

# XANES Study of Tungsten $L_{III}$ Discontinuity in Some Rare Earth Tungstates

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The shape and near edge structure of the  $L_{III}$  absorption discontinuity of tungsten in some rare earth tungstates,  $RE_2(WO_4)_3$ , were studied using a 40 cm Cauchois-type transmission x-ray spectrograph. Molecular orbital theory was used to interpret the fine structure.

## INTRODUCTION

In recent years the study of rare earth metals and their compounds has attracted considerable interest because of their technological potential.<sup>1-4</sup> Amongst the rare earth compounds, the HRET (heavy rare-earth tungstates) system is particularly important. The compounds of this family are typical insulators at room temperature and they become semiconductors at elevated temperatures.<sup>5,6</sup>

As is well known,<sup>7,8</sup> the study of x-ray absorption discontinuity provides valuable information on the electronic structure and chemical bonding in various types of materials. Several theories have been put forward to explain the fine structure observed close to the discontinuities, which is called XANES (x-ray absorption near edge structure). Molecular orbital theory is particularly useful, especially when the absorbing atom is surrounded by ligands in such a way that one can think in terms of the existence of molecules in the materials.

We report in this paper an x-ray absorption study of rare-earth tungstates,  $Gd_2(WO_4)_3$  and  $Dy_2(WO_4)_3$ , which show insulator to semiconductor transition. These compounds have similar structures, usually described as a defect scheelite structure,<sup>9,10</sup> in which the tungsten atom exists in the radical  $(WO_4)^{2-}$  form with a coordination number of four and the rare-earth ion has a coordination number of eight.<sup>11</sup> The radical  $(WO_4)^{2-}$ , with tetrahedral symmetry, is common to all compounds of the system and the near environment is basically the same in each case.

## EXPERIMENTAL

The compounds were prepared and characterized at the Physical Laboratory of the Mineral Exploration Corp., Nagpur.

The  $L_{III}$  absorption spectra of the compounds were recorded on a Cauchois-type 40-cm, bent crystal x-ray spectrograph. An x-ray tube with a copper target, operated at 20 kV and 10 mA, was employed as the source of radiation. The (100) reflecting planes of mica were used for recording the spectra. Several spectra for each sample were recorded using different absorption thicknesses, and that giving the best contrast and structure was selected. Several spectra using the proper absorption thickness were recorded for each sample to ensure reproducibility.

Microphotometer traces with a magnification of  $\times 100$  were taken on a Carl-Zeiss (MD 100) microphotometer for each spectrum at different heights on the same film. The reference lines used for measurement of the wavelength of the  $L_{III}$  discontinuity of tungsten were  $WL_{\gamma_1}$  and  $WL_{\beta_2}$  whose wavelengths were taken from the International Tables for x-ray wavelengths.<sup>12</sup>

## RESULTS

The structure associated with the  $L_{III}$  discontinuity of tungsten in the tungstates as observed on the microphotometer traces was studied. The discontinuities had similar shapes in both compounds. A typical curve showing the near edge fine structure associated with the  $L_{III}$  discontinuity of tungsten in  $Gd_2(WO_4)_3$  is given in Fig. 1.

The shape of the tungsten  $L_{III}$  discontinuity in these compounds is different from that observed in either tungsten metal or its oxides,  $WO_2$  and  $WO_3$ , for which the discontinuity shows the usual arc tangent absorption curves. It can therefore be inferred that the shape in Fig. 1 is a unique feature of the  $(WO_4)^{2-}$  radical.

The maxima and minima on the curve (Fig. 1) correspond to the minima and maxima of the absorption coefficient, respectively. A prominent white line labelled b is

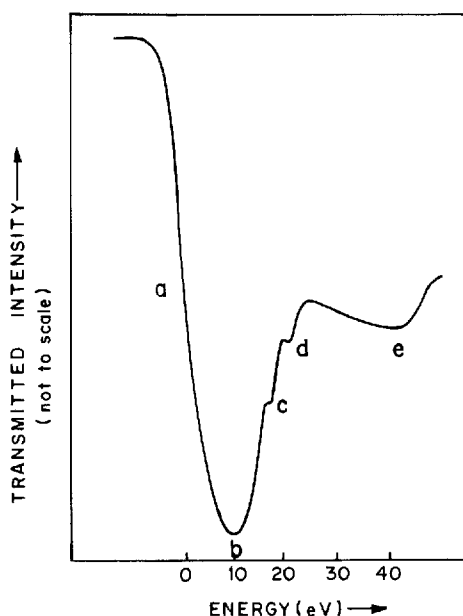


Figure 1. Tungsten  $L_{III}$  absorption discontinuity in  $Gd_2(WO_4)_3$ .

obtained, along with other maxima c, d and e. The energy differences between a, the inflection point on the main edge, and the other maxima are given in Table 1.

a	b	c	d	e	$ \Delta(b-c) $
0	10.1	17.7	21.3	44	7.6

## DISCUSSION

For the interpretation of the different features of the discontinuity, we shall make use of the molecular orbital diagram for  $(ReO_4)^-$ , as given by Pendharkar and Mande.<sup>13</sup> Such an approach was used by Apte and Mande<sup>14</sup> to interpret the shape and the near edge structure associated with the K absorption edge of manganese in its compounds and more recently by Sugiura *et al.*<sup>15</sup> to study the  $L_{III}$  and K edges of ruthenium and chlorine, respectively, in some complex compounds.

For the formation of molecular orbitals, the tungsten atom contributes 6 electrons and the four oxygen atoms contribute 24 electrons. Since the  $(WO_4)^{2-}$  ion has a double negative charge, we have to distribute 32 electrons in the molecular orbitals, which are formed by taking into consideration the metal 5d, 6s and 6p orbitals and the ligand 2s and 2p ( $\sigma$ ,  $\pi$ ) orbitals. After distributing the 32 valence electrons in the  $1a_1$ ,  $1t_2$ ,  $1e$ ,

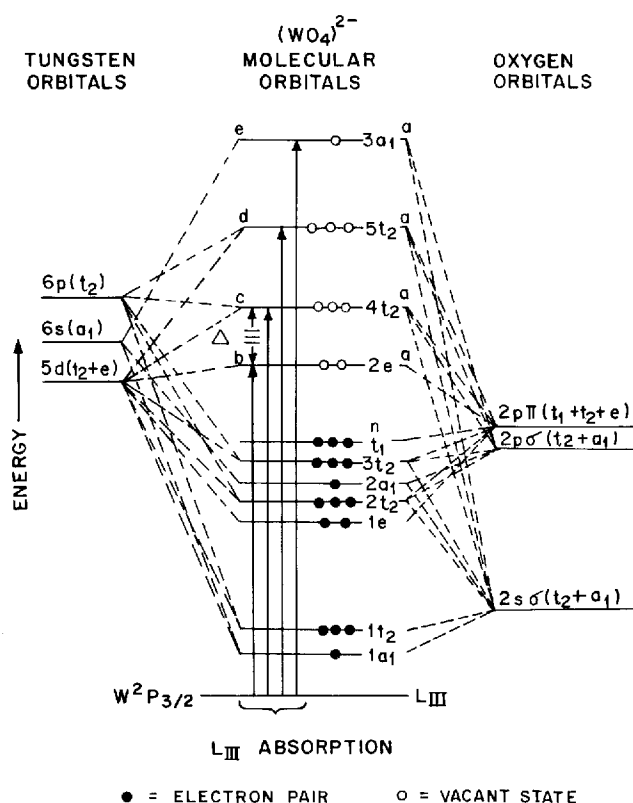


Figure 2. Qualitative molecular orbital energy level diagram for the tetrahedral  $(WO_4)^{2-}$  ion.

$2t_2$ ,  $2a_1$ ,  $3t_2$  and  $t_1$  orbitals, the  $2e$ ,  $4t_2$ ,  $5t_2$  and  $3a_1$  orbitals are left entirely vacant, as shown in Fig. 2.

The molecular orbital diagram for  $(WO_4)^{2-}$  shown in Fig. 2 is only qualitative, built on considerations of LCAO and molecular orbital formulation with respect to the first coordination shell, without taking into account the several complicating effects discussed by Pendharkar and Mande.<sup>13</sup>

The white line corresponding to absorption maximum b is very intense, since it corresponds to the transition  $2P_{3/2}$  to the molecular orbital level  $2e$ , which has strong  $d$  symmetry contributed by the absorbing tungsten atom.

The maxima c, d and e correspond to the transitions from  $2P_{3/2}$  level to  $4t_2$ ,  $5t_2$  and  $3a_1$  respectively.

It is possible to obtain an estimate of the crystal field splitting  $\Delta E$ , the energy separation between the two non-degenerate MO levels of  $d$  symmetry ( $t_2$  and  $e$ ) from our experimental curves. This energy separation is found to be 7.6 eV. Since no optical data on these compounds were found in the literature, no comparison could be made. However, this value is approximately the same (6.4 eV) as that obtained with tetrahedral compounds of rhenium,<sup>13</sup> which is not surprising since the rhenium (75) and tungsten (74) are adjacent in the Periodic Table.

## REFERENCES

1. S. Flugge (Ed.), *Handbuch der Physik XVIII/1*, p. 389. Springer-Verlag, Berlin, Heidelberg (1968).
2. K. N. R. Taylor, *Contemp. Phys.* **11**, 423 (1970).
3. K. N. R. Taylor, *Adv. Phys.* **20**, 551 (1971).
4. F. H. Spedding, *Encyclopaedia Britannica*, 15th edn, p. 515 (1974).
5. B. K. Verma and H. B. Lal, *Mater. Res. Bull.* **16**, 1579 (1981).
6. N. Dar and H. B. Lal, *Mater. Res. Bull.* **14**, 1263 (1979).

7. C. Bonnelle and C. Mande (Eds), *Advances in X-ray Spectroscopy*. Pergamon Press, Oxford (1982).
8. B. K. Agarwal, *X-ray Spectroscopy*. Springer-Verlag, Berlin, Heidelberg (1979).
9. A. F. Wells, *Structural Inorganic Chemistry*, 2nd edn, p. 391 Oxford University Press, Oxford (1950).
10. A. F. Wells, *Structural Inorganic Chemistry*, 4th edn, p. 487 Oxford University Press, Oxford (1979).
11. P. B. Jamieson, S. C. Abrahams and J. L. Bernstein, *J. Chem. Phys.* **50**, 86 (1969).
12. Y. Cauchois and C. Senemaud, *International Tables of Selected Constants, Wavelengths of X-ray Emission Lines and Absorption Edges*. Pergamon Press, Oxford (1978).
13. A. V. Pendharkar and C. Mande, *Chem. Phys.* **7**, 244 (1976).
14. M. Y. Apte and C. Mande, *J. Phys. Chem. Solids* **41**, 307 (1980).
15. C. Sugiura, M. Kitamura and S. Muramatsu, *J. Chem. Phys.* **84**, 4824 (1986).