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Luminescence of Eu(III) in $(NH_4)_3YCl_6$: Nonradiative Transitions Induced by the Second Coordination Sphere

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The quantum efficiency of the luminescence of Eu(III) in $(NH_4)_3YCl_6$ is considerably suppressed due to the presence of high-frequency oscillators (NH_4^+) in the second coordination sphere of the europium ion. Additional evidence for this effect is found in the vibronic emission lines of Gd(III) in $(NH_4)_2GdCl_5$. © 1992 Academic Press, Inc.

Introduction

Meyer *et al.* (*1–3*) have shown that the so-called ammonium chloride route to prepare anhydrous lanthanide trichlorides from the oxides is a two-step procedure. In the first step, a complex chloride $(NH_4)_3LnCl_6$ (Ln = Tb–Lu, Y) is formed at ~230°C, and in the second step this complex chloride decomposes at ~400°C into the trichloride and ammonium chloride. The complex chloride undergoes several phase transitions. The high-temperature phase has a cubic structure of the $(NH_4)_3FeF_6$ type, which is closely related to elpasolite. The low-temperature phases can be considered as distortions from the high-temperature phase.

In this paper we describe and discuss the luminescence of Eu(III) in $(NH_4)_3YCl_6$. There are several reasons to investigate this system. Marley *et al.* (*4*) have shown that the elpasolite structure is an excellent model system to investigate the luminescence of trivalent lanthanide ions. It may be possible to derive structural details of the $(NH_4)_3YCl_6$ low-temperature phase from the Eu(III) emission in this lattice. More interesting, in our opinion, is the fact that the $EuCl_6^{3-}$ octahedron in $(NH_4)_3YCl_6$: Eu(III) is imbedded in a "sea" of ammonium ions: six on the corners of an octahedron and eight on the corners of a cube around the $EuCl_6^{3-}$ octahedron (in the distorted modification these numbers may be slightly different). The ammonium ions have high-frequency vibrations (up to some 3000 cm^{-1}). It is well known that high-frequency vibrations in the first coordination sphere of Eu(III) suppress the quantum efficiency of the Eu(III) luminescence drastically (*5, 6*). It would be interesting to see whether the second coordination sphere can also be of influence in this respect. The present work shows that this is indeed the case.

Experimental

Samples were prepared following Meyer's recipe (*1*). The Eu(III) concentration amounts to 2 mole%. The optical measurements were performed as described

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before (7) using a Perkin–Elmer spectrofluorometer equipped with a liquid helium cryostat. Quantum efficiencies were estimated by comparison with standard phosphors. The samples were handled in a dry box since they are hygroscopic.

Results and Discussion

Undoped $(NH_4)_3YCl_6$

The undoped host lattice shows a broad band emission with a maximum at ~440 nm upon excitation with $\lambda \leq 250$ nm. Its intensity is low and partly quenched at room temperature. The diffuse reflection spectrum shows an absorption band with a maximum at about 230 nm. Its intensity is too low to be due to the host lattice itself. Therefore, we ascribe these phenomena to oxygen or hydroxyl in or on the samples. In view of the hygroscopic nature of the samples, this is an obvious assumption. Comparable phenomena have been observed by us before (*8*). This luminescence does not interfere with the Eu(III) luminescence, as we will see below.

Eu(III)-doped $(NH_4)_3YCl_6$

Samples $(NH_4)_3YCl_6$: Eu(III) show an additional broad absorption band around 300 nm. Excitation into this band yields the characteristic Eu(III) emission with a temperature independent intensity ($T \leq 300$ K). The emission spectrum at 4.2 K is given in Fig. 1. The corresponding excitation spectrum shows weak intra-$4f^6$-configuration lines and a dominating broad band with a maximum at about 310 nm, corresponding to the reflection spectrum.

This broad band is ascribed to the Eu(III)–Cl(–I) charge-transfer transition. It has the same position as reported in the literature for Eu(III)–chloride complexes (for some data see Ref. (9)). The emission spectrum shows the well-known emission transitions from the $^5D_0$ level to the ^7F_J levels.

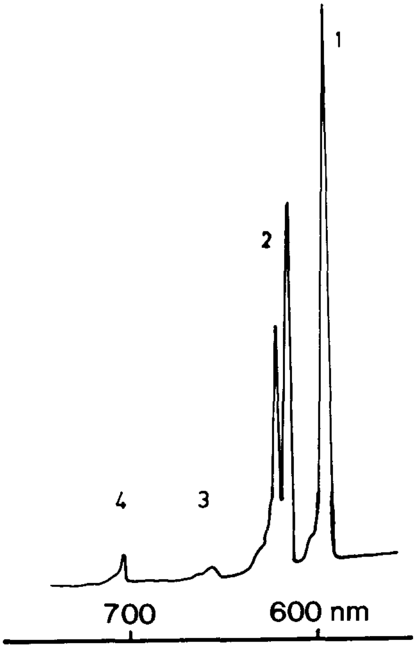

FIG. 1. Emission spectrum of the Eu(III) luminescence of $(NH_4)_3YCl_6$: Eu at 4.2 K. Excitation wavelength 310 nm. The figures 1 to 4 give the J value of the emission transitions $^5D_0$–^7F_J.

Dominating are the $^5D_0$–$^7F_1$ and $^7F_2$ lines, indicating a site symmetry close to inversion symmetry (*10*), as is to be expected for octahedral $EuCl_6^{3-}$. The $^5D_0$–$^7F_2$ emission line intensity shows that the distortion from cubic symmetry occurs in such a way that the inversion center at the lanthanide site is lost.

On the longer-wavelength side of the $^5D_0$–$^7F_{1,2}$ transitions a vibronic transition is observed. For $^5D_0$–$^7F_2$ this is to be expected, but for $^5D_0$–$^7F_1$ it is more exceptional (*11*). Since the latter transition is parity allowed (magnetic-dipole transition), the transition has to be considered as a phonon replica due to the Frank Condon offset. For the unsplit $^5D_0$–$^7F_1$ transition the vibrational frequency is found to be (275 ± 25) cm^{-1}. This is in agreement with the frequency of the ν_1 mode of the $EuCl_6^{3-}$ octahedron (*12*).

The intensity of this vibronic transition is

5% of that of the corresponding electronic transition, yielding for the Huang–Rhys factor the value of $S = 0.05$ (see also Ref. (*11*)).

These spectral data show that the Eu(III) ion in $(NH_4)_3YCl_6$ occupies the Y sites with a (distorted) octahedral chloride-ion coordination. However, the following observations seem to be at variance with such an assignment:

(i) The emission spectrum does not show any emission from higher ^5D levels. For Cs_2NaYCl_6 : Eu(III) this is the case (*4*), as is to be expected in view of the low vibrational frequencies of the $EuCl_6^{3-}$ complex ($\nu \leq 300$ cm^{-1}). These low frequencies suppress the nonradiative rates of relaxation processes like $^5D_2 \rightarrow {}^5D_1$ and $^5D_1 \rightarrow {}^5D_0$ (*6, 10*).

(ii) The quantum efficiency (q) of the Eu(III) emission of $(NH_4)_3YCl_6$: Eu is low: for charge-transfer excitation $q \leq 10\%$, for excitation in the ^5D_J levels $q \leq 20\%$. The former value was obtained by comparison with standard phosphors, the latter from the excitation spectrum using a method described elsewhere (*13*). What matters here is the fact that these values are far from 100%. The somewhat lower value for charge-transfer excitation may be due to nonradiative losses from the charge-transfer state (*6, 10*), but also for excitation within the $4f^6$ configuration the value of q is much lower than expected. In Cs_2NaYCl_6 : Eu there are no indications for nonradiative losses of any importance, nor is there an influence of concentration quenching (*14*).

Observations (i) and (ii) seem to indicate that in $(NH_4)_3YCl_6$ the high-frequency vibrations of the ammonium ions induce nonradiative transitions in the Eu(III) ion. It is hard to find a different explanation. In the undistorted structure the Eu(III) ion has 8 NH_4^+ ions at 4.8 Å and 6 at 5.5 Å. Since these distances refer to the center of gravity of the NH_4^+ ion, and although the distorted structure is unknown, it is certain that every Eu(III) ion will have more than 10 N–H oscillators within a distance of 5 Å. The present results show that the properties of the second coordination sphere may influence the transitions on the central Eu(III) ion.

This is not the case in $Eu_2Mg_3(NO_3)_{12} \cdot 24\, H_2O$ (*15*). Here the Eu(III) ions are bidentately coordinated by six nitrate ions. The quantum efficiency of the Eu(III) emission is high, which suggests that the nitrate ions shield the Eu(III) ions from the water molecules in the second coordination sphere. Note that the nitrate ion is slightly larger than the chloride ion (*16*).

Another example of the influence of the second coordination sphere on a rare-earth spectrum has been reported for $Gd(ClO_4)_3 \cdot 6H_2O$ (*17*). In this compound every Gd(III) is coordinated octahedrally by six water molecules (Gd–O distance 2.35 Å). The second coordination sphere consists of four chlorate ions (Gd–Cl distance 4.22 Å). The emission spectrum of this compound consists of the $^6P_{7/2} \rightarrow {}^8S$ transition of Gd(III) followed by vibronic transitions which are not only due to water, but also to the perchlorate ion.

In view of the observations on the perchlorate we also took a short look on the Gd(III) emission in $(NH_4)_3YCl_6$ and in $(NH_4)_2GdCl_5$. The sample $(NH_4)_3YCl_6$: Gd(III), prepared in the same way as the Eu(III)-doped sample, shows Gd(III) emission consisting of the $^6P_{7/2} \rightarrow {}^8S$ transition at 313.5 nm. Due to the low Gd concentration, the absorption strength ($^8S \rightarrow {}^6I_J$) is weak and the emission intensity is too low to allow the observation of vibronic lines.

Meyer *et al.* (*1, 2*) have shown that the intermediary complex chloride of gadolinium has a different stoichiometry, viz. $(NH_4)_2GdCl_5$ with K_2PrCl_5 structure (*2*). This implies that Gd(III) is in seven coordination. The polyhedra form linear rows with composition $GdCl_5^{2-}$. This compound was prepared according to Ref. (*1*) and shows strong Gd(III) emission. The emission spec-

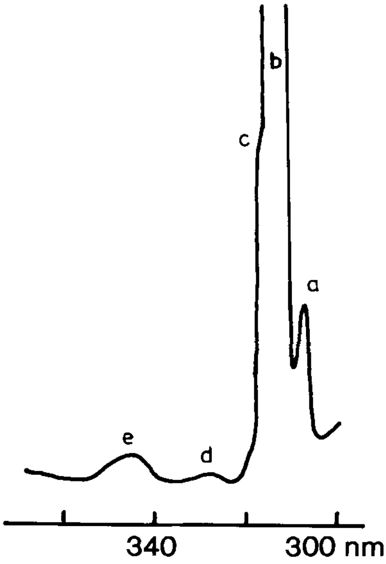

FIG. 2. The emission spectrum of $(NH_4)_2GdCl_5$ at 300 K. Excitation wavelength 250 nm. The letters a to e are explained in the text. Feature b is off scale.

trum at 300 K is given in Fig. 2. That at 4.2 K is not relevant for our study, since it consists mainly of Gd(III) trap emission due to energy migration over the $GdCl_5^{2-}$ rows (see, e.g., Ref. (*18*). Since the shortest Gd–Gd distance is 4.5 Å (*19*), this migration agrees with criteria evaluated before (*18*).

The room temperature emission spectrum shows, in sequence of increasing wavelength (compare Fig. 2), the following features:

a. the thermally activated $^6P_{5/2} \rightarrow {}^8S$ transition at about 308 nm,

b. the dominating $^6P_{7/2} \rightarrow {}^8S$ transition at 313.5 nm,

c. a shoulder on *b* at about 316 nm,

d. a very weak feature at 328 nm (~1400 cm^{-1} below the $^6P_{7/2} \rightarrow {}^8S$ transition),

e. a weak feature at about 347 nm (~3100 cm^{-1} below the $^6P_{7/2} \rightarrow {}^8S$ transition).

Feature *e* is assigned to a vibronic line due to coupling with the ν_3 mode of the ammonium ion (3100 cm^{-1} Ref. (*19*)), and feature *d* to a vibronic line due to coupling with the ν_4 mode (1400 cm^{-1}, Ref. (*19*)). These modes are the infrared-active modes of the ammonium ion and should turn up with the higher vibronic intensity (*20*). Feature *e* has an integrated intensity of about 2% of the electronic origin $^6P_{7/2} \rightarrow {}^8S$, feature *d* about 0.5%. Due to the weakness of the vibronic lines these data are not very accurate. Nevertheless they show convincingly that the vibrations of the second coordination sphere (ammonium ion) couple with the movements of the 4*f* electrons on the central metal ion. The Gd(III) ion has 12 ammonium ions in the second coordination sphere (*2*, *21*).

Feature *c* could not be resolved from the electronic $^6P_{7/2} \rightarrow {}^8S$ transition; it is estimated to be ~250 cm^{-1} below the electronic line and assigned to a vibronic line due to coupling with the Gd–Cl vibrations (see also above). Feature *c* is several times more intense than features *d* and *e*, as is to be expected for coupling with the first and the second coordination sphere, respectively.

Finally, the present results confirm our earlier warning (*6*) that the nonradiative $^5D_0$–^7F rate on the Eu(III) ion depends not only on the number of oscillators but also on their interaction with, i.e. distance to, the Eu(III) ion.

In conclusion, we have presented evidence for coupling between the vibrational modes of the second coordination sphere and the electronic transitions within the $4f^n$ configuration of the central lanthanide ion. The present compositions are very suitable for a study of this effect, since the lanthanide-chloride polyhedron is coordinated by a large number of ammonium ions.

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