

## EVIDENCE FOR THE INFLUENCE OF AN EFFECTIVE CHARGE ON THE POSITION OF THE CHARGE-TRANSFER BAND OF $\text{Eu}^{3+}$ IN SOLIDS

H.E. HOEFDRAAD, F.M.A. STEGERS and G. BLASSE

*Department of Solid State Chemistry, Physical Laboratory, University of Utrecht, Utrecht, The Netherlands*

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Evidence is given for the influence of the effective charge on the position of the charge-transfer band of the  $\text{Eu}^{3+}$  ion occupying the crystallographic site of cations with a different formal charge (viz.  $\text{Ca}^{2+}$ ,  $\text{Zr}^{4+}$ ) in oxides.

The spectral position of the first charge-transfer (CT) band of a molecular or ionic complex is determined by the oxidizing character of the central metal ions and by the properties of the set of ligands [1, 2]. In solids the presence of an effective charge may also be of importance. The central metal ion bears a formal effective charge if it replaces a metal ion with different charge in the host lattice concerned [3]. The  $\text{Eu}^{3+}$  ion on the site of a  $\text{Ca}^{2+}$  ion in a calcium compound, for example, is effectively positive but on the site of a  $\text{Zr}^{4+}$  ion in a zirconium compound it is effectively negative. It is to be expected that ligand-to-metal CT bands are situated at relatively low energy if the metal ion bears an effectively positive charge and at relatively high energy if the metal ion bears an effectively negative charge.

Almost no attention has been paid to this effect, which may be due to the fact that much of the work on CT spectra has been performed in liquids where it is impossible to define an effective charge. An example where such an effect has been claimed is the system  $\text{CaSO}_4\text{-V, Tb}$  where the fact that the  $\text{Tb}^{3+}$  emission is not quenched by the  $\text{Tb}^{4+}\text{-V}^{4+}$  CT state has been explained by noting that  $\text{Tb}^{3+}$  on a  $\text{Ca}^{2+}$  site has an effectively positive charge and  $\text{V}^{5+}$  on an  $\text{S}^{6+}$  site has an effectively negative charge [4]. Thus, it was argued, the CT band should be expected at higher energies than in  $\text{YPO}_4\text{-V, Tb}$  where the  $\text{Tb}^{3+}$  luminescence is quenched rapidly if P is replaced by V [5, 6].

We now present some direct evidence for the exist-

tence of such an effect. We have recently proposed a model to explain the strong variation of the position of the first CT band of  $\text{Eu}^{3+}$  [7] and of the tetravalent lanthanides [2] in oxides. It was noted that in octahedral VI coordination the position of the first CT band is more or less fixed ( $42 \pm 1$  kK) thus obeying Jørgensen's rules concerning the optical electronegativities [8]. A suitable system to study the effect of effective charge on the spectral position of CT bands is, therefore, the  $\text{Eu}^{3+}$  ion incorporated in three different compounds on octahedral sites which are occupied in the pure compound by di-, tri- and tetravalent metal ions, respectively. To limit the effect of different ionic radii we considered  $\text{Ca}^{2+}$  as the divalent and  $\text{Zr}^{4+}$  as the tetravalent ion.

The results are the following: in  $\text{CaO-Eu}^{3+}$  the CT band is located at  $\approx 36$  kK [9], in  $\text{Y}_2\text{O}_3\text{-Eu}^{3+}$  at 41.7 kK [10] and in  $\text{ZrP}_2\text{O}_7\text{-Eu}^{3+}$  at 45 kK or higher. The spectral shift due to the presence of an effective charge (4–5 kK) is much larger than the small variation in the position of the CT band of octahedrally coordinated  $\text{Eu}^{3+}$  in a large number of compounds where it does not bear an effective charge (1–2 kK). These data indicate, therefore, directly the existence of an influence of the effective charge on the oxidizing character of central metal ion.

Unfortunately it is extremely difficult to obtain more examples. In VI coordination the CT bands of the host lattice often interfere, because they appear in the same region of the spectrum. Furthermore it cannot

be excluded that in other cases different effects will obscure the effective charge influence. We consider  $\text{Eu}^{3+}$  in VIII-coordination to illustrate this remark. For this coordination the position of the CT band is also determined by the Eu—O distance [7], which in turn is influenced by the formal charge of the  $\text{Eu}^{3+}$  ion.

As an illustration we compare  $\text{YPO}_4\text{—Eu}^{3+}$  and  $\text{CaSO}_4\text{—Eu}^{3+}$ , P. In both compounds  $\text{Eu}^{3+}$  is in VIII coordination. In the former it is effectively neutral, in the latter effectively positive. The position of the CT band has been reported for  $\text{YPO}_4\text{—Eu}^{3+}$  at 45 kK [10] and determined by us for  $\text{CaSO}_4\text{—Eu}^{3+}$ , P at 38 kK. This large shift may partly be due to the influence of the effective charge, but on the other hand the Eu—O distance in the calcium compound cannot easily be compared with that in the yttrium compound on the basis of the ionic radii of both host ions. Therefore, the magnitude of the shift of the CT band due to an effective charge on the  $\text{Eu}^{3+}$  ion in VIII coordination cannot easily be estimated.

We conclude that the influence of an effective charge on the position of CT bands is not easy to demonstrate, but that the most suitable example for such a study, viz. octahedrally coordinated  $\text{Eu}^{3+}$  in oxides, presents strong evidence for such an effect which must be quite general.

$\text{ZrP}_2\text{O}_7\text{—Eu}^{3+}$  was prepared by firing recrystallized  $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{Eu}_2\text{O}_3$  in oxygen

of  $1100^\circ\text{C}$ .  $\text{CaSO}_4\text{—Eu}^{3+}$ , P was prepared by firing  $\text{CaCO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Eu}_2\text{O}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  in oxygen at  $1000^\circ\text{C}$ . Samples were checked by X-ray analysis using  $\text{Cu K}\alpha$  radiation. The spectral position of the CT band of the  $\text{Eu}^{3+}$  ion was determined from the excitation spectra of the red  ${}^5\text{D}_0\text{—}{}^7\text{F}_{1,2}$  emission as were all literature values cited. The excitation spectra were measured on a Perkin—Elmer MPF-3L spectrofluorimeter at 300 K and corrected for the lamp intensity using sodium salicylate. Due to the low lamp intensity above 40 kK we could only determine a lower limit for the CT band position of  $\text{ZrP}_2\text{O}_7\text{—Eu}^{3+}$ .

## References

- [1] C.K. Jørgensen, *Modern aspects of ligand field theory* (North-Holland, Amsterdam, 1971).
- [2] H.E. Hoefdraad, *J. Inorg. Nucl. Chem.*, to be published.
- [3] F.A. Kröger, *The chemistry of imperfect crystals* (North-Holland, Amsterdam, 1964).
- [4] W.T. Draai and G. Blasse, *Phys. Stat. Sol.* 21a (1974) 569.
- [5] R.G. De Losh, T.Y. Tien, E.F. Gibbons, P.J. Zacamanides and H.L. Stadler, *J. Chem. Phys.* 53 (1970) 681.
- [6] G. Blasse, *J. Luminescence* 1, 2 (1970) 766.
- [7] H.E. Hoefdraad, to be published.
- [8] C.K. Jørgensen, *Absorption spectra and chemical bonding* (Pergamon Press, New York, 1962).
- [9] W. Lehmann, *J. Luminescence* 6 (1973) 455.
- [10] G. Blasse, *J. Solid State Chem.* 4 (1972) 52.