

In the  $\text{FeSb}_2\text{O}_4$  the yield of  $\text{Sb}^{\text{V}}$  was higher: 8 per cent of the radioactive fraction was in the pentavalent state. In the  $\text{Sb}_2\text{O}_3$ , the  $\text{Sb}-\text{O}$  has 46 per cent partial ionic character, but in the  $\text{FeSb}_2\text{O}_4$  the bond is more covalent [3, 6].

If the internal conversion processes account for the formation of the higher oxidation state, the low yield of  $\text{Sb}^{\text{V}}$  in the trivalent irradiated antimony compounds, could be due to a very rapid electron transfer mechanism, perhaps via the formation of  $F$  type centres. But this transfer is somewhat reduced by covalent character of the bond.

Upon annealing, the yield of  $\text{Sb}^{\text{V}}$  in  $\text{FeSb}_2\text{O}_4$  decreases as in  $\text{Sb}_2\text{O}_3$ . Its annealing patterns are temperature dependent (see Fig. 1a). In addition, Maddock's rule is obeyed (Fig. 1b). The higher the temperature, the higher the number of electron donor centres which diffuse towards the trapped recoil atom. Further, migration of oxide ions might be involved in this mechanism; so that one should expect anionic vacancies to be generated. Such vacancies behave, as Maddock [7] showed, as "incipient  $F$  centres", the function of which is to facilitate the reduction steps in thermal annealing, acting as electron donors.

Instituto de Ciencias  
Asunción  
Paraguay  
South America

J. F. FACETTI

6. A. F. Wells, *Structural Inorganic Chemistry* p. 670. Clarendon Press, Oxford (1960).

7. S. M. Milenkovic and A. G. Maddock, *Radiochim. Acta* **8**, 222 (1967).

---

*J. inorg. nucl. Chem.*, 1971, Vol. 33, pp. 4356-4357. Pergamon Press. Printed in Great Britain

## A relation between charge-transfer spectra and ionization potentials

(Received 20 April 1971)

THE CHARGE-transfer spectra of highly-charged cations with noble-gas configuration in oxides (e.g. niobate or tungstate groups) have been investigated during recent years [1, 2]. In the u.v. region of the spectrum these groups show a strong optical absorption due to transfer of electronic charge from the surrounding oxygen ligands ( $2p$  orbitals) to the central cation (empty  $d$  orbitals). This note reports on a relation between the spectral position of these charge-transfer bands and the value of the  $n^{\text{th}}$  ionization potential of the central  $M^{n+}$  ion.

From a classical point of view, the energy  $\Delta E$  required to transfer an electron from the ligands to the central metal ion, is given by  $\Delta E = -I_n + E_L + \Delta M$  [3]. Here  $I_n$  is the  $n^{\text{th}}$  ionization potential of the metal ion  $M^{n+}$ ,  $E_L$  the electroaffinity of the ligand and  $\Delta M$  the change in Madelung, polarization and related energies. From this equation we might expect a linear relation between  $\Delta E$  and  $I_n$  in the case of a series of isomorphous compounds in which only  $M^{n+}$  is varied.

In Fig. 1 the experimental values of  $\Delta E$  vs.  $I_n$  have been plotted for a number of compounds. The straight lines connecting isomorphous compounds are parallel. The perovskites  $\text{Sr}_3\text{MoO}_6$ ,  $\text{Sr}_3\text{WO}_6$ ,  $\text{Sr}_2\text{GdNbO}_6$ , and  $\text{Sr}_2\text{GdTao}_6$  containing isolated  $\text{MoO}_6$ , etc. octahedra are on a straight line. The slope of these lines is about  $-0.08$ . From the equation given above a value of  $-1$  is expected. This indicates the existence of an effective screening-constant that is constant for the (isoelectronic) groups wherein the charge-transfer transition occurs. It probably corresponds to the fact that the electron returning to the metal ion does not come from infinity to a free ion. The process occurs in a dielectric.

1. G. Blasse and A. Bril, *Z. phys. Chem.* **57**, 187 (1968).

2. G. Blasse and A. Bril, *J. Luminesc.* **3**, 109 (1970).

3. See e.g. H. L. Schaefer, *Z. phys. Chem.* **3**, 222 (1955).

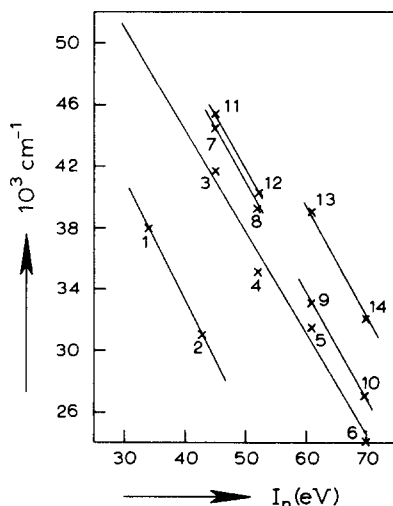


Fig. 1. The spectral position of the charge-transfer band ( $10^3 \text{ cm}^{-1}$ ) of a number of oxides containing  $\text{Me}^{n+}$  ions with noble-gas configuration vs. the  $n^{\text{th}}$  ionization potential  $I_n$  (eV). 1— $\text{CaZrO}_3$ ; 2— $\text{CaTiO}_3$ ; 3— $\text{Sr}_2\text{GdTaO}_6$ ; 4— $\text{Sr}_2\text{GdNbO}_6$ ; 5— $\text{Sr}_3\text{WO}_6$ ; 6— $\text{Sr}_3\text{MoO}_6$ ; 7— $\text{YTao}_4$ ; 8— $\text{YNbO}_4$ ; 9— $\text{Gd}_2\text{WO}_6$ ; 10— $\text{Y}_2\text{MoO}_6$ ; 11— $\text{Mg}_4\text{Ta}_2\text{O}_9$ ; 12— $\text{Mg}_4\text{Nb}_2\text{O}_9$ ; 13— $\text{CaWO}_4$ ; 14— $\text{CaMoO}_4$ .  $I_4 = 34$  for Zr and 43 for Ti;  $I_5 = 45$  for Ta and 52 for Nb;  $I_6 = 61$  for W and 70 for Mo.

The fact that the lines in Fig. 1 do not coincide must be due to different values of  $\Delta M$ . If one considers, for example, the series  $\text{Mg}_4\text{Ta}_2\text{O}_9$ ,  $\text{YTao}_4$ , and  $\text{Ba}_2\text{GdTaO}_6$  it is clear that the Madelung energies will be different.

The relations of Fig. 1 can be used to predict the position of the charge-transfer band of other, isoelectronic groups. Two examples given here:

(a)  $\text{Zr}^{4+}$ . The 4<sup>th</sup> ionization potential of Zr amounts to 34 eV. The charge-transfer band of isolated  $\text{Zr}^{4+}$  in oxides is then expected to be situated at about  $50,000 \text{ cm}^{-1}$ . For  $\text{BaZrSi}_3\text{O}_9$  with isolated  $\text{ZrO}_6$  octahedra we observed a strong band at about  $52,000 \text{ cm}^{-1}$  [4].

(b)  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ . For these ions (with  $I_3 = 25$ , 20, and 20, respectively) the charge-transfer band is expected at such high energies that the edge absorption of these compounds (between 45,000 and  $50,000 \text{ cm}^{-1}$ ) must be due to another transition (e.g.  $2p \rightarrow 3s$  on the  $\text{O}^{2-}$  ion as proposed by Jørgensen [5]).

Solid State Chemistry Department  
Physical Laboratory  
University of Utrecht, Sorbonnelaan 4  
Utrecht  
The Netherlands

G. BLASSE

4. G. Blasse and A. Bril, *J. solid-state Chem.* **2**, 105 (1970).
5. C. K. Jørgensen, R. Pappalardo and E. Rittershaus, *Z. Naturforsch.* **20a**, 54 (1965).