

The Ultraviolet Absorption Bands of Bi^{3+} and Eu^{3+} in Oxides

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The position of the uv absorption bands of Bi^{3+} ($^1S_0 \rightarrow ^3P_1$ transition) and of Eu^{3+} (charge-transfer transition) in a number of oxides are discussed. The position of the Bi^{3+} band seems to be determined by the covalency of the lattice; that of the Eu^{3+} band by other, mainly unknown, effects.

1. Introduction

The Bi^{3+} ion is expected to show two strong absorption bands in the ultraviolet region of the spectrum, viz., the transitions $^1S_0 \rightarrow ^3P_1$ and 1P_1 (1).

The Eu^{3+} ion shows a charge-transfer absorption band in this region (2). The position of both bands depends strongly on the nature of the surrounding ions. In the sequence of ligands F, Cl, Br, I, for example, these bands shift to lower energies.

It seemed interesting to compare the position of these bands in a number of host lattices that can contain Eu^{3+} as well as Bi^{3+} without charge-compensation. In this way it is possible to find whether the influence of the host lattice on the position of the absorption bands is the same for Bi^{3+} ("Rydberg" transition) as for Eu^{3+} (charge-transfer transition).

2. Results

Results are summarized in Table I. These data were taken from earlier papers, viz., (3) for Bi^{3+} , (4) for Ce^{3+} and (5) for Eu^{3+} , and represent the $^1S_0 \rightarrow ^3P_1$ transition of Bi^{3+} , the energy difference between the $4f$ state and the centre of the $5d$ state of Ce^{3+} as derived or estimated from the transitions between the $4f$ state and the $5d$ crystal field components, and the charge-transfer transition of Eu^{3+} . The host lattices are arranged according to the position of the Bi^{3+} band.

3. Discussion

(a) Bi^{3+}

From Table I it is seen that the position of the Bi^{3+} and the Ce^{3+} absorption band shifts to lower energy in the given sequence of host lattices and that the position of the Eu^{3+} band is not related to this sequence. In the case of Bi^{3+} and Ce^{3+} we are involved with a transition on the cation itself ("Rydberg" transition). It is well known that these transitions depend strongly on covalency effects (6). Recently Duffy and Ingram (7) have proposed a quantitative relation between the position of the $^1S_0 \rightarrow ^3P_1$ transition of ns^2 ions and the nephelauxetic ratio factor h of the host lattice. The factor h comes from the factorization of the nephelauxetic ratio β (derivable from $d-d$ spectra) as proposed by Jørgensen (8): $1 - \beta = hk$, where h relates to the ligands and k to the central metal ion. From the position of the Bi^{3+} absorption band given in Table I we derived the factor h for each lanthanide site in the host lattices given using the relation proposed by Duffy and Ingram. These values of h are also given in Table I. An inspection of these values reveals the following:

- (i) A typical value of h for oxygen does not exist. The value of h varies from 1.0 to 2.0. Even within the series of borates h varies from 1.2 to 1.6;
- (ii) The sequence of host lattices arranged according to increasing h is not unreasonable from a chemical point of view. If we take the yttrium

TABLE I
SPECTRAL DATA (IN kK) OF Bi^{3+} , Ce^{3+} AND Eu^{3+} IN SOME OXIDES

Host lattice	Bi^{3+} ($^1S_0-^3P_1$)	h	Ce^{3+} ($4f$ -centre $5d$)	Eu^{3+} charge-transfer	coordination
YPO_4	43.0	1.0	~ 36.5	~ 45	4 + 4
LaPO_4	41.5	1.1	—	37.0	8
LaBO_3	40.4	1.2	~ 36	37	9
YBO_3	38.5	1.4	~ 35	42.7	6
YOF	37.8	1.4	—	~ 43	4O, 4F
Y_2SO_6	37.8	1.4	—	37.0	?
Lu_2SO_6	37.0	1.5	—	37.0	?
$\text{YAl}_3\text{B}_4\text{O}_{12}$	36.7	1.5	35.4	40.5	6
La_2SO_6	36.4	1.5	—	34.5	?
CaYBO_4	35.8	1.6	~ 34	41.7	6
LiYSiO_4	35.7	1.6	—	42.7	6
ScBO_3	35.1	1.6	32.5	~ 43	6
La_2O_3	32.5	1.8	—	33.7	7
Y_2O_3	30.1	2.0	—	41.7	6
YOCl	30.1	2.0	~ 33	35.4	4O, 5Cl
LaOCl	30.0	2.0	—	33.3	4O, 5Cl

compounds with known crystal structure and oxygen anions only, the sequence is YPO_4 , YBO_3 , $\text{YAl}_3\text{B}_4\text{O}_{12}$, CaYBO_4 , LiYSiO_4 , and Y_2O_3 . That h (and, therefore, the covalency) increases in this series, may be argued as follows. In YPO_4 the Y ion has four nearest oxygen neighbors; these are in a nearly linear Y–O–P configuration, so that the oxygens are strongly polarized from the Y ion to the small and highly charged P ion resulting in a low degree of covalency at the Y site (9). In YBO_3 and $\text{YAl}_3\text{B}_4\text{O}_{12}$, each oxygen surrounding an yttrium site has at least one different small ion (B, Al) as neighbor with angle Y–O–B(Al) in the order of 110° . The degree of covalency at the Y-site is then expected to be larger than in YPO_4 (with larger angle). In CaYBO_4 and LiYSiO_4 a similar situation is found but a number of oxygen ions are polarized by one and the same small ion. In Y_2O_3 , finally, no small cations are present. In fact, the oxygen ions are surrounded rather regularly by four yttrium ions so that there is practically no anion polarization. These considerations show that the values of h are not surprising and that the relation of Duffy and Ingram may be used with some confidence for solid oxides too.

(iii) Taking $h = 2.0$ for an oxide lattice without small cations we note that the value $h = 1.4$ for YOF is the average of $h = 2.0$ and the h value of fluorine [0.8; see Ref. (8)]. The value $h = 2.0$ for the oxychlorides is equal to the value of 2.0 for Y_2O_3 and 2.0 for chlorine (8).

(b) Ce^{3+}

It is interesting to see that the value of the energy difference between the $4f$ state and the centre of the $5d$ state indicate the same sequence of host lattices as the values for Bi^{3+} . In Fig. 1 we have plotted the value of this energy difference versus the h value of the host lattice obtained from the position of the Bi^{3+} band in that lattice. The relation is linear. Note, however, that the Bi^{3+} band is more sensible to a variation

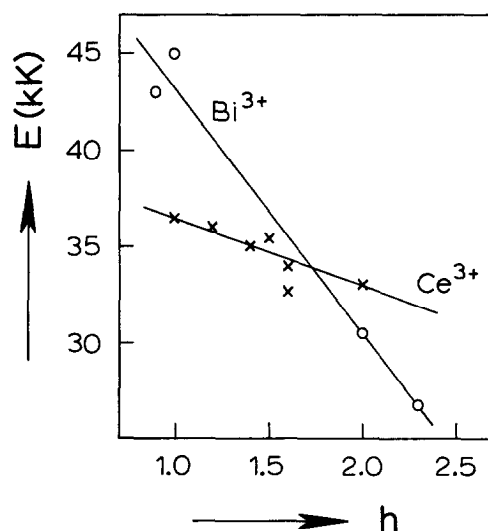


FIG. 1. The relation of Duffy and Ingram [Ref. (7)] for Bi^{3+} ($^1S_0-^3P_1$) and the energy difference between the $4f$ state and the centre of the $5d$ state of Ce^{3+} v. h .

of h than the $4f$ centre– $5d$ distance of Ce^{3+} as should be expected since to a first and good approximation the $4f$ orbitals do not interact with the surroundings.

(c) Eu^{3+}

Table I shows that the position of the Eu^{3+} charge-transfer band is not determined by the value of h . As pointed out by Jørgensen (10) the position of the charge-transfer band of a given metal ion in a series of ligands is given by the optical electronegativity x_{opt} . Since the relation between h and x_{opt} seems to be linear for a number of ligands (see Fig. 2), the present result is surprising, especially because the Eu^{3+} and Bi^{3+} ion were introduced in the same crystallographic sites. This shows that other factors are determining the position of the charge-transfer band in oxides. One of these may be the coordination number of the Eu^{3+} ion. There is a tendency to find the charge-transfer band at lower energies for higher

coordination numbers. This is also shown in Table I. This correlation has been supposed by other authors before, e.g., for Eu^{3+} halides (11), tungstates (12) and Fe chlorides (13). On the other hand, the position of the charge-transfer band is also determined by the potential field at the O^{2-} ions that surround the Eu^{3+} ions (14).

In conclusion we see that the position of the Rydberg transition of Bi^{3+} in oxides is determined by factors completely different from those determining the position of the Eu^{3+} charge-transfer band. This is in contradiction with the data for, e.g., halides, where both bands shift to lower energy in the sequence F, Cl, Br, I.

References

1. D. S. McCLURE, "Electronic Spectra of Molecules and Ions in Crystals," Academic Press, New York, 1959.
2. C. K. JØRGENSEN, *Mol. Phys.* **5**, 271 (1962).
3. G. BLASSE AND A. BRIL, *J. Chem. Phys.* **48**, 217 (1968); *Philips Res. Rep.* **23**, 461 (1968).
4. G. BLASSE AND A. BRIL, *J. Chem. Phys.* **47**, 5139 (1967).
5. G. BLASSE, *J. of Luminescence* **1**, **2**, 766 (1970), and references cited therein.
6. See, e.g., C. K. JØRGENSEN, "Absorption Spectra and Chemical Bonding," Chapt. 10, Pergamon Press, New York, 1962.
7. J. A. DUFFY AND M. D. INGRAM, *J. Chem. Phys.* **54**, 443 (1971).
8. Reference (6, Chapter 7).
9. Compare similar arguments in G. Blasse, *J. Appl. Phys.* **36**, 877 (1965).
10. C. K. JØRGENSEN, "Orbitals in Atoms and Molecules," Academic Press, New York, 1962.
11. J. C. BARNES AND H. PINCOTT, *J. Chem. Soc.* 842 (1966).
12. F. A. KRÖGER, "Some Aspects of the Luminescence of Solids," Elsevier, Amsterdam, 1948.
13. H. L. SCHLAEFER, *Z. Physik. Chemie (N.F.)* **3**, 222 (1955).
14. G. BLASSE, *J. Chem. Phys.* **45**, 2356 (1966).

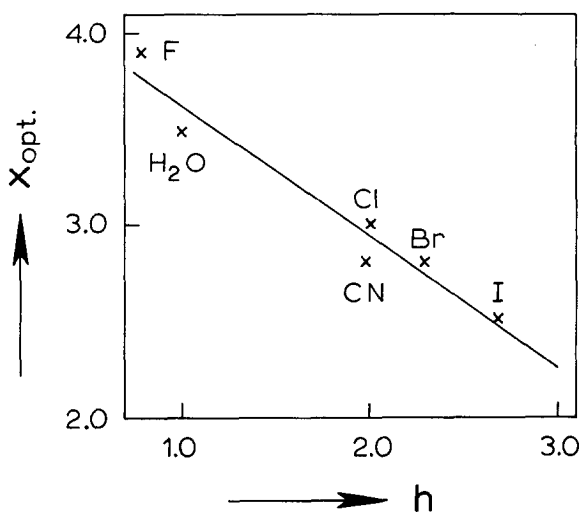


FIG. 2. The optical electronegativity x_{opt} v. the factor h for some ligands. Data from Ref. (8) and Ref. (10).