

X-ray K-absorption edge shifts due to chemical combination

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Abstract. A possible explanation is given of the chemical shifts of x-ray K-absorption edges of metals when they undergo a chemical combination and form compounds. It is proposed that when a metal forms a compound its Fermi edge changes. It explains the numerical order as well as the nature of the chemical shifts. A fairly good agreement between the calculated and observed values has been obtained.

Keywords. Chemical shifts; x-ray K absorption edges

1. Introduction

A considerable amount of experimental work (Agarwal and Verma 1970; Padalia *et al* 1973; Sapre and Mande 1972; Vishnoi 1970) has been done during the last few years on chemical shifts of the x-ray K-absorption edges of metals when they form compounds. Several qualitative explanations based on molecular orbital theory and hybridization etc have been put forward by these workers from time to time but none of these theories could give the quantitative order or nature of the chemical shifts of the x-ray K-absorption edges of metals when they form compounds. Recently the chemical shifts of the x-ray L-absorption edges of some compounds of Pb and Bi have been reported (Srivastava *et al* 1979a). In this paper we present the calculations for the chemical shifts of the x-ray K-absorption edges of V, Cr, Mn, Fe, Co, Ni, Cu and Zn.

2. Physical concept

The K-absorption edge in x-ray spectra corresponds to a transition of K-core electrons to the bottom of the conduction band (E_c) above the Fermi level (E_F). The difference in energy between the edge of a compound and its metal is called the chemical shift. In the x-ray absorption curve, the K-edge corresponds to the first inflection point (see figure 1). Similarly, in principle one can also get the first inflection point in the x-ray emission curve that corresponds to a transition from the top of the valence band (E_v) to the K-level. In the case of a metal, the inflection points of the emission and absorption curves coincide (figure 1), because in this case they both correspond to the Fermi level (E_F^M), while in the case of a semi-conductor, the inflection points of emission and absorption are not coincident since the top of the valence band (E_v^S) is

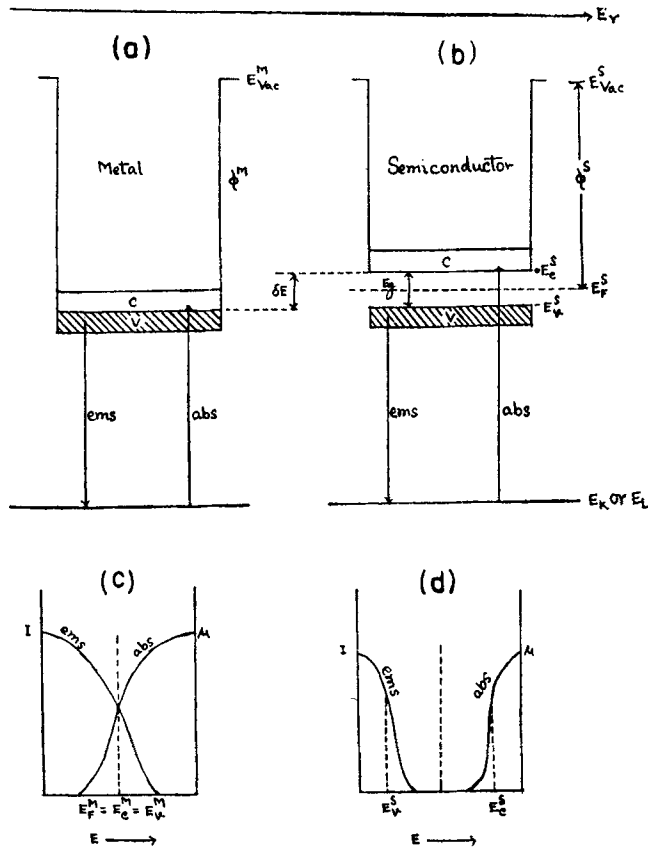


Figure 1. a, b. Schematic energy diagram of a metal and intrinsic semiconductor. C=conduction band, V=valence band, E_c =bottom of the conduction band, E_v =top of valence band, E_k =K level, E_g =band gap. Superscripts M and S stand for metal and semi-conductor respectively, E_F =Fermi energy. c, d. X-ray emission and absorption curve for the metal and semi-conductor.

separated from the bottom of the conduction band (E_c^S) by an energy gap (E_g) as shown in figure 1. Thus the chemical shift is the difference in the inflection points of the absorption curves of a compound and its metal. In view of figure 1, the chemical shifts can be defined as

$$\delta E_c = E_c^S - E_c^M, \tag{1}$$

where M and S stand for metal and semi-conductor respectively. For metals we know that

$$E_c^M = E_F^M, \tag{2}$$

while for semi-conductors the Fermi energy is defined as (Dekker 1957)

$$E_F^S \approx \frac{1}{2} (E_c^S + E_v^S), \tag{3}$$

$$\text{and } E_g = (E_c^S - E_v^S). \quad (4)$$

From (3) and (4) we get

$$E_F^S \approx E_c^S - E_g/2. \quad (5)$$

But $E_g/2$ is a very small quantity for most of the semi-conductors and to a first approximation can be neglected.

$$\text{Hence } E_F^S \approx E_c^S. \quad (6)$$

Using (6) and (2) in (1) we get

$$\delta E_c \approx E_F^S - E_F^M. \quad (7)$$

Thus to a first approximation the chemical shift can be calculated from (7), *i.e.* from the energy difference between the Fermi energy of a compound (E_F^S) and its metal (E_F^M). In other words, when a metal goes into a chemical combination and forms a compound its Fermi energy changes. As a result the x-ray absorption edge in the compound would be shifted with respect to its position in the metal. Vainshtein (1950), Kakuschadze (1961), Appleton (1964) and Ulmer (1969) have reported this fact long ago.

To calculate the Fermi energy of a compound, we use the relation between Fermi energy and plasmon energy derived by Pines (1964) as

$$E_F = 3.68/r_s^2 \text{ ryd} = 0.2948 (\hbar\omega_p)^{4/3} \text{ eV}, \quad (8)$$

where (Marton *et al* 1955; Rooke 1968)

$$\hbar\omega_p = (12/r_s^3)^{1/2} \text{ ryd} = 28.8 (Z \sigma/W)^{1/2} \text{ eV}, \quad (9)$$

$$r_s = r_0/a_0 \text{ (a dimensionless parameter),}$$

Z is the effective number of electrons taking part in plasma oscillations, σ is the specific gravity and W is the molecular weight. In the case of transition elements, the recent observed plasma loss values (Jenkins and Chung 1971; Sutherland and Arakawa 1968; Vehse and Arakawa 1969) show that Z is one, which has also been recently justified by the present authors (Srivastava *et al* 1979 b and Srivastava 1980). In oxygen the effective value for Z is 2 and 6 (Glasstone 1964). The effective Z value for S, Br and I is 2, 7 and 7 respectively.

Equation (9) holds for a free electron model but to a first approximation it is good for dielectrics also. According to Kittel (1977) plasma oscillations in dielectrics are physically the same as in metals. This fact can be substantiated from the work

of Raether (1965) and Philipp and Ehrenreich (1963), who have shown that the plasmon frequency for dielectrics is

$$\omega_{pd}^2 = \omega_p^2 / (1 - \delta\epsilon_0), \quad (10)$$

where $\delta\epsilon_0$ is a very small quantity and can be neglected to a first approximation. Philipp and Ehrenreich (1963) have shown that the calculated values of $\hbar\omega_{pd}$ and $\hbar\omega_p$ are in fair agreement with their observed values of plasmon energy for dielectrics.

Equations (8) and (9) show that the Fermi energy depends upon Z , and W , hence the Fermi energy for a metal will be different from its compound. The change in the Fermi energy when a metal forms a compound is given by (7).

The δE_c value has been calculated for various compounds of V, Cr, Mn, Fe, Co, Ni Cu and Zn and it has been found that they are of the same order of magnitude as the chemical shifts reported by several workers (see table 1).

Table 1. K-edge shift in x-ray absorption spectra of compounds.

Metal/ compound	Z	σ	W	E_F (eV)	δE_F (eV)	Experimental shift δE_c (eV)	References
1	2	3	4	5	6	7	
V	1	5.96	50.95	6.2243	—	—	
VB ₂	7	5.10	72.59	15.2132	9.9889	6.82 ± 0.42	(a)
VC	5	5.77	62.96	15.4633	9.2390	9.38 ± 0.47	(a)
VN	4	6.13	64.96	13.5914	7.3671	7.06 ± 0.30	(a)
VO	7	5.758	66.95	18.5532	12.3289	11.28 ± 0.59	(a)
V ₂ O ₃	20	4.87	149.90	19.5213	13.2970	10.75 ± 0.40	(a)
V ₂ O ₄	26	4.339	165.90	20.1225	13.8982	12.41 ± 0.47	(a)
V ₂ O ₅	32	3.357	181.90	18.3169	12.0926	12.75 ± 0.28	(a)
VF ₃	22	3.636	107.95	20.2281	14.0038	12.61 ± 0.35	(a)
V ₂ S ₃	20	4.7	198.10	15.8308	9.6065	7.35 ± 0.30	(a)
Cr	1	7.20	52.01	6.961	—	—	
Cr ₂ (SO ₄) ₃	44	3.012	392.22	12.64	5.679	7.12	(b)
Cr ₂ S ₃	20	3.77	200.20	13.474	6.613	6.9	(c)
Cr ₂ O ₃	8	5.21	152.02	10.97	4.009	6.83	(b)
Mn	1	7.20	54.94	6.7140	—	—	
MnO	7	3.7	70.93	13.2940	6.580	5.4	(d)
MnO ₂	13	5.026	86.93	21.5114	14.7974	15.2	(c)
Mn ₂ O ₃	20	4.50	157.86	17.8918	11.1778	12.45	(b)
Mn ₂ O ₄	27	4.856	228.79	17.9532	11.2392	10.20	(e)
MnO(OH)	14	3.26	87.94	16.8053	10.0913	11.75	(b)
MnCl ₂	15	2.977	125.84	13.0430	6.3290	5.84 ± 0.52	(f)
MnSO ₄	27	3.25	151.0	18.1212	11.4072	9.7	(b)
Fe	1	7.86	55.85	7.0407	—	—	
FeO	7	5.7	71.84	17.5824	10.5417	9.2	(d)
Fe ₂ O ₃	20	5.24	159.70	19.6506	12.6099	12.1	(d)
FeS	7	4.84	87.92	13.7799	6.7392	6.5	(g)
Fe ₂ (SO ₄) ₃	92	3.097	399.90	20.7582	13.7175	13.9	(g)
Fe(NO ₃) ₂ 9H ₂ O	136	1.684	404.02	17.8234	10.7827	8.89	(h)

(Contd.)

Table 1 (Contd.)

	1	2	3	4	5	6	7	8
Co		1	8.9	68.94	7.3779	—	—	
CoS		7	5.45	91.01	14.5751	7.1972	7.41 ± 1.0	(i)
CoS ₂		13	4.269	123.07	15.3022	7.9243	8.99 ± 1.0	(i)
CoSe		7	7.65	137.90	14.6954	7.3175	3.99 ± 1.0	(i)
Co ₂ O ₃		8	5.18	165.88	10.32	2.9421	2.20 ± 0.3	(j)
CoC ₂ O ₄		17	3.021	146.96	12.91	5.5321	5.47 ± 0.3	(j)
CoCO ₃		11	4.13	118.95	13.705	6.3271	7.34 ± 0.3	(j)
Co(NO ₃) ₂ ·6H ₂ O	43		1.87	291.05	11.04	3.6621	6.67 ± 0.3	(j)
CoSO ₄ ·7H ₂ O	39		1.948	281.12	10.87	3.4921	4.36 ± 0.3	(j)
Ni		1	8.90	58.71	7.394	—	—	
NiS		7	5.65	90.76	14.96	7.566	9.09 ± 0.3	(k)
NiSe		7	8.46	137.65	14.79	7.396	5.0	(l)
Ni ₂ O ₃		20	4.83	165.42	18.23	10.836	10.09 ± 0.3	(k)
NiSO ₄ ·7H ₂ O	87		1.948	280.87	18.58	11.186	11.38 ± 0.3	(k)
NiBr ₂		15	4.68	218.52	12.13	4.736	4.99 ± 0.3	(k)
Cu		1	8.92	63.54	7.030	—	—	
CuO		3	6.40	79.54	10.09	3.06	3.87 ± 0.6	(g)
CuSO ₄		11	3.603	159.61	10.28	3.25	4.88 ± 0.6	(g)
CuI		8	5.62	190.61	9.938	2.908	2.20 ± 0.6	(g)
Cu(CH ₃ COO) ₂	35		1.93	181.64	13.46	6.43	9.72 ± 0.6	(g)
Zn		1	7.14	65.38	5.944	—	—	
ZnO		3	5.606	81.38	9.088	3.144	3.0	(m)
ZnSO ₄		11	3.74	161.44	10.46	4.516	5.35	(m)
Zn(NO ₃) ₂		19	2.065	189.49	9.109	3.165	3.96	(n)

Letters in paranthesis represent the references.

(a) (Salem *et al* 1978a), (b) (Kulkarni and Mande 1971b), (c) (Lindh 1925), (d) (Sanner 1941), (e) Padalia *et al* 1973), (f) (Salem *et al* 1978b), (g) (Verma and Agarwal 1968), (h) (Kulkarni and Mande 1971a), (i) (Kondawar and Mande 1976), (j) (Nigam and Gupta 1973), (k) (Gupta and Nigam 1972b), (l) (Mande and Nigavekar (1969), (m) (Gupta and Nigam 1972a), (n) (Saxena *et al* 1974).

δE_c may be positive or negative, depending upon $E_F^S \geq E_F^M$. Thus (7) can give the sign of the chemical shifts which also corresponds well with the observed values.

The difference in the calculated and observed values of the chemical shifts may be due to the fact that we have neglected $E_g/2$ in the calculation of E_F^S and also we have not taken account of the shift in the inner levels.

Hence the present method can give not only an approximate value of the chemical shifts but also the nature of the shift.

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