S <sub>7/2</sub>
35,874 <sup>c</sup>	vw	<sup>6</sup> I <sub>J</sub> → <sup>8</sup> S <sub>7/2</sub>
35,492 <sup>c</sup>	vw	<sup>6</sup> I <sub>J</sub> → <sup>8</sup> S <sub>7/2</sub>
33,110	vvw	<sup>6</sup> P <sub>3/2</sub> → <sup>8</sup> S <sub>7/2</sub>
32,625	w	<sup>6</sup> P <sub>5/2</sub> → <sup>8</sup> S <sub>7/2</sub>
32,025 <sup>d</sup>	vs	<sup>6</sup> P <sub>7/2</sub> → <sup>8</sup> S <sub>7/2</sub> (eo)
~31,850	w	Lattice modes vibronics (eo—175 cm <sup>-1</sup> )
31,390	w	SO <sub>4</sub> (ν <sub>4</sub> ) vibronic (eo—635 cm <sup>-1</sup> )
30,910	w	SO <sub>4</sub> (ν <sub>3</sub> ) vibronic (eo—1115 cm <sup>-1</sup> )
30,420 <sup>e</sup>	vvw	H <sub>2</sub> O(ν <sub>2</sub> ) vibronic (eo—1605 cm <sup>-1</sup> )
28,695 <sup>f</sup>	vw	H <sub>2</sub> O(ν <sub>1</sub> , ν <sub>3</sub> ) vibronic (eo—3330 cm <sup>-1</sup> )

<sup>a</sup> v, very; w, weak; s, strong.

<sup>b</sup> b, bending; s, stretching.

<sup>c</sup> Only present in  $\text{Gd}_{0.8}\text{Y}_{1.2}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ .

<sup>d</sup> eo, electronic origin.

<sup>e</sup> Not present in  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{D}_2\text{O}$ , has shifted to about same energy as much stronger SO<sub>4</sub>(ν<sub>3</sub>) vibronic.

<sup>f</sup> Shifts to 29,585 cm<sup>-1</sup> in  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{D}_2\text{O}$ , i.e. (eo—2440 cm<sup>-1</sup>).

generation measurement, we agree with the centric structure and thus assume a single Gd<sup>3+</sup> site. Furthermore, the spectral studies in the present paper show that there is only one <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> emission line, in agreement with the centric symmetry (i.e., one Gd<sup>3+</sup> site). In structures which possess two distinct crystallographic sites for Gd<sup>3+</sup>, such as Y<sub>2</sub>O<sub>3</sub>, 8 lines have been observed for this transition (8).

In the structure determination of  $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  (6) the Ln<sup>3+</sup> ion is found to be eight coordinated, with four oxygens belonging to water molecules and the other four to sulfate groups. The shortest Ln<sup>3+</sup>–Ln<sup>3+</sup> distance is about 5 Å. The high emission intensity of the <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition in  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  implies that there is little concentration quenching for the <sup>6</sup>P<sub>7/2</sub> levels (9). The higher <sup>6</sup>I<sub>J</sub> and <sup>6</sup>D<sub>J</sub> levels, however, are nearly quenched for this compound, but are readily observable in the dilute Y<sub>1.2</sub>Gd<sub>0.8</sub>(SO<sub>4</sub>)<sub>3</sub> · 8H<sub>2</sub>O system, where the average Gd<sup>3+</sup>–Gd<sup>3+</sup> distance is about 7 Å. This observation implies that the critical

distance for Gd<sup>3+</sup>–Gd<sup>3+</sup> energy transfer is greater than 5 Å (but less than 7 Å) for the <sup>6</sup>D<sub>J</sub> and <sup>6</sup>I<sub>J</sub> levels.

The assignments of the electronic <sup>6</sup>P<sub>J</sub> → <sup>8</sup>S<sub>7/2</sub> transitions are straightforward (10) and appear in Table I. The <sup>6</sup>P<sub>3/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition is rarely observed in emission measurements. The experimental values of the relative integrated emission intensities of the <sup>6</sup>P<sub>7/2</sub>, <sup>6</sup>P<sub>5/2</sub> and <sup>6</sup>P<sub>3/2</sub> → <sup>8</sup>S<sub>7/2</sub> transitions are 1, 4 × 10<sup>-2</sup>, and 5 × 10<sup>-5</sup>, respectively. If the radiative rates were equal for these three transitions, we would expect relative intensities of 1, 4 × 10<sup>-2</sup>, and 2 × 10<sup>-3</sup>. These values were calculated, assuming thermal equilibrium, from the expression (2J + 1) exp(–E/kT), where E is the energy difference between the level concerned and the <sup>6</sup>P<sub>7/2</sub> level, k is Boltzmann's constant, and T is the temperature. In this expression (2J + 1) is the (upper) energy level degeneracy and J is the angular momentum quantum number, J = |L + S|. The line ratios which we observe imply that the radiative rate of the <sup>6</sup>P<sub>3/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition is considerably less than that of the <sup>6</sup>P<sub>5/2</sub>, <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transitions.

Detrio (11) has calculated oscillator strengths for transitions of Gd<sup>3+</sup> in SrF<sub>2</sub> (C<sub>4v</sub> site symmetry). The <sup>6</sup>P<sub>5/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition has an oscillator strength approximately half that of the <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition. The magnetic dipole contribution to the <sup>6</sup>P<sub>3/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition is zero and, in addition, the electric dipole contribution is small. Thus consideration of the relative oscillator strengths (radiative rates) for these three transitions partially explains the deviation of the experimental results from expectations which assume thermal equilibrium. Furthermore, the actual oscillator strengths in  $\text{Gd}_{0.8}\text{Y}_{1.2}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  may differ from the values given in Ref. (11) since the Gd<sup>3+</sup> site symmetry (and therefore the crystal field) will be different (C<sub>1</sub> vs C<sub>4v</sub> site symmetry). This consideration precludes a quantitative comparison.

The vibronic lines in  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  fall into two natural categories: those due to coupling with lattice vibrations and those due to coupling with the internal vibrations of the sulfate and water groups. These two categories are well separated in energy, with the internal vibrations lying between 400 and  $4000\text{ cm}^{-1}$  and the lattice (external) vibrations lying below  $400\text{ cm}^{-1}$ . The general assignment of the vibronic features is straightforward and is given in Table II. Of interest are the relative intensities of the  $\text{SO}_4$  and  $\text{H}_2\text{O}$  vibronics. In  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  the relative intensity ratios of the  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  electronic transition to the  $\text{SO}_4$  ( $\nu_3$ ) and  $\text{H}_2\text{O}$  ( $\nu_1, \nu_3$ ) vibronics are about 100:3.0:0.3. For comparison in  $\text{NaLa}_{0.5}\text{Gd}_{0.5}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  this ratio is 100:2.5:0.5 (12). Thus, the  $\text{Gd}^{3+}$ - $\text{H}_2\text{O}$  vibronic coupling, normalized to the number of  $\text{H}_2\text{O}$  molecules in the coordination sphere of the  $\text{Gd}^{3+}$  ion, is stronger in  $\text{NaLa}_{0.5}\text{Gd}_{0.5}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  than in  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ . The total integrated vibronic intensity in  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is about 10% that of the electronic  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  transition intensity.

The vibronic transitions we observe are in good agreement with the infrared spectrum of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  (13, 14). This is a result of the preferred coupling of the even parity  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  electronic transition with the odd parity infrared active vibrations. For this material, a group theoretical analysis predicts 120 infrared active vibrations (14). The relatively low spectral resolution of the vibronic data ( $\sim 20\text{ cm}^{-1}$ ) precludes observation of all the transitions, but the complexity of the vibronic spectrum due to the large number of vibrations remains obvious. In  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  there are four  $\text{H}_2\text{O}$  and four  $\text{SO}_4$  groups surrounding the  $\text{Gd}^{3+}$  ion, which accounts for the considerable complexity of the  $\text{H}_2\text{O}$  vibronics at 5 K. This complexity is specifically due either to a variety of sites for the  $\text{H}_2\text{O}$  molecules in the unit cell or to correlation field splitting of vibrational transitions from  $\text{H}_2\text{O}$

TABLE II  
THE VIBRONIC EMISSION LINES ASSOCIATED WITH THE ELECTRONIC  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  TRANSITION OF  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  AT 5 K UNDER 269 nm UV EXCITATION

Energy relative to electronic origin ( ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition)	Intensity <sup>a</sup>	Assignment	Transverse optic phonon energies <sup>b</sup>
0		${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}$	—
145	s	Lattice modes	129, 140
355	s	Lattice modes	351
472, 532	w	$\nu_2(\text{SO}_4^{2-})$	409–512
626	m	$\nu_4(\text{SO}_4^{2-})$	567, 658
705	m		700
830	vw	$\text{H}_2\text{O}$ librations	828
1008	m		$\nu_1(\text{SO}_4^{2-})$
1085, 1138	vs	$\nu_3(\text{SO}_4^{2-})$	1094, 1151
1642	w	$\text{H}_2\text{O}$ bending ( $\nu_2$ )	1642
3183	vw	OH stretch ( $\nu_1$ and $\nu_3$ )	3170
3238	m		3232
3296	vw		3292
3350	m		3358
3428	w		3422
3485	w		3462

Note. All values are in  $\text{cm}^{-1}$ .

<sup>a</sup> v, very; w, weak; s, strong.

<sup>b</sup> Transverse optic phonon energies determined by Kramers-Kronig analysis of infrared reflectance data (13).

molecules in identical sites. The former possibility appears more likely since, when  $\text{D}_2\text{O}$  partially replaces  $\text{H}_2\text{O}$  (i.e., in the dilute limit), the infrared spectrum of the  $\text{D}_2\text{O}$  O–D stretching vibrations remains complex, whereas one might expect little or no correlation splitting in this situation. A detailed discussion of the infrared and Raman data will appear elsewhere (14). We note that in the structural studies of  $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , the positions of the 64 hydrogen atoms per unit cell were not determined, complicating analysis of the water vibronics. Finally, it is possible that  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  undergoes a structural phase transition to a lower symmetry than  $\text{C}2/\text{c}$  upon cooling, which could also increase the complexity of the 5 K vibronics. Temperature-dependent structural studies will be necessary to resolve this issue.

The  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  emission in  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is intense, indicating little quenching

due to either  $Gd^{3+}-Gd^{3+}$  energy transfer or the presence of  $H_2O$  molecules with their high energy OH stretching vibrations. The latter observation may reflect the high energy of the  ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$  transition which, to be nonradiatively relaxed, requires excitation of about 10 OH stretching quanta. Such a high order process is unlikely. We have also observed that the compounds  $Ln_2(SO_4)_3 \cdot 8H_2O$ , where  $Ln = Tb^{3+}$  or  $Eu^{3+}$ , luminesce efficiently, which again indicates that the coupling between the rare earth ion and the  $H_2O$  molecules is weaker in this structure than in  $NaLa_{0.5}Gd_{0.5}(SO_4)_2 \cdot H_2O$  (12).

In conclusion, we have reported observation of complex vibronic spectra in  $Gd_{2-x}Y_x(SO_4)_3 \cdot 8H_2O$  under X-ray or UV excitation. The  $Gd^{3+}$  ion is an excellent probe of such transitions since there are no electronic transitions at lower energy than the  ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$  transition. This allows easy and unambiguous observation of the vibronic transitions.

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*Note added in proof.* Recent measurements with higher spectral resolution ( $\sim 10 \text{ cm}^{-1}$ ) have resolved the crystalfield components of the  ${}^6P_{3/2} \rightarrow {}^8S_{7/2}$  and the

${}^6P_{7/2} \rightarrow {}^8S_{7/2}$  transitions. We observe three lines for the former transition and four for the latter, as expected for the  $Gd^{3+}$  ion located at a single site of  $C_1$  symmetry.

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