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The Intensity of Vibronic Transitions in the Spectra of the Trivalent Europium Ion

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Abstract

The intensity of the vibronic transitions in the spectra of the Eu^{3+} ion are reported and discussed for a large number of host lattices. The vibronic intensity is compared to the intensity of the electronic (magnetic-dipole) transitions $^7F_0$–$^5D_1$ or $^5D_0$–$^7F_1$. The latter are structure independent. The ratios obtained in this way vary by two orders of magnitude. In some cases they depend on the Eu^{3+} concentration. In a few cases even the magnetic-dipole lines carry relatively strong vibronic lines. These observations are discussed in terms of existing theories. There is qualitative agreement. The position of the absorption band of the ligands appears to play an important role.

Introduction

Recently the vibronic transitions in the emission spectra of a large number of Gd^{3+}-containing compositions have been reported and discussed [1, 2]. These transitions were observed for all types of host lattices. Their intensity varied considerably. These variations were discussed in terms of existing theories [3–6].

In this paper we want to consider comparable data for the Eu^{3+} ion ($4f^6$). We have compiled data on the intensities of vibronic transitions in Eu^{3+} spectra which were obtained over a number of years. These data were extended by literature data as far as such are available.

The $^6P_{7/2} \rightarrow {}^8S$ emission transition of Gd^{3+} is very suitable to study vibronic transitions, because the spectral region on the longer wavelength side is completely free from electronic transitions. The same is true for the $^7F_0 \rightarrow {}^5D_2$ absorption transition of Eu^{3+}. Therefore we studied the vibronic transitions belonging to this electronic transition in the excitation spectrum of the Eu^{3+} luminescence of the compositions involved.

In addition we tried to investigate the vibronic transitions belonging to the $^5D_0$–$^7F_2$ emission transition of the Eu^{3+} ion. This, however, is not a suitable case for the study of vibronic lines, because the crystal field splitting of the final $^7F_2$ level is often considerable and because overlap of vibronic lines with other electronic lines takes place (e.g. $^5D_0$–$^7F_3$). Data of this type appeared to be rather inaccurate. Note that the parent electronic transitions mentioned are all of the $\Delta J = 0, 2$ type. According to theory this is a prerequisite for the occurrence of relatively strong vibronic transitions [4, 6].

The compilation of data shows that the vibronic intensity varies by two orders of magnitude when the host lattice is varied. A qualitative explanation has been given using existing theories.

Experimental

Table 1 shows the compositions which have been studied. Their preparation has been described in the literature cited. A few samples were prepared especially for the present purpose. This was done by the usual solid-state techniques using appropriate firing temperatures. Samples were checked for purity by X-ray powder diffraction. The measurements were performed on a Perkin-Elmer spectrofluorometer MPF-44B equipped with a liquid helium cryostat.

Results

Table 1 presents the results obtained in this study. Some representative spectra are given in Figs. 1 and 2. Table 1 gives the ratio r between the total vibronic intensity belonging to the parent electronic lines, $^7F_0 \rightarrow {}^5D_2$ or $^5D_0 \rightarrow {}^7F_2$, and the intensity of the corresponding (electronic) magnetic-dipole transition $^7F_0 \rightarrow {}^5D_1$ or $^5D_0 \rightarrow {}^7F_1$, respectively. In this way r presents a value which can be compared for Eu^{3+} in different host lattices. This is based on the fact that the magnetic-dipole transitions mentioned are allowed transitions, so that their intensities are practically not influenced by a change in the surroundings of the Eu^{3+} ion.

The situation in the case of Eu^{3+} is more surveyable than the case of Gd^{3+} [2]. In the latter case we compared the vibronic intensity with the parent

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TABLE 1. Total integrated vibronic intensity in the $^7F_0$–$^5D_2$ and $^5D_0$–$^7F_2$ transitions of the Eu^{3+} ion relative to the corresponding electronic magnetic-dipole transitions for several compositions at liquid helium temperature

Composition	$\frac{I(^7F_0-^5D_2)_{vibr}}{I(^7F_0-^5D_1)_e}$	$\frac{I(^5D_0-^7F_2)_{vibr}}{I(^5D_0-^7F_1)_e}$	Reference
$SrTiO_3$:Eu	$\geqslant 10$	5	9, 11
Sr_2TiO_4:Eu, Na		~1	12
$Eu_2Mg_3(NO_3)_{12}\cdot 24H_2O$	>5	~1	13
$LaTiSbO_6$:Eu		~1	14
$Gd_2(MoO_4)_3$:Eu	4		15
$Eu_2(MoO_4)_3$	10		15
Ba_2EuNbO_6	3.2	0.4	16
$EuNbO_4$	2.8	0.8	16
$Gd_2Sn_2O_7$:Eu	~2	0.2	17
$KEu(WO_4)_2$	1.94		18
$LiEuF_4$	1.7	0.1	16
$Na_5Gd(WO_4)_4$:Eu	1.5	0.8	8
$Na_5Eu(WO_4)_4$	~5	0.8	8
$Gd_2(WO_4)_3$	1.5	~1	19
Eu_2O_2S	$\geqslant 1$	~0	20
Monoclinic Eu tellurite	1.1	0.25	21
$ScBO_3$:Eu	1.0	0.65	22
$LuTaO_4$:Eu	1.0	0.2	23
$BaGd_2(MoO_4)_4$:Eu	1.0	0.4	24
$EuMgAl_{11}O_{19}$	1.0	0.3	25
$CaWO_4$:Eu	0.92		18
GdOCl:Eu	0.9	0.25	26
YOCl:Eu	0.9	0.3	26
$NaEu(WO_4)_2$	0.72		18
Tetragonal Eu tellurite	0.8	0.1	21
Sr_2LaBeO_5:Eu	0.7	0.1	27
Cs_2NaYCl_6:Eu	0.55	0.4	28
$SrLaAlO_4$:Eu	0.6	0.2	29
Eu_3ReO_8	0.6	0.13	30
LaOCl:Eu	$\leqslant 0.5$	0.4	26
$LaAlO_3$:Eu	0.4	0.15	29
GdB_3O_6:Eu (crystalline and glass)	0.3		31
$CaSO_4$:Eu	~0.1	0.1	32
$BaLa_4(WO_4)_7$:Eu	0.1		33
$[Eu \subset bpy\cdot bpy\cdot bpy]^{3+}$	~0.15	0.1	34
$GdTiNbO_6$:Eu		~0.1	14
$LaTiTaO_6$:Eu		~0.1	14

electronic intensity. However, this electronic intensity contains magnetic-dipole and forced-electric-dipole contributions. The latter are host-lattice dependent. In the case of Eu^{3+} we relate the total vibronic intensity to that of an electronic magnetic-dipole transition which is structure independent. As a consequence the r values in Table 1 can be more reliably compared than those for Gd^{3+} in ref. 2.

The magnetic-dipole oscillator strengths for the $^7F_0 \rightarrow {^5D_1}$ and $^5D_0$–$^7F_1$ transitions of Eu^{3+} have been calculated by Ofelt [7]. Their values are 1.48×10^{-8} and 8.85×10^{-8}, respectively. Using the r values in Table 1, the approximate total vibronic oscillator strength can be directly found. It is clear that the vibronic oscillator strength is of the order of magnitude of the electronic magnetic-dipole oscillator strength. However, in some cases it can be a factor of 10 larger, in others smaller (see Table 1).

It must be realized that the tabulated r values are not very accurate. This is inherent in the measurement of the spectra. The features concerned are very weak. Further we compare the broad vibronic region with the sharp-line magnetic-dipole transition. Nevertheless, the r values from the excitation transitions (transitions starting on the $^7F_0$ level) are rather reliable. The inaccuracy may be some 30%. However,

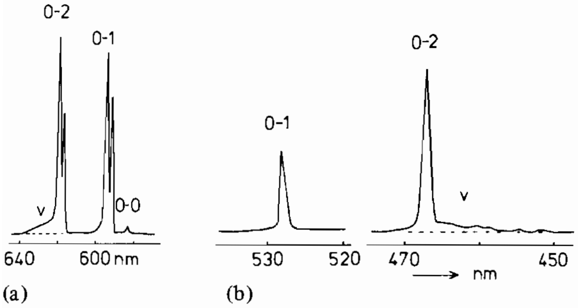

Fig. 1. (a) Emission spectrum of LaAlO$_3$:Eu at 4.2 K showing $^5D_0-^7F_2$ vibronics. (b) Excitation spectrum of the emission of LaAlO$_3$:Eu at 4.2 K showing $^7F_0-^5D_2$ vibronics.

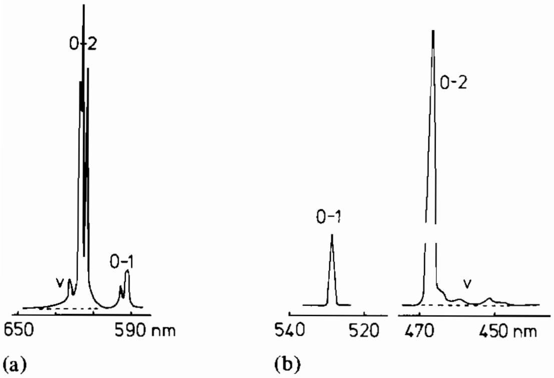

Fig. 2. (a) Emission spectrum of Gd$_2$(WO$_4$)$_3$:Eu at 4.2 K showing $^5D_0-^7F_2$ vibronics. (b) Excitation spectrum of the emission of Gd$_2$(WO$_4$)$_3$:Eu at 4.2 K showing $^7F_0-^5D_2$ vibronics.

the r values from the emission transitions (transitions starting on the $^5D_0$ level) are considerably less accurate. This is due to the fact that the vibronic transitions involved are sometimes hard to distinguish from weak electronic lines in the spectrum.

Nevertheless we can arrive at some reliable conclusions which will be discussed in the next section.

(a) The r values from the emission spectra are always lower than those from the excitation spectra.

(b) In a few cases the r value depends on the Eu^{3+} concentration. This has been investigated in more detail by van Vliet and Blasse [8]. This is only the case for the excitation transitions, not for the emission transitions.

(c) The r values vary by two orders of magnitude. Compare, for example, SrTiO$_3$:Eu^{3+} and CaSO$_4$:Eu with $r \geqslant 10$ and $r \sim 0.1$ in the excitation spectra, respectively.

(d) In some cases the magnetic-dipole transition ($\Delta J = 1$) carries also vibronic transitions although this seems to be in contradiction to the selection rule ($\Delta J = 0, \pm 2$) [4, 6]. In the case of SrTiO$_3$:Eu they are even relatively strong in the emission spectrum [9].

Discussion

In ref. 2 we have briefly reviewed the theories on vibronic rare-earth transitions and shown that the oscillator strength of these transitions can be approximated by the expression [4–6]

$$P_v \sim \nu(g + n\alpha R^{-3})^2(\Xi(1,2))^2\langle J\|U^{(2)}\|J'\rangle^2 \times \frac{1}{2J+1}\langle 0\|T^{(1)}\|p\rangle^2 \qquad (1)$$

Here P_v is the oscillator strength of the vibronic transition involved, ν its frequency, n the number of ligands around the Eu^{3+} ion, g and α the charge and the polarisability of the ligand, R the Eu–ligand distance, Ξ (1,2) is defined by eqn. 14 in ref. 10 and takes care of the opposite-parity mixing, J and J' are the total quantum numbers of the initial and final electronic states, the first matrix element is that of the reduced tensor operator $\|U^{(2)}\|$, and the second matrix element that of the electric-dipole operator connecting the initial (0) and the final (p) vibrational states. It should be realized that increasing covalency of the Eu^{3+}–ligand bond implies an increase of the vibronic intensity [2, 4].

Let us now try to discuss the conclusions of the preceding section using eqn. (1).

(a) The r values obtained from the excitation spectra ($^7F_0-^5D_2$ vibronics) and emission spectra ($^5D_0-^7F_2$ vibronics) are not equal. Equation (1) shows that they should be different. First, the oscillator strengths of the magnetic-dipole transitions, to which the vibronic transitions are compared, are not equal (see above). Second, the matrix element $\langle J\|U^{(2)}\|J'\rangle^2$ is different for the two transitions involved: 0.0008 for $^7F_0-^5D_2$ and 0.0032 for $^5D_0-^7F_2$ [35]. Third, the value of ν is different; about 21.7 kK for the $^7F_0-^5D_2$ vibronics and 16.0 kK for the $^5D_0-^7F_2$ vibronics.

Because of this the r value from the excitation spectra should be twice that from the emission spectra. Table 1 shows that in a number of cases this is close to the experimental result, especially if one takes the inaccuracy of the r value into consideration. However, in many cases the r values differ by more than a factor of 2, so that the disagreement cannot be ascribed to the experimental inaccuracies. This is especially the case for the concentrated Eu^{3+} compositions. Therefore we now turn to the discussion of conclusion (b).

(b) Since it is hard to imagine that the terms $(g + n\alpha R^{-3})^2$ and $\langle 0\|T^{(1)}\|p\rangle^2$ in eqn. (1) will be different for the two transitions, we are left with term Ξ (1,2). Hoshina *et al.* [20] were the first to report the dependence of the vibronic intensity on the Eu^{3+} concentration. Later this was confirmed for other systems (ref. 8; see also Table 1). However, this dependence was only observed for the vibronic lines in the excitation spectra, and not for those in the emission spectra. Hoshina *et al.* [20] ascribed this to a preferential admixture of the septet charge-transfer state into the ^7F levels.

The vibronic intensity is in fact determined by the admixture of the opposite-parity state into the initial level [36], i.e. for the $^7F_0 \rightarrow {}^5D_2$ transition into the $^7F_0$ level and for the $^5D_0 \rightarrow {}^7F_2$ transition into the $^5D_0$ level. More recent measurements from this laboratory [8] did not exclude the proposal made by Hoshina *et al.*

Therefore we assume that in all compositions for which the two tabulated r values differ by more than a factor of two, there is a stronger admixture of opposite-parity states in the ^7F levels than in the ^5D levels. This would have an influence on the value of $\Xi(1,2)$.

In this connection it is noted that Judd [4] has shown that the dynamic coupling contribution to the vibronic intensity contains a factor $(1 - \sigma_2)^2$ which allows for the screening of quadrupole fields by the outer shells of the rare-earth ions. If the ligand wavefunctions penetrate the outer shells of the rare-earth ions, the screening is reduced. We have allowed for this effect by stating above that higher covalency results in a stronger dynamic coupling contribution, i.e. in a higher vibronic intensity. An admixture of the opposite-parity states into the ^7F levels will, therefore, also imply an increase of the dynamic coupling contribution and increase the difference between the r values for a given composition. A further analysis of this effect seems to be desirable, but lies beyond the scope of this paper.

(c) The large variation of r through Table 1 warrants further comments. In nearly all compositions the Eu^{3+} ion is coordinated by oxygen. The polarisability (α) of oxygen is probably very different in the compositions involved [37]. The frequency dependence of α can be taken into account by the formula

$$\alpha = \frac{e^2}{m} \sum_j \frac{f_{ij}}{\nu_{ij}^2 - \nu^2} \qquad (2)$$

Here ν is the frequency involved, ν_{ij} the absorption frequency of the transition $i \rightarrow j$, and f_{ij} the corresponding oscillator strength [38]. The value of ν_{ij} enters also the denominator of the factor $\Xi(1,2)$. Therefore eqn. (1) predicts an increasing vibronic intensity for a decreasing value of the absorption frequency of the Eu^{3+} surroundings.

Table 1 shows, as far as we know for the first time, a clear illustration of this frequency dependence. Let us consider the value of r from the emission spectra to exclude the concentration effects. Starting with $SrTiO_3$:Eu (absorption frequency $\simeq 25\,000$ cm^{-1}), r (emission) (r(em.)) is 5, a very high value. A group of compositions with absorption frequencies at about $30\,000$ cm^{-1} ($Eu_2Mg_3(NO_3)_{12} \cdot 24H_2O$, Sr_2TiO_4:Eu, $LaTiSbO_6$:Eu, $Gd_2(WO_4)_3$:Eu) show r(em.) about 1; those with the absorption frequency around $35\,000$ cm^{-1} (Ba_2EuNbO_6, LaOCl:Eu) have r(em.) slightly below 0.5. If the absorption frequency moves to higher than $40\,000$ cm^{-1} ($LiEuF_4$, $CaSO_4$:Eu), r(em.) drops down to 0.1.

The frequency dependence discussed above yields a factor of about 30 if one compares $\nu_{ij} = 25\,000$ and $40\,000$ cm^{-1} for $\nu = 16\,000$ cm^{-1}. The experimental values are in between 5 ($\nu_{ij} \simeq 25\,000$ cm^{-1}) and 0.1 ($\nu_{ij} \simeq 40\,000$ cm^{-1}). We consider this as a surprisingly good agreement, since the r values are inaccurate and other factors in eqn. (1) have been neglected (for example the matrix element $\langle 0 \| T^{(1)} \| p \rangle$).

Instead of comparing all data, it is also useful to compare a few related compositions. Consider, for example, the results for $LaTiSbO_6$:Eu and $LaTiTaO_6$:Eu. The absorption edges are not very different [14]. The lattice parameters show that the oxygen volume is larger in $LaTiSbO_6$:Eu than in $LaTiTaO_6$:Eu. This implies that the oxygen polarisability is also larger [37]. Indeed the vibronic intensity is higher in $LaTiSbO_6$:Eu.

The comparison of the perovskite-type compositions is also interesting. The difference between the vibronic intensities of the Eu^{3+} ion in $SrTiO_3$ and $LaAlO_3$ is striking. Above we have already argued that the low-lying absorption edge of $SrTiO_3$ is the main reason for the high vibronic intensities in the case of $SrTiO_3$. Note that the intensities in the case of Cs_2NaYCl_6:Eu, an ordered perovskite, are much closer to those for $LaAlO_3$:Eu than those for $SrTiO_3$:Eu. This illustrates our argument given before [2] that the polarisability of Cl^- is more than compensated by the larger ionic radius which augments the value of R in eqn. (1).

(d) In some cases the intensity of the vibronic lines belonging to the electronic magnetic-dipole transition is considerable. In $SrTiO_3$:Eu [9] the ratio of the intensity of all the $^5D_0$–$^7F_1$ vibronics to that of the electronic line is about 3. In $Eu_2Mg_3(NO_3)_{12} \cdot 24H_2O$ [13] it amounts to 0.3. In $CaWO_4$:Eu [18] this ratio is 0.04 for the $^7F_0$–$^5D_1$ transition.

According to eqn. (1) these vibronic transitions are forbidden in view of the factor $\langle J \| U^{(2)} \| J' \rangle$. They have to be considered as the classical one-phonon vibronic replicas [2, 6, 40]. Using the expression e^{-S} for the relative amount of electronic intensity, S being the Huang–Rhys parameter [39] we can derive for S the following values: $S = 1.4$ ($SrTiO_3$), $S = 0.2$ ($Eu_2Mg_3(NO_3)_{12} \cdot 24H_2O$), and $S = 0.04$ ($CaWO_4$).

These S values are much higher than those usually assumed for the trivalent rare-earth ions ($S = 0.01$, refs. 2 and 6). This is another indication that the opposite-parity mixing is not equally effective in the two electronic states between which the optical transition takes place. It must be realised that the $\Delta J = 2$ vibronic transitions contain also a contribution of replicas of this type.

Conclusions

The intensity of the vibronic transitions in the spectra of the Eu^{3+} ion is reported and compared in a large number of host lattices. The results are compared with existing theories. An important factor appears to be the position of the optical absorption transition of the Eu^{3+} surroundings. If it is at low energy, the vibronic intensity is strong. The Huang–Rhys factor becomes relatively large. Recently Berry *et al.* [41] have shown that the antipyrine ligand is also able to induce impressive vibronic transitions due to the high polarisability of the ligand.

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