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The Charge-Transfer Absorption Band of Eu^{3+} in Oxides

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The position of the charge-transfer band of Eu^{3+} in the absorption spectra of a number of oxides is discussed. It is shown that this position is more or less fixed in octahedral *VI* coordination and that it varies in *VIII* and *XII* coordinations as a function of the effective ionic radius of the relevant host lattice ion.

Introduction

The red luminescence of the Eu^{3+} ion has found technical application. As a consequence, a considerable amount of optical data on this ion in a large variety of compounds have become available in the last decade. It has been suggested that the efficiency of this luminescence is determined by the spectral position of the charge-transfer (c.t.) band in the uv region (*1*, *2*). Till now the variation of the position of this c.t. band as a function of the lattice was not understood. It has been noted that the band position varies considerably from ~48 kK in $ScPO_4{:}Eu^{3+}$ (*3*) to 30.5 kK in $SrLaLiWO_6{:}Eu^{3+}$ (*4*). This experimental fact is not in accordance with Jørgensen's relation between the position of a c.t. band (σ) and the optical electronegativities (χ) of the central ion (M) and the ligand (X) (*5*):

$$\sigma = [\chi_{\text{opt}}(X) - \chi_{\text{uncorr}}(\text{M})]\cdot 30 \text{ kK}.$$

In Ref. (*6*) we have proposed a model that explains the variation of the c.t. band position of tetravalent lanthanide (Ln) ions in *VIII* coordination in oxidic lattices. It seemed interesting to try to extend this model to the Eu^{3+} c.t. band. Furthermore we will try to give some rules concerning the position of this band in compounds in which the Eu^{3+} ion has the same coordination number, but a different stereochemistry.

Results

All data were taken from the literature (*3*, *4*, *7–13*) and are summarized in Tables I, II, and III. We use only data relating to the Eu^{3+} ion on the site of trivalent lanthanide ions or on the site of Y^{3+} and Sc^{3+} in oxidic lattices.

Discussion

Table I shows that the position of the Eu^{3+} c.t. band does not shift appreciably in the case of a (more or less regular) octahedral coordination of the Eu^{3+} ion by oxygen ions in lanthanide compounds (including Y and Sc compounds). The ionic radii of the relevant host lattice ions vary from Sc^{3+} ($r_{VI} = 0.745$ Å) to Gd^{3+} ($r_{VI} = 0.938$ Å); the ionic radius of Eu^{3+} in *VI* coordination is $r_{VI} = 0.947$ Å (*14*). This is consistent with observations for tetravalent Ln ions (*6*). For a regular octahedron this band can be ascribed to the transition $\pi t_{1g} \rightarrow f$.

Accepting an average band position of 42 kK in octahedral *VI* coordination and using Jørgensen's definition (*5*) we arive at a value of $\chi_{\text{uncorr}} = 1.8$ for the Eu^{3+} ion with $\chi_{\text{opt}}(O^{2-}) = 3.2$. This is only slightly lower than the value reported for Eu^{3+} complexes with halogen ligands in solutions, i.e., 1.89 for Eu^{3+} in $EuCl_6^{3-}$ (*15*).

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TABLE I

POSITION OF THE c.t. BAND OF Eu^{3+} IN OCTAHEDRAL *VI* COORDINATION IN OXIDES

Compound	Crystal structure	Reference	σ(kK)
$ScBO_3:Eu^{3+}$	Calcite	(*7*)	43
$NaLuGeO_4:Eu^{3+}$	Olivine	(*8*)	43.4
$LiLuSiO_4:Eu^{3+}$	Olivine	(*8*)	43.2
$NaLuSiO_4:Eu^{3+}$	Olivine	(*8*)	43.1
$LiLuO_2:Eu^{3+}$	α-$LiFeO_2$	(*9*)	43.0
$LiLuGeO_4:Eu^{3+}$	Olivine	(*8*)	41.6
$NaYGeO_4:Eu^{3+}$	Olivine	(*8*)	43.1
$LiYSiO_4:Eu^{3+}$	Olivine	(*8*)	42.7
$YBO_3:Eu^{3+}$	Calcite	(*10*)	42.7
$LiYO_2:Eu^{3+}$	α-$LiFeO_2$	(*9*)	42.0
$Y_2O_3:Eu^{3+}$	Bixbyite	(*11*)	41.7
$CaYBO_4:Eu^{3+}$	Y_2BeO_4	(*11*)	41.7
$LiYGeO_4:Eu^{3+}$	Olivine	(*8*)	41.4
$GdBO_3:Eu^{3+}$	Vaterite	(*7*)	42.5
$NaGdGeO_4:Eu^{3+}$	Olivine	(*8*)	41.6
$LiGdO_2:Eu^{3+}$	α-$HAlO_2$	(*9*)	41.3
$Gd_2O_3:Eu^{3+}$	Bixbyite	(*7*)	41.1
$NaGdO_2:Eu^{3+}$	α-$LiFeO_2$	(*9*)	41.1

Turning to *VIII* coordination it is seen in Table II that the position of the first excitation band shifts from very high energies for Eu^{3+} on the site of Sc^{3+} ($r_{VIII} = 0.87$ Å) to very low energies for Eu^{3+} on the site of La^{3+} ($r_{VIII} = 1.18$ Å).

The same line of reasoning as was used in the case of the tetravalent Ln ions applies here. Again the position of the $2t_{2g}$ ligand m.o. (*6*) relative to the t_{1g} ligand m.o. is strongly dependent on the energetic position and the extent of delocalization of the metal ion *d*-orbitals and the magnitude of the interaction terms of both sets of ligand t_{2g} m.o.'s with the metal t_{2g} *d*-orbitals. Thus the Eu–O distance becomes a factor that strongly determines the c.t. band position in the case of cubic *VIII* coordination.

For an oxygen *XII* coordination with (more or less regular) cubic symmetry only data for Eu^{3+} on the site of a Gd^{3+} or a La^{3+} ion have been reported. The data point to the existence of an effect similar to that observed for Eu^{3+} in *VIII* coordination (see Table III). This is not unexpected since in this coordination there are also two sets of ligand t_{2g} m.o.'s and two sets of ligand e_g m.o.'s; furthermore, note that the crystal-field splitting in both coordinations is similar (*16*).

We thought it interesting to compare data on the c.t. band of Eu^{3+} ions with the same

TABLE II

POSITION OF THE c.t. BAND OF Eu^{3+} IN *VIII* COORDINATION IN OXIDES

Compound	Crystal structure	Reference	σ(kK)
$ScPO_4:Eu^{3+}$	Zircon	(*3*)	~48
$YPO_4:Eu^{3+}$	Zircon	(*11*)	~45
$Y_3Ga_5O_{12}:Eu^{3+}$	Garnet	(*12*)	42.5
$YTaO_4:Eu^{3+}$	Fergusonite	(*13*)	40.8
$Gd_2Zr_2O_7:Eu^{3+}$	Disordered fluorite	(*12*)	38.1
$LaPO_4:Eu^{3+}$	$CePO_4$	(*11*)	37

TABLE III

POSITION OF THE c.t. BAND OF Eu^{3+} IN *XII* COORDINATION IN OXIDES

Compound	Crystal structure	Reference	σ(kK)
$GdGaO_3:Eu^{3+}$	Perovskite	(*12*)	40.5
$GdAlO_3:Eu^{3+}$	Perovskite	(*12*)	38
$LaAlO_3:Eu^{3+}$	Perovskite	(*12*)	32.3
$SrLaLiWO_6:Eu^{3+}$	Ordered perovskite	(*4*)	30.5

coordination number but with different stereochemistry. Only a few data are known for the Eu^{3+} c.t. band in a trigonal prismatic *VI* coordination, i.e., 40.5 kK in $YAl_3B_4O_{12}$ (*11*), 40.1 kK in $GdAl_3B_4O_{12}$ (*12*), and 41.3 kK in $NaGdSiO_4$ (*8*). Here the position of the c.t band appears to be more or less fixed, as in octahedral *VI* coordination. Accepting an average band position of 40.5 kK from the available data we arrive at $\chi_{\text{uncorr}} = 1.85$ for the Eu^{3+} ion in trigonal prismatic *VI* coordination. This is somewhat higher than the value for octahedral *VI* coordination and well within the limits of experimental error.

One clear discrepancy should be mentioned. For Eu^{3+} on a La^{3+} site in octahedral *VI* coordination only one datum is reported, i.e., $NaLaO_2{:}Eu^{3+}$ with the α-$LiFeO_2$ structure, which is an ordered rocksalt structure. The c.t. band is reported to be situated at 36 kK (*9*) which is much too low for an octahedral *VI* coordination [$r_{VI}(La^{3+}) = 1.045$ Å]. At the moment we cannot explain this discrepancy. It seems worthwhile to reinvestigate $NaLaO_2{:}Eu^{3+}$.

In Ref. (*6*) we found for the tetravalent Ln ions in *VIII* coordination a second maximum, which we attributed to a transition ligand $t_{1g} \rightarrow f$. For Eu^{3+} in oxides no reliable data are available, one of the difficulties being the absorption of the host lattice, which is often expected in the same region of the spectrum.

It has been suggested that the variation of the c.t. absorption band of Eu^{3+} in oxides can be explained by the variation of the potential at the O^{2-} anion (*12*). This, however, cannot be a major factor, since the consequence of this would be that the magnitude of the variation would be roughly the same for all coordinations.

In conclusion, we can state the following concerning the position of the Eu^{3+} c.t. band in oxidic lattices:

(1) The coordination of the Eu^{3+} ion is a determining factor. In octahedral *VI* coordination the band position is more or less fixed, and in cubic *VIII* and *XII* coordinations the band position varies as a function of the host lattice.

(2) The variation in *VIII* and *XII* coordinations is proportional to the Eu–O distance. With increasing bond length the band shifts to lower energies.

These rules may be used as a strong indication of the exclusion of certain surroundings in unknown structures. Eu^{3+} in Y_2SO_6, for example, has the c.t. band at 37 kK (*11*). This seems to exclude *VI* coordination for Y in this compound.

Finally, these rules relate the value of the quantum efficiency of Eu^{3+} luminescence for excitation into the c.t. band to the structural details of the host lattices applied.

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