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Emission spectrum from Eu^{3+} ions in anhydrous $EuCl_3$

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Abstract

While the emission spectrum from Eu^{3+} ion doped into lanthanum trichloride has been thoroughly studied, that from pure $EuCl_3$ has not been reported correctly. We have recorded the emission spectrum from anhydrous $EuCl_3$ at 77 K with high resolution. As reported in the literature for other UCl_3-type lanthanide trichlorides, the Eu^{3+} ion in $EuCl_3$ exhibits an emission spectrum which is indicative of a D_{3h} site symmetry for the Eu^{3+} ion, even though X-ray diffraction data from $EuCl_3$ support a Eu^{3+} ion site symmetry of C_{3h}.

Introduction

$EuCl_3$ is frequently used as a precursor in several synthetic procedures, for example in the preparation of EuOCl [1]. Knowledge of the precursor's emission spectrum can be useful in determining the purity of the starting materials and final products as well as facilitating the interpretation of the spectra of these materials. The emission spectrum from Eu^{3+} ions doped into anhydrous lanthanum trichloride has been extensively studied [2]. Pant *et al.* [3] reported what they believed to be emission from anhydrous $EuCl_3$ but, upon inspection of their results by us, we have concluded that the reported emission spectrum resulted not from $EuCl_3$, but rather from EuOCl. This finding is supported by the comparison of their emission spectrum to that from EuOCl [1] and also by the evaluation of the synthetic procedure which they employed [3]. Therefore, further comparison of these literature results [3] to our emission data from anhydrous $EuCl_3$ is unwarranted.

The lanthanide trichlorides exhibit a UCl_3-type hexagonal crystal structure [4], space group C^2_{6h}-$P6_3/m$ (ITC No. 176). This structure can be approximated as a tricapped trigonal prism with the three equatorial positions distorted by a slight rotation around the C_3 axis. In $EuCl_3$, the angle of this rotation is equal to 1.4°

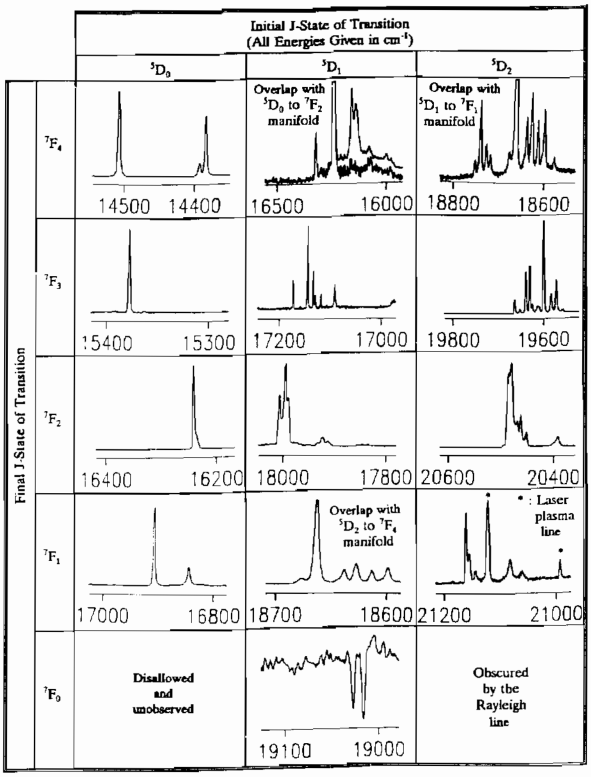

Fig. 1. Emission spectrum from Eu^{3+} ion in anhydrous $EuCl_3$ at 77 K (excitation at 465.8 nm).

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[4]. This small rotation is all that distorts the Eu^{3+} ion's site symmetry from the D_{3h} symmetry of a regular tricapped trigonal prism.

Experimental

Anhydrous $EuCl_3$ (certified 99.9%, Cerac, Inc.) was obtained and sealed into glass capillaries under a helium atmosphere. Both Raman scattering and X-ray diffraction analysis of the samples confirmed that the compound exhibited the expected UCl_3-type crystal structure.

The compound was resonantly excited to the $^5D_2$ state by 200 mW of the 465.8 nm line from a six watt argon-ion laser (Coherent Radiation). The sample was cooled by immersion of the sample capillary in liquid nitrogen (77 K). The emitted light was collected at 90° from the incident laser excitation and dispersed by a 1-meter double monochromator (Jobin Yvon-Instruments SA), having a resolution of 0.5 cm^{-1} at 514 nm. The collected light was detected by a photon counting system, which employed a cooled photomultiplier tube (Hamamatsu) and multichannel analyzer (Nicolet) interfaced with an AT personal computer using 'Spectra Calc' software (Galactic Industries Corp.).

Results and discussion

The Eu^{3+} ion emission bands from anhydrous $EuCl_3$ are shown in Fig. 1. A compilation of the observed transitions and the calculated energies (cm^{-1}) of the electronic levels relative to the Eu^{3+} ion's $^7F_0$ ground state is given in Table 1. The assigned energies of the observed transitions are believed to have an experimental error of less than 2 cm^{-1}. An approximate uncertainty in the calculated relative energies is less than 6 cm^{-1}. The $^5D_1$ to $^7F_0$ transitions were observed as absorption maxima; all other transitions were observed as emission characteristics (Fig. 1).

As stated in 'Introduction', anhydrous $EuCl_3$ deviates slightly from the ideal tricapped trigonal prism and 'perfect' D_{3h} metal ion site symmetry. This deviation should impose a C_{3h} site symmetry upon the Eu^{3+} ion. Group theory predicts that a Eu^{3+} ion in either a D_{3h} or a C_{3h} site should have: no allowed $^5D_0$ to $^7F_0$ transition; two allowed $^5D_0$ to $^7F_1$ transitions; one allowed $^5D_0$ to $^7F_2$ transition; and two allowed $^5D_0$ to $^7F_3$ transitions.

TABLE 1. Relative electronic energy levels and experimentally observed transition energies (cm^{-1}) from the Eu^{3+} ion in anhydrous $EuCl_3$

Final *J* state of transition (cm^{-1})		Initial *J* state of transition (cm^{-1})					
		$^5D_0$	$^5D_1$		$^5D_2$		
		A_1' 17258	E'' 19015	A_2' 19026	E' 21480	E'' 21494	A_1' 21505
$^7F_4$							
2905	A_1''				17492		18598
2876	A_2''	14382					18627
2867	E'	14391		16158	18613	18627	18637
2753	E'	14505	16262		18727	18741	18752
$^7F_3$							
1925	A_2''		17090		19555	19569	19580
1898	A_1''		17117	17128	19580	19598	19608
1882	E'	15376	17132	17144	19598	19611	19622
1866	A_2'				19615	19628	19637
1844	E''		17171		19637	19651	19662
$^7F_2$							
1091	A_1'		17924		20391		
1026	E''		17989	18002	20451	20469	20480
1019	E'	16239	17996	18007	20462	20474	20485
$^7F_1$							
414	A_2'	16844	18598	18612	21060	21092	
352	E''	16906	18663	18677	21122	21144	21155
$^7F_0$							
0	A_1'		19015	19026	Rayleigh line overlap		

All these expected transitions are observed as emission maxima with the exception of the singlet-to-singlet transition of the last set (Fig. 1). Distinguishing between the D_{3h} and C_{3h} site symmetries can be accomplished by careful inspection and analysis of the $^5D_0$ to $^7F_4$ manifold. The $^5D_0$ to $^7F_4$ manifold of Eu^{3+} ion emission should contain three transitions for a D_{3h} metal ion site, or four transitions for a C_{3h} metal ion site; three are observed (Fig. 1). The $^5D_1$ to $^7F_3$ manifold can be similarly employed for interpretive purposes. Six transitions should be seen in this manifold for a D_{3h} metal ion site, compared to seven transitions for a C_{3h} metal ion site; six are observed (Fig. 1). We therefore describe the Eu^{3+} ion's emission as resulting from the ion in a D_{3h} symmetry site. The difference between the assigned Eu^{3+} ion site symmetry based upon the analysis of the X-ray diffraction or luminescence data is believed to stem from the very small deviation from ideal D_{3h} symmetry. This same apparent contradiction has been seen from the analysis of the emission spectra of other similar compounds, including other lanthanide trichlorides [2, 5].

In summary, the deviations from the D_{3h} or C_{3h} symmetry reported by Pant *et al.* [3] can be attributed to the mistaken identity of their sample's composition. The emission spectrum from pure anhydrous $EuCl_3$, as with the other lanthanide trichlorides, has been found to exhibit the emission characteristics of a Eu^{3+} ion occupying a D_{3h} symmetry site without any observed effect of the slight distortion from this site symmetry which has been detected by X-ray analysis. Perhaps one might observe the effects of this slight distortion from D_{3h} site symmetry by analysis of the Eu^{3+} ion's emission spectrum obtained from $EuCl_3$ cooled to lower temperatures than that used in the present work. However such effects were not seen at 4.5 K in Eu^{3+} ion doped lanthanide trichlorides [2].

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References

1 G. D. Del Cul, *Ph.D. Dissertation,* The University of Tennessee, Knoxville, TN, 1990; G. D. Del Cul, G. M. Murray, S. E. Nave, C.-T. P. Chang, G. M. Begun and J. R. Peterson, *Eur. J. Solid State Inorg. Chem., 28* (1991) 155.
2 L. G. DeShazer and G. H. Dieke, *J. Chem. Phys., 38* (1963) 2190; G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals,* Interscience, New York, 1968, p. 243.
3 P. C. Pant, B. C. Bhatt and T. C. Pant, *Indian J. Phys., 58B* (1984) 541.
4 B. Morosin, *J. Chem. Phys., 49* (1968) 3007.
5 W. Urland, *J. Less-Common Met., 148* (1989) 151; R. S. Rana, J. Shertzer and F. W. Kaseta, *Lanthanide Actinide Res., 2* (1988) 295; E. V. Sayre and S. Freed, *J. Chem. Phys., 24* (1956) 1213; H. G. Brittain and J. V. Posluszny, *Thermochim. Acta, 118* (1987) 25.