

The x-ray L_{III} absorption discontinuity of ytterbium in the metal and in some of its compounds

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Abstract. The shape and fine structure of the x-ray L_{III} absorption discontinuity of ytterbium ($Z = 70$) has been studied in the pure metal and in several of its compounds. The shape and the near edge structure of the discontinuity in the metal reflects the band structure. A molecular orbital interpretation for the fine structure near the absorption edge has been proposed for the spectrum of the sesqui-oxide. The average bond lengths for the systems studied have been determined from the measurements on the fine structure employing Lytle's and Levy's methods and are compared with the available crystallographic data in the case of the metal, oxide and fluoride.

Keywords. X-ray L_{III} discontinuity; fine structure; bond length; rare earth spectra.

1. Introduction

The rare earth elements and their compounds have evoked great interest in the past few years because of their peculiar properties and industrial potential. Since x-ray absorption spectroscopy provides a very useful technique to study the electronic structure of materials, we have studied the L_{III} absorption edge of ytterbium in the pure metal and in some of its compounds. As the pure metal was not available till recently, L absorption studies of ytterbium (Kunzl 1932, Allais 1942, Troneva 1963, 1964, Blokhin and Wainshtein 1964, Vainshtein *et al* 1965) have been restricted to the oxide and a very few other compounds. Only recently a study of the white line associated with the L_{III} absorption edge of some rare earth elements including ytterbium (Dubey and Shrivastava 1972) has been reported. In the present paper we report the shape and extended fine structure of the discontinuity in the metal and in eight of its compounds namely, ytterbium sesqui-oxide Yb_2O_3 , fluoride YbF_3 , chloride $YbCl_3 \cdot 6H_2O$, bromide $YbBr_3 \cdot 6H_2O$, nitrate $Yb(NO_3)_3 \cdot 5H_2O$, sulphate $Yb_2(SO_4)_3 \cdot 8H_2O$, acetate $Yb(C_2H_3O_2)_3 \cdot 6H_2O$, and oxalate $Yb(C_2O_4)_3 \cdot 10H_2O$. The chemical shift of the main edge in the compounds with respect to its position in the metal is also reported.

The ytterbium atom ($Z = 70$) has as its outer electronic configuration $4f^{14}5s^25p^6 6s^2$. As is well known (Gschneidner 1969), this atom can exist in two valence states; a divalent one with the participation of the two 6s electrons in bonding as in the metal and some compounds, and a trivalent one with the participation of an additional electron from the 4f shell as in the case of its more common compounds.

2. Experimental Procedure

The spectra were recorded on Kodak x-ray photographic films employing a 400 mm Cauchois type bent crystal spectrograph. A well tested mica crystal was used as analyser and reflections from the (100) planes of the crystal were utilised giving a dispersion of 12.62 xu per mm on the films. A sealed Machlett x-ray tube having a tungsten target operated at 15 kV and 12 mA was employed as the source of x-radiation. The materials studied were obtained from Rare Earth Products Ltd., England. The optimum experimental conditions employed including the preparation of suitable absorbing screens have been as given by Mande (1960), and Pendharkar and Mande (1972). Microphotometer records with magnification $\times 100$ of the spectra were obtained employing a Spectroline Scanner manufactured by the Applied Research Laboratory, California, U.S.A.

3. Results

The shape and the extended fine structure of the L_{III} absorption discontinuity of ytterbium in all the systems studied are shown in figure 1. These curves, drawn

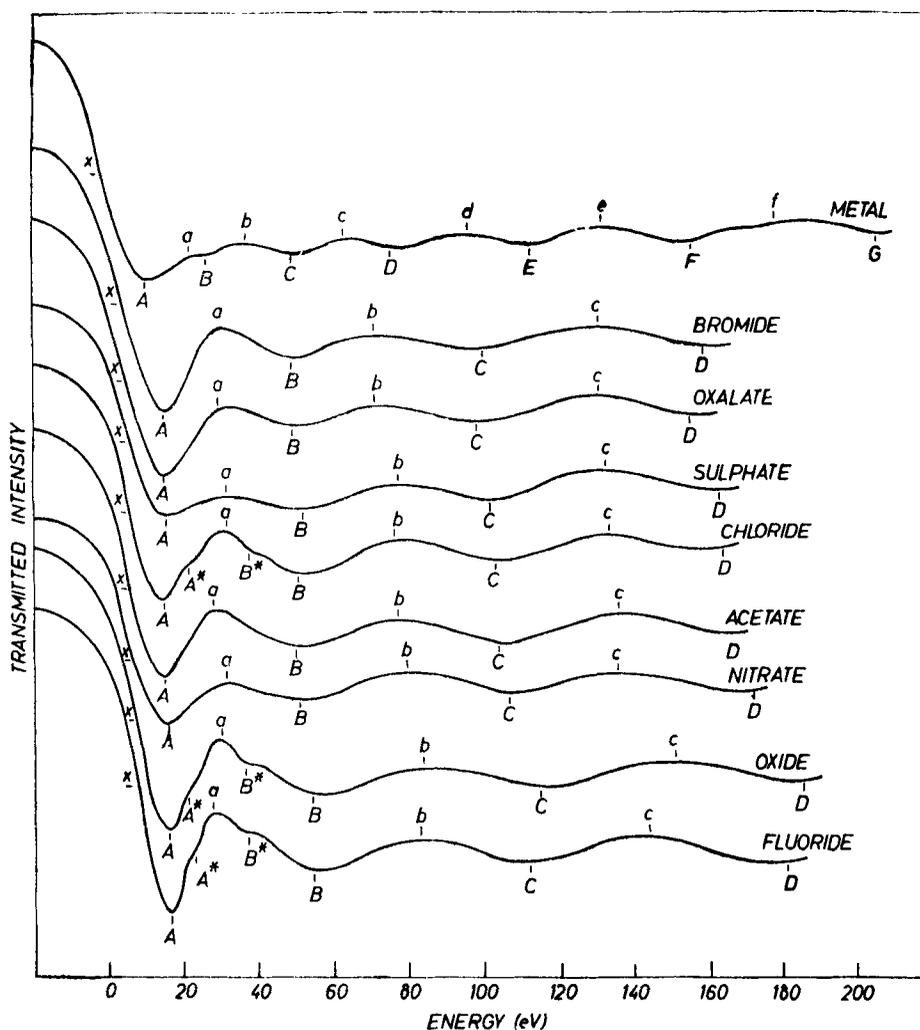


Figure 1. The position, shape and fine structure of the x-ray L_{III} absorption discontinuity of ytterbium in the metal and in its compounds.

Table 1. Position of the x-ray L_{III} absorption discontinuity of ytterbium in the metal and in its compounds.

System	L_{III} edge (xu)	Energy (eV)	Shift ΔE (eV)	$\delta E(A - x)$ (eV)
Metal	1384.54	8936.14	—	9.8
Bromide	1383.65	8941.85	5.7	9.4
Oxalate	1383.59	8942.26	6.1	9.0
Sulphate	1383.59	8942.26	6.1	9.4
Chloride	1383.53	8942.67	6.5	9.0
Acetate	1383.53	8942.67	6.5	9.0
Nitrate	1383.53	8942.67	6.5	9.4
Oxide	1383.34	8943.90	7.8	8.2
Fluoride	1383.27	8944.30	8.2	8.2

The chemical shifts are given in column 4. The last column gives the energy separation between the white line and the inflexion point on the main discontinuity.

after averaging the results obtained from a very large number of microphotometer records, represent the transmitted intensity as a function of energy and consequently the maxima and minima in these correspond to the minima and maxima respectively in the values of the absorption coefficient.

Table 1 gives the position of the main absorption discontinuity as measured at the inflexion point (X), that of the white line in the immediate vicinity of the discontinuity and the energy separation between them in the case of the metal and the compounds. The chemical shift of the discontinuity in the different compounds with respect to its position in the metal is also included in this table. In table 2 are given the positions of the maxima and minima in the extended fine structure for the systems investigated. The maximum error involved in the measurements of the energies, as determined statistically, is ± 1.0 eV for the peaks upto 50 eV and ± 2.0 eV for those beyond it.

It is worthwhile to note the following interesting features of the spectra.

(i) The main absorption discontinuity in the case of the compounds is found to shift to the high energy side with respect to its position in the case of the metal. The magnitude of the shift is in the following sequence: bromide < oxalate, sulphate < chloride, acetate, nitrate < oxide < fluoride.

(ii) The pronounced absorption maximum in the immediate vicinity towards the high energy side of the absorption discontinuity, often referred to as the white line, is most intense in the spectra of the oxide and the fluoride and the absorption maxima A, B and C are visible on the films even to the naked eye.

(iii) The overall shape of the discontinuity is found to be more or less similar for the compounds taken as a group but quite different from that for the metal.

Table 2. Energies (eV) of the absorption maxima and minima in the fine structure of the x-ray L_{III} absorption discontinuity of ytterbium in the metal and in its compounds with respect to that of the inflexion point on the main discontinuity.

System	<i>A</i>	<i>A*</i>	<i>a</i>	<i>B*</i>	<i>B</i>	<i>b</i>	<i>C</i>	<i>c</i>	<i>D</i>
Metal*	9.8		22.9		26.2	36.4	49.1	63.2	75.6
Bromide	9.4		24.5		45.1	67.4	94.8	126.6	153.5
Oxalate	9.0		24.5		43.5	64.9	93.2	125.8	149.3
Sulphate	9.4		25.4		45.9	71.6	95.7	136.7	157.8
Chloride	9.0	14.7	25.4	31.1	44.3	70.3	97.3	126.6	157.8
Acetate	9.0		22.1		43.5	70.7	98.2	135.0	160.3
Nitrate	9.4		24.5		44.3	72.4	100.7	130.0	166.2
Oxide	8.2	13.9	22.9	30.3	46.8	77.0	107.4	143.5	179.0
Fluoride	8.2	14.7	18.8	28.3	46.8	75.7	103.2	136.8	174.8

* Metal: *d*(96.9), *E*(113.9), *e*(132.3), *F*(157.6), *f*(180.2), *G*(206.8).

The amplitudes of the peaks and the energy separation between the successive maxima are comparatively smaller in the case of the metal.

(iv) In the spectra for the oxide, fluoride and chloride, besides the main features appearing in those for the other compounds two additional absorption maxima, one manifested in the form of a shoulder at *A** and the other at *B**, are observed. These are found to be most prominent in the spectrum of the oxide.

4. Discussion

The x-ray L_{III} absorption spectrum corresponds to the transitions of the photoelectrons ejected from the $2p_{3/2}$ sub-shell of the absorbing atom to the unoccupied available levels of appropriate symmetry. In the case of the metal the inflexion point on the main absorption discontinuity is considered to represent the Fermi level. Recent relativistic augmented plane wave calculations (Johansen and Mackintosh 1970) employing a muffin tin potential suggest that in ytterbium metal there is a strong hybridisation of the *sp* and *d* bands near the Fermi level. According to these calculations the outer electronic structure of ytterbium is characterised by a *6sp* band starting at 4.6 eV below the Fermi level, hybridised with a broad *5d* band which overlaps the Fermi level and extends to approximately 6 eV above it. Thus, in the case of the metal the white line results from the favoured transition of the inner $2p_{3/2}$ electrons to the unfilled *5d* states of high density in the conduction band. The broadening of the *5d* band through hybridisation is reflected in the large energy separation (9.8 eV) between the inflexion point and white line. There is yet another factor which may be contributing to the broadening of the white line. As has been shown earlier, one often obtains for the metals a plasmon peak in the fine structure of x-ray absorption discontinuities (Mande and Joshi 1968, Pimpale and Mande 1973). For ytterbium metal the plasmon energy calculated according to the formula given by Bohm and Pines (1953) comes out to be 9.14 eV which is

nearly equal to the energy separation of 9.8 eV between the inflexion point and the white line. The plasmon peak will therefore not be very clearly resolved in the spectrum but will contribute to the broadening of the white line which is a situation somewhat similar to that in the case of the L_{III} absorption spectrum of rhodium (Ekstig 1966).

In the case of compounds, it has been shown that the chemical shift of the absorption discontinuity with respect to its position in the metal is towards the high energy side when the absorbing atom is a cation and that it increases with increasing effective ionic charge (Sapre and Mande 1972, Sapre and Mande 1973). For all the compounds which we have studied, the shift is to the high energy side and lies in the range 5.7–8.2 eV. The present work shows that, amongst the halides, the effective charge on the ytterbium ion is largest in the fluoride and least in the bromide which is in agreement with the electronegativity data. From the study of the chemical shift of the $K\alpha_1$ emission line of ytterbium in some of its compounds it has been shown (Smirnov *et al.* 1970) that the ionicity of the chemical bond is greater for the fluoride than for the oxide, which also is in confirmity with our result. It may be pointed out that the increase in the effective charge of the absorbing atom is associated with greater ionicity of chemical bonding which, in turn, results in greater dehybridisation of the wave functions and a consequent increased shift of the absorption edge to the high energy side accompanied with a sharper and more pronounced white line. In the spectra of all the compounds studied the existence of an intense white line implies the predominance of d-like character in the conduction band. This inference is in agreement with that obtained earlier from the study of the density of states in the conduction band of some rare earth oxides (Bergwall and Nigavekar 1969) employing the x-ray isochromat method.

We shall now discuss the near edge fine structure obtained in the spectrum of ytterbium oxide (Yb_2O_3) in the light of the molecular orbital theory. In compounds, it has been shown (Fischer 1970, Pendharkar and Mande 1972) that the fine structure close to the absorption edge originates from the distribution and availability of molecular orbitals of appropriate symmetry formed as a result of the interaction between the orbitals of the metal atom and those belonging to the ligands. Ytterbium oxide (Yb_2O_3) has a Tl_2O_3 structure (Pert 1962) with the metal atoms having octahedral coordination in four slightly different types of cubic substructures. One-fourth of the metal atoms are at the centre of symmetry of an octahedron with six equidistant oxygen atoms whereas the remaining ones form three disordered cubic substructures, the metal atom in each case being surrounded by an octahedron of six oxygen atoms but with unequal metal-oxygen distances. For these four cubic substructures the metal-oxygen distances are 2.25 Å, 2.31 Å, 2.23 Å and 2.21 Å. Hence in ytterbium oxide the metal atoms occupy octahedral sites with only a slight distortion of the octahedra. Also it is well known that in this compound the metal ion is in the trivalent state which is formed by the participation of the two 6s electrons and a 4f electron promoted to the valence band (Gschneidner 1969). We consider that this electron goes to the next available 5d level. We have therefore adapted the molecular orbital diagram for octahedral coordination after Ballhausen and Gray (1965) and following Fischer (1970) and Pendharkar and Mande (1973) we have constructed for Yb_2O_3 the molecular orbital diagram shown in figure 4.

For the MO levels, the six oxygen atoms contribute thirtysix electrons, two from the 2s and four from the 2p (σ and π) orbitals of each atom. The 5d orbitals of ytterbium interact with the 2p orbitals of the ligands to form the $2e_g$, $1t_{2g}$, $2t_{2g}$ and $3e_g$ molecular orbital levels, the first two being bonding and the latter two antibonding orbitals. The e_g orbitals form π bonds and the t_{2g} orbitals form σ bonds. The 6s and 6p orbitals of the metal interact with the 2p orbitals of oxygen to form $2a_{1g}$, $2t_{1u}$, $3t_{1u}$, $3a_{1g}$ and $4t_{1u}$ molecular orbital levels. In addition, the metal 5d, 6s and 6p orbitals interacting with the ligand 2s orbitals give rise to $1a_{1g}$, $1t_{1u}$ and $1e_g$ molecular orbital levels. The t_{2u}^n and t_{1g}^n arise out of the non-bonding oxygen 2p lone pairs. As is evident from the molecular orbital diagram, the $2t_{2g}$ and $3e_g$ levels have d symmetry, the $3a_{1g}$ level has s symmetry and the $4t_{1u}$ level has p symmetry. Thus, the levels upto t_{1g}^n are fully occupied and the levels $2t_{2g}$, $3e_g$, $3a_{1g}$ and $4t_{1u}$ are left unoccupied to which the transitions of electrons ejected from the inner levels can take place. In so far as the $2p_{3/2}$ electrons are concerned transitions can take place only to the three former levels, the latter corresponding to a $p \rightarrow p$ transition being forbidden according to the dipole selection rules. Thus, the white line A, the shoulder A* on its rising part and B* can be attributed to the transitions to the $2t_{2g}$, $3e_g$ and the $3a_{1g}$ MO levels respectively. The intensity of absorption, which is a function of the transition probability and the available density of states of appropriate symmetry, will be maximum for the transition corresponding to the $2t_{2g}$ level since it can accommodate six electrons, less for the $3e_g$ level which can accommodate four electrons and least for the $3a_{1g}$ level which, besides having s symmetry, can accommodate only two electrons. This inference is in good agreement with our curve for the oxide (figure 1). The energies corresponding to the molecular orbital levels as obtained from the positions of A, A* and B* are given in table 2. We thus obtain 5.7 eV for the crystal field splitting (Δ) of the d levels for the sesquioxide.

It is not possible to build MO diagrams for the other systems studied because of their complex crystallographic structures. However, the absorption maxima A, A* and B* appearing in the spectra of the fluoride and the chloride in the same energy region may be attributed, by extrapolation, to the formation and availability of molecular orbital levels of suitable symmetry. It is difficult to give an unambiguous assignment for these peaks.

We shall now interpret the extended fine structure obtained for the systems on the basis of Lytle's (1966) and Levy's (1965) theories which are essentially short range order theories in the sense that in both the near neighbour atoms are considered to be most important in determining the nature of the fine structure. According to Lytle's theory, an absorption maximum occurs whenever the equation $E = (h^2/8mr_e^2) Q$ is satisfied.

In this equation E represents the energies (in eV) of the absorption maxima in the fine structure measured with respect to that of the inflexion point on the main discontinuity; Q are the zero roots of the half order Bessel function which appears in the radial part of the solution of the equation set up for the ejected photoelectron wave interacting with the potential array surrounding the absorbing atom; r_e is the value of the radius (in Å) of the sphere of volume equivalent to that of the

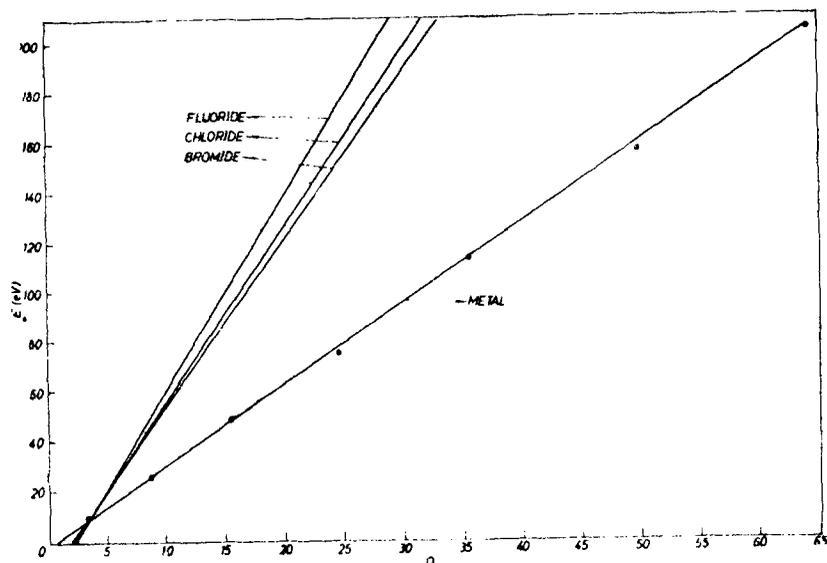


Figure 2. Lytle plots (E vs Q) for ytterbium metal and its halides.

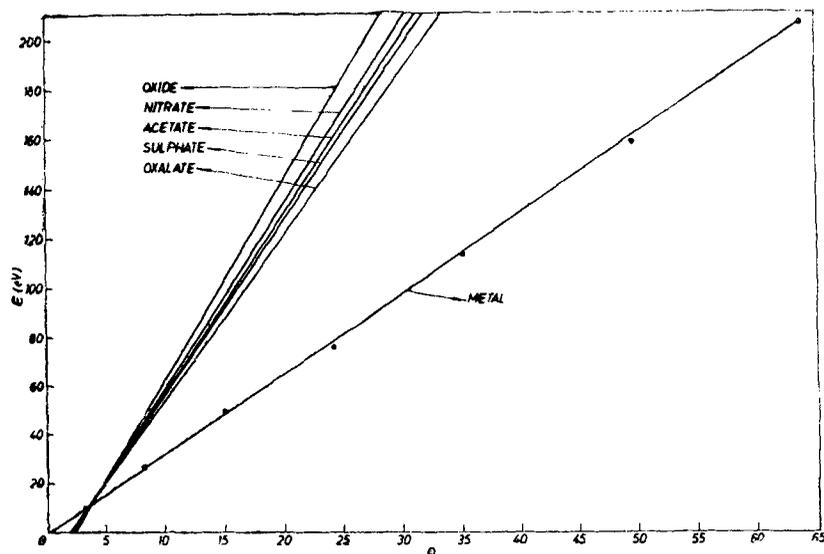


Figure 3. Lytle plots (E vs Q) for ytterbium metal, oxide, nitrate, sulphate, acetate and oxalate.

atomic polyhedron constructed around the absorbing atom after the method originally demonstrated by Wigner and Seitz and discussed by Slater (1956); m is the mass of the electron; and h is the Planck's constant.

The E vs Q plots for the metal and the halides (figure 2) and the oxide, nitrate, sulphate, acetate and oxalate (figure 3) show that the slope of the E vs Q plot is much smaller for the metal than that for the compounds taken as a group, as expected from the lesser magnitude of the energy separation between the successive absorption maxima in the case of the metal. It is also seen that the plot for the

Table 3. Values of interatomic spacings and of equivalent sphere radii for ytterbium metal and its compounds calculated employing Levy's and Lytle's methods.

System	Lytle's method		Levy's method	
	M-slope of E vs Q plot	$r_s = (37 \cdot 60/M)^{\dagger}$ (Å)	$\delta E(b-B)$ (eV)	$r = (151/\delta E)^{\dagger}$ (Å)
Metal	3.25	3.40	10.2	3.84
Oxalate	6.67	2.37	21.4	2.65
Bromide	6.80	2.35	22.3	2.60
Sulphate	7.07	2.30	25.7	2.42
Chloride	7.14	2.29	26.0	2.40
Acetate	7.22	2.28	27.2	2.35
Nitrate	7.43	2.24	28.1	2.31
Fluoride	7.86	2.18	28.9	2.28
Oxide	8.06	2.15	30.2	2.23

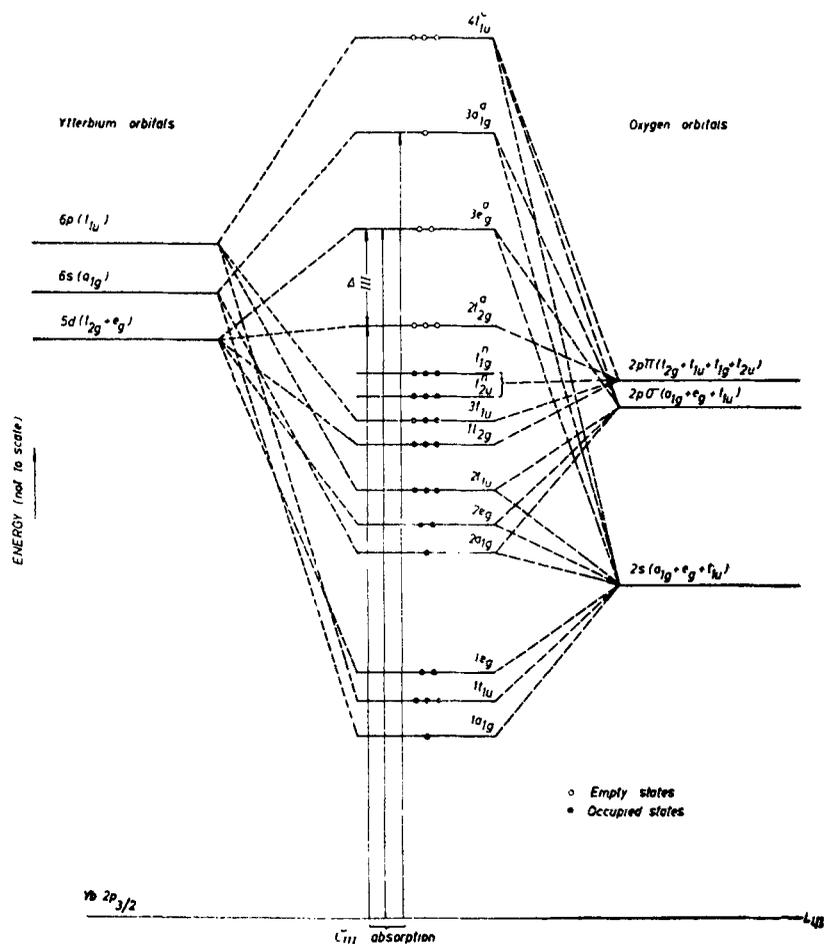


Figure 4. Molecular orbital diagram indicating the energy sequence of the MO levels for ytterbium sesquioxide (Yb₂O₃).

metal passes almost through the origin whereas those for the compounds do not. This can be attributed to the approximations inherent in Lytle's theory and is in accordance with the modified theory of Chivate *et al* (1968). The values of r_s obtained from these plots [$r_s = (37.60/M)^{\frac{1}{2}}$ where M is the slope] are given in table 3. It will be seen that amongst the halides the slope is largest for the fluoride implying that for this compound the interatomic spacing is the least.

Following the recent application of Levy's method of determining the bond length from the extended fine structure of x-ray absorption edges to the case of L_{III} absorption (Pendharkar and Mande 1973), we consider the absorption maximum B to represent the escape energy of the 2p electron. It may be noted that B is the first absorption maximum beyond the molecular orbital region discussed earlier. The energy separation δE (in eV) between the absorption maximum B and the subsequent minimum b is then a measure of the radius of the first coordination sphere around the absorbing atom through the Bragg relation $r = (151/\delta E)^{\frac{1}{2}}$. The bond lengths thus calculated for all the compounds studied are also included in table 3.

It is interesting to compare the values of the equivalent sphere radii and the bond lengths which we have obtained with the values determined using regular crystallographic techniques such as x-ray diffraction, neutron diffraction, etc., in the cases of the metal, oxide and fluoride for which the data are available. However, it may be remarked that in x-ray absorption it is not possible to distinguish between the first neighbour distances of individual metal atoms having different coordinations and hence the values of bond lengths which we have determined are average values. The values of r_s are also, for similar reasons, average values.

Ytterbium metal is known to have, in the phase which exists at room temperature, a face centered cubic structure (Spedding *et al* 1956) with unit cell parameter $a = 5.4862 \pm 0.0004 \text{ \AA}$. The fluoride crystallises in orthorhombic structure (Wyckoff 1963) with the ytterbium atom having as its neighbours eight fluorine atoms at distances between 2.25–2.32 \AA and one more at 2.6 \AA . The metal-oxygen distances in Yb_2O_3 as mentioned earlier, lie between 2.21–2.31 \AA . It is seen that there is a fair agreement between the values which we have obtained using Levy's method and those from diffraction techniques. However, the values of r_s obtained from Lytle's method are found to be consistently slightly lesser than the values of bond length obtained from both Levy's method and crystallographic techniques. This is due to the fact that whereas Levy's method gives the bond length directly, Lytle's method does not. The interatomic spacing has to be derived in the latter method from r_s by multiplying it with a factor (greater than unity) appropriate to the geometry of the system (Lytle 1966). This multiplying factor is known to be 1.140 for systems which crystallise in the face centred cubic lattice which is the structure for the metal. In this manner, the interatomic spacing for ytterbium metal is found out to be 3.87 \AA . It is also possible to calculate the value of the unit cell parameter a from the value of r_s for the metal since in the case of face centred cubic structures, $a = 1.612 r_s$ (Lytle 1966). We thus obtain the value of the unit cell parameter for the metal as 5.48 \AA which is in excellent agreement with the value ($5.4862 \pm 0.0004 \text{ \AA}$) obtained by Spedding *et al* (1956) using the x-ray diffraction technique.

5. Concluding remarks

The present study shows that x-ray absorption spectroscopy can be very useful in obtaining important information such as electronic structure, interatomic spacing, crystal field splitting, etc. It may be mentioned that Levy's method gives the interatomic spacings to a fair degree of accuracy. However, using Lytle's method, it is not possible to determine the values of interatomic spacings in the case of systems having complex structures for which the requisite multiplying factors are not known. The fact that interatomic spacing has to be derived from the value of r_s , which is only approximately equal to the former, must be borne in mind. It appears that this point is often not taken into account while making comparison of the values of the parameter r_s with those of interatomic spacing (Bhide and Bahl 1972, Shrivastava and Nigam 1972-73, Padalia *et al* 1973).

In the present work, for the first time, the crystal field splitting of the d levels has been obtained for the sesquioxide of ytterbium through the application of the molecular orbital theory. Similar studies of various systems of some other rare earth elements are in progress and will be communicated shortly.

References

- Allais M L 1942 *Cah. Phys.* **7** 13
 Ballhausen and Gray 1965 *Molecular orbital theory* (New York : Benjamin)
 Bergwall S and Nigavekar A S 1969 *Phys. Kondens Mater.* **10** 107
 Bhide V G and Bahl M K 1972 *J. Phys. Chem. Solids* **33** 1669
 Blokhin S M and Wainshtein E J 1964 *Dokl. Akad. Nauk SSSR* **158** 694
 Bohm D and Pines D 1953 *Phys. Rev.* **92** 609
 Chivate P, Damle P S, Joshi N V and Mande C 1968 *J. Phys. C. (Proc. Phys. Soc.) Ser. 2* **1** 1171
 Dubey V S and Shrivastava B D 1972 *Phys. Status Solidi (b)* **53** K51
 Ekstig B 1966 *Uppsala Univ. Instt. Phys. UUIP* 508
 Fischer D 1970 *J. Appl. Phys.* **41** 3561
 Gschneidner K A Jr 1969 *J. Lesscommon metals* **17** 13
 Johansen G and Mackintosh A R 1970 *Solid State Commun.* **8** 121
 Kunzl V 1932 *Collect. Czech. Chem. Commun.* **75** 191 468
 Levy R M 1965 *J. Chem. Phys.* **43** 1846
 Lytle F W 1966 *Advances in x-ray analysis* **9** 398 (Plenum Press, New York)
 Mande C 1960 *Ann. Phys. (Paris)* **5** 1559
 Mande C, Pendharkar A V and Chakrovorti M C 1972 *Proc. Indian Acad. Sci. Sec. A* **75** 209
 Mande C and Joshi N V 1968 *Proc. Int. Conf. X-ray Spectroscopy and Structure of Matter* (Kiev Institute of Metal Physics Ukr. SSR) 57
 Padalia B D, Gupta S V and Krishnan V 1973 *J. Chem. Phys.* **58** 2084
 Pendharkar A V and Mande C 1973 *Pramana* **1** 104
 Pert A 1962 *Bull. Soc. Fr. Mineral. Cristallogr.* **85** 267
 Pimpale A and Mande C 1973 *Pramana* **1** 147
 Sapre V B and Mande C 1972 *J. Phys. C* **5** 793
 Sapre V B and Mande C 1973 *J. Phys. Chem. Solids* **34** 1351
 Shrivastava U C and Nigam H L 1972-73 *Coord. Chem. Rev.* **9** 275
 Slater J C 1956 *Handbuch der physik* **19** 1 ed S Flugge (Springer Verlag, Berlin)
 Smirnov Yu P, Sumbaev O I, Petrovich E V, Zykov V S, Egorov A I and Grushko A I 1970 *Sov. Phys.-JETP* **30** 622
 Spedding F H, Daane A H and Hermann K W 1956 *Acta Crystallogr.* **9** 599
 Troneva N V 1963 *Izv. Akad. Nauk SSSR Ser. Fiz.* **27** 403
 Troneva N V 1964 *Izv. Akad. Nauk SSSR Ser. Fiz.* **28** 809
 Vainshtein E E, Blokhin S M and Paderno Yu B 1965 *Sov. Phys. Solid State* **6** 2318
 Wyckoff R W G 1963 *Crystal structures*, Second Edition (Interscience Publishers, New York)