Luminescence from the Eu^{3+} Ion in D_{4d} Symmetry

G. BLASSE

Physical Laboratory, University of Utrecht, P.O.B. 80.000, 3508 TA Utrecht, The Netherlands

(Received September 17, 1987)

The emission of the Eu^{3+} ion ($4f^6$) is well known and has been studied intensively [1, 2]. It is often used as a probe of site symmetry. Actually the emission spectrum of the Eu^{3+} ion is very simple, since the emitting level ($^5D_0$) is nondegenerate. Usually the emission transitions $^5D_0-^7F_{0,1,2}$ are studied. The $^5D_0-^7F_0$ transition is weak anyhow, the $^5D_0-^7F_1$ transition (magnetic dipole) dominates if the Eu^{3+} ion is on a site with inversion symmetry, the $^5D_0-^7F_2$ transition (forced electric-dipole) dominates if there is no inversion centre [1, 3].

A very peculiar site symmetry in this aspect is D_{4d}. This predicts the following number of lines in the Eu^{3+} emission spectrum: $^5D_0-^7F_0$:0, $^5D_0-^7F_1$:1, $^5D_0-^7F_2$:0, $^5D_0-^7F_4$:2. The $^5D_0-^7F_2$ transition is forbidden under this site symmetry, although inversion symmetry is definitely absent. We have found one example of such a case, *viz.* the emission of Eu^{3+} in lanthanide decatungstates [4]. In this letter we draw attention to the fact that this site symmetry occurs in good approximation also in nonmolecular solids. The emission colour of the Eu^{3+} ion on sites with this symmetry is different from what is expected at first sight.

Structural Data

In the Eu^{3+}–decatungstate molecule the site symmetry of the Eu^{3+} ion is D_{4d} if only the nearest neighbours are considered. In the solid the symmetry is lowered to C_2 [4]. This D_{4d} symmetry is usually not observed in non-molecular solids. However, we found at least two compounds where D_{4d} symmetry is a good approximation to the real site symmetry, *viz.* GdB_3O_6 and YF_3.

The crystal structure of GdB_3O_6 has been solved by Abdullaev *et al.* [5]. The lanthanide ions occupy distorted ten-coordinated polyhedra with site symmetry C_2. However, by using a fourfold axis parallel [001], it can be seen that D_{4d} is a good approximation for the site symmetry. Two O^{2-} ions are nearly on that axis, and the remaining eight are in the neighbourhood of the corners of two squares perpendicular to that axis and 45° rotated relative to each other. This coordination polyhedron has no inversion symmetry, not even in approximation.

The crystal structure of YF_3 is described as containing nine-coordinated lanthanide ions in a tricapped trigonal prism. However, one of the nine nearest neighbours is further away (2.6 Å) than the others (~2.3 Å) [6]. It is clear that such a site lacks inversion symmetry completely. The eight nearest F^- ions form approximately two squares, rotated 45° relative to each other and both perpendicular to the axis connecting Y^{3+} and the ninth F^- ion. This can also be considered as D_{4d} symmetry where the axis mentioned is the fourfold one.

Spectral Results and Discussion

Table I shows the integrated intensities of the Eu^{3+} emission lines of Eu^{3+}–decatungstate [4], YF_3:Eu^{3+} [7] and GdB_3O_6:Eu^{3+} [8]. If these compositions are irradiated with ultraviolet light, they show an orange (not a red) emission. This is due to the fact that the intensity of the $^5D_0-^7F_1$ transition is much higher than that of the $^5D_0-^7F_2$ transition. Usually this is interpreted as an indication that the Eu^{3+} ion occupies a site with a symmetry near to inversion symmetry. This, however, is by no means the case in the compositions under consideration. The low $^5D_0-^7F_2$ intensity is due to the approximate D_{4d} symmetry which forbids this transition.

The fact that the $^5D_0-^7F_2$ transition is nevertheless observed with a non-negligible intensity is due to the deviation from exact D_{4d} symmetry. Undoubtedly the hypersensitive character of this transition

TABLE I. Integrated Emission Intensities for the Eu^{3+} Ion in Three Compositions with Approximate D_{4d} Site Symmetry (the $^5D_0-^7F_1$ (magnetic dipole) intensity has been set 10)

Composition	$^5D_0-^7F_0$	$^5D_0-^7F_1$	$^5D_0-^7F_2$	$^5D_0-^7F_4$
Eu^{3+}–decatungstate	<0.1	10	2	4
YF_3:Eu^{3+}	0.1	10	2	6
GdB_3O_6:Eu^{3+}	0.1	10	2	5

0020-1693/88/$3.50

[1–4] is responsible for the fact that a small deviation from D_{4d} symmetry is sufficient to result in a sizeable intensity.

That the actual site symmetry is lower than D_{4d} follows also from the number of $^5D_0-^7F_1$ and $^5D_0-^7F_4$ emission lines. The number expected for D_{4d} symmetry [2] is only observed if the resolving power is not too high. Otherwise a more extended splitting is observed. Its width is, however, small.

In conclusion, a low $^5D_0-^7F_2$ emission intensity does not prove that the site symmetry of the Eu^{3+} ion is near inversion symmetry. This is only true if the $^5D_0-^7F_4$ transition has also a low intensity. Otherwise the Eu^{3+} ion may occupy a site with (approximate) D_{4d} symmetry.

References

1 G. Blasse, in K. A. Gschneidner, Jr. and L. Eyring (eds.), 'Handbook on the Physics and Chemistry of Rare Earths', North Holland, Amsterdam, 1979, Chap. 34.
2 R. D. Peacock, *Struct. Bonding (Berlin), 22,* 83 (1975).
3 G. Blasse, A. Bril and W. C. Nieuwpoort, *J. Phys. Chem. Solids, 27,* 1587 (1966).
4 G. Blasse, G. J. Dirksen and F. Zonnevijlle, *J. Inorg. Nucl. Chem., 43,* 2847 (1981).
5 G. K. Abdullaev, Kh. S. Mamedov and G. G. Dzhafarov, *Sov. Phys. Crystallogr., 20,* 161 (1975).
6 A. F. Wells, 'Structural Inorganic Chemistry', 4th edn., Clarendon, Oxford, 1975.
7 G. Blasse and A. Bril, *Philips Res. Rep., 22,* 481 (1967).
8 Hao Zhiran and G. Blasse, *Mater. Chem. Phys., 12,* 257 (1985).