

Chemical shifts of the x-ray K or L_{III} absorption edges

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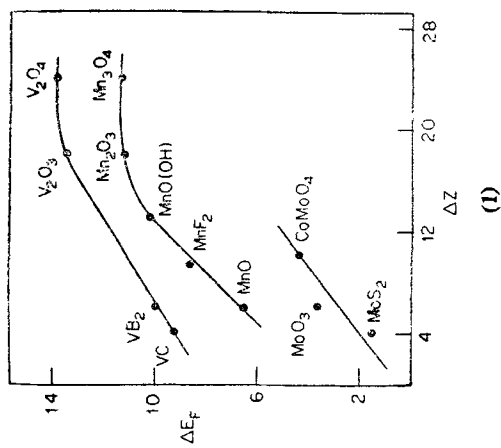
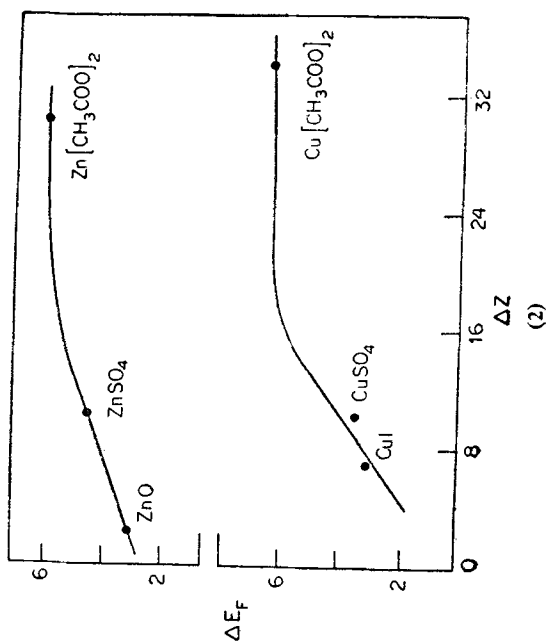
Abstract. The x-ray K or L-absorption edge shifts of V, Mn, Mo, Zn, Cu, Co, Pb, Ga, Fe and Y, when they undergo chemical combination and form compounds, have been calculated. It has been found that the major contribution to the chemical shift comes from the change in the Fermi energy of a metal when it forms a compound. The calculated values for the change in Fermi energy correspond well with the values observed by several workers for the chemical shift.

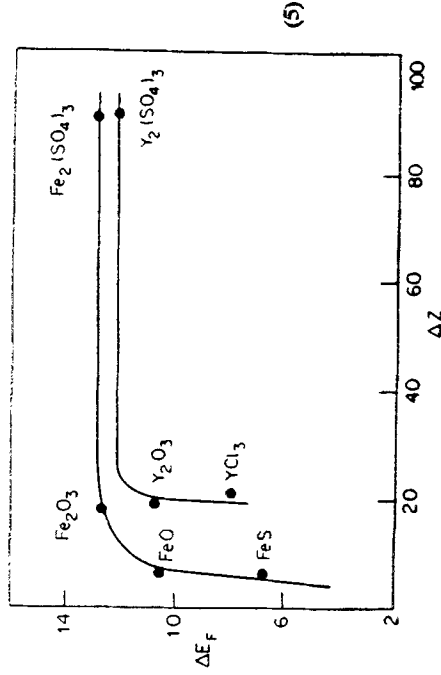
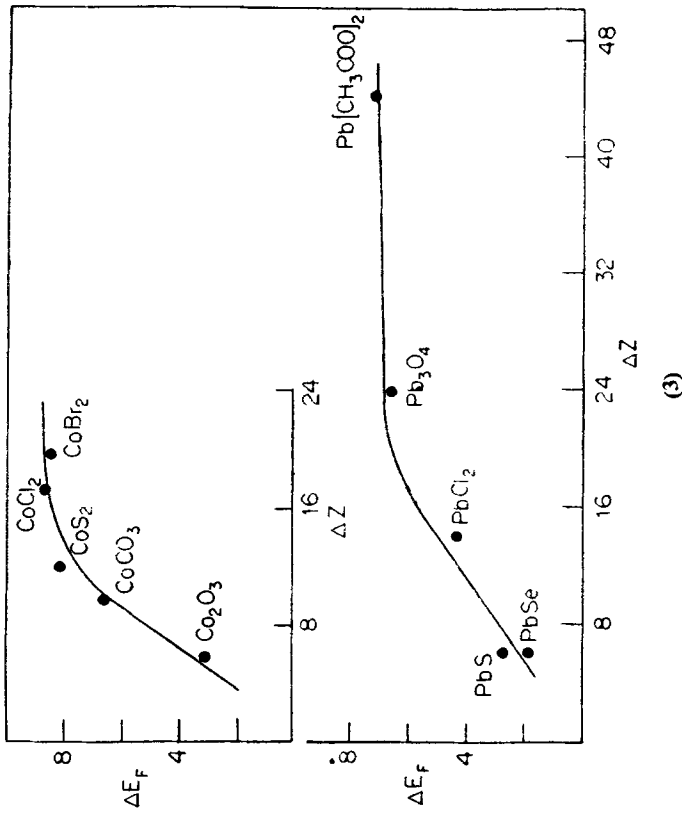
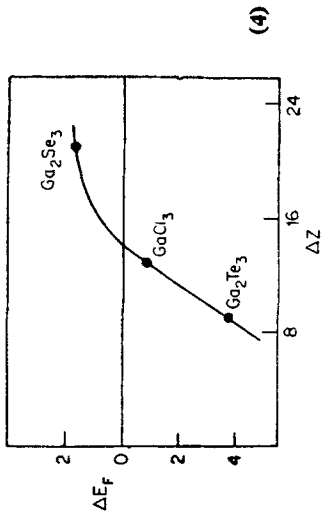
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In recent years great interest has been shown in giving various possible explanations for the experimentally observed chemical shifts in x-ray absorption edges. Attempts have been made to correlate chemical shift empirically with the ionic or covalent character of the bond, valency, hybridization and electronegativity, etc. (Agarwal and Verma 1970; Dey and Agarwal 1971; Bhide and Bahl 1972; Kawata and Maeda 1978). Recently Salem *et al* 1978 have reported that the chemical shift of K-absorption edge of vanadium in some of its compounds is due to effective ionic charge. But none of the authors mentioned above have been able to give the numerical order or nature (*i.e.*, sign of the shift) of the observed chemical shift.

A survey of the literature shows that the problem of correlating the experimentally observed x-ray absorption edge shifts with the calculated value of the chemical shift requires a more systematic investigation. Many workers believe that the change in the chemical environment of a metal, when it forms a compound is due to redistribution of electronic charge in particular orbitals (Seigbahn *et al* 1967; Lindberg *et al* 1970; Vishnoi 1970; Pendharkar and Mande 1973). This indicates that Fermi level should change because of redistribution of charge in the orbitals. Blokhin (1961); Kakuschadze (1961) and Appleton (1964) have also pointed

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Figures 1-5. Plot of Fermi energy shift ($\Delta E_F = \Delta E_g$) versus change in effective number of electrons (ΔZ).

out that the Fermi energy of a metal changes when it undergoes a chemical combination and forms a compound. The authors have used this method (Srivastava *et al* 1979) recently for Pb and Bi. We also know that K or L- edge in an x-ray absorption spectrum corresponds to a transition of an electron from the corresponding core level to the first unoccupied vacancy in or above the Fermi surface. Thus, if the Fermi surface of a metal changes on chemical combination, its absorption edge will also change. Blokhin (1961) has used Sommerfeld expression for the Fermi energy as

$$E_F = \frac{h^2}{8m} \left[\frac{3n}{\pi} \right]^{2/3} \quad (1)$$

Differentiating this, we get

$$\begin{aligned} \Delta E_F &= \left[\frac{h^2}{12m} \left(\frac{3}{\pi} \right)^{2/3} n^{-1/3} \right] \Delta n \\ &= \text{constant } \Delta n. \end{aligned} \quad (2)$$

This change in Fermi energy should correspond to the chemical shift. Thus

$$\begin{aligned} \Delta E_F &= \Delta E_C = \text{constant } \Delta n \\ &= \text{constant } \Delta Z. \end{aligned} \quad (3)$$

Thus chemical shift varies linearly with the change in the number of electrons (ΔZ) in the Fermi surface. A plot of ΔE_F versus ΔZ for V, Mn, Mo, Zn, Cu, Co, Pb, Ga, Fe and Y metals and their compounds have been shown in figures 1 to 5. It has been found that ΔE_F varies linearly with ΔZ upto $\Delta Z = 20$. Sapre and Mande 1973 have also observed linear variation of chemical shift with q_p upto $q_p = 1.3$. In order to get the numerical value of E_F one can express equation (1) in terms of plasmon energy as

$$E_F = 0.29484 (\hbar\omega_p)^{4/3} \text{ eV} \quad (4)$$

where

$$\hbar\omega_p = 28.8 \left(\frac{Z\sigma}{W} \right)^{1/2} \text{ eV.} \quad (5)$$

Z is the effective number of electrons taking part in plasma oscillations, σ is the specific gravity and W is the molecular weight.

The expression for $\hbar\omega_p$ given in equation (5) is valid for the free electron gas model but to a first approximation can be used for dielectrics too (Srivastava *et al* 1979).

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

$$\omega_{pd}^2 = \omega_p^2 / (1 - \delta\epsilon_0). \quad (6)$$

Table 1. Comparison of change in Fermi energy (ΔE_F) with observed chemical shift (ΔE_c).

Metal/ compound	$Z^{a,b}$	Calculated ΔE_F in eV	Experimental C.S. ΔE_c in eV
V	1
VC	5	9.24	9.38 ± 0.47^c
VB ₂	7	9.99	6.82 ± 0.42^c
V ₂ O ₃	20	13.30	10.75 ± 0.40^c
V ₂ O ₄	26	13.90	12.41 ± 0.47^c
Mn	1
MnO	7	6.58	5.4^d
MnF ₂	10.6	8.66	7.57 ± 0.52^e
MnO (OH)	14	10.09	11.75^f
Mn ₂ O ₃	20	11.18	12.45^f
Mn ₃ O ₄	27	11.24	10.20^g
Mo	1
MoS ₂	5	1.57	2.4^h
MoO ₃	7	3.68	2.8^h
CaMoO ₄	11	4.30	3.4^h
Zn	1
ZnO	3	3.14	3.0 ± 0.3^i
ZnSO ₄	11	4.52	5.35 ± 0.3^i
Zn(CH ₃ COO) ₂	31	5.99	4.37 ± 0.3^i
Cu	1
CuI	8	2.91	2.20 ± 0.6^j
CuSO ₄	11	3.25	4.88 ± 0.6^j
Cu (CH ₃ COO) ₂	35	6.43	9.72 ± 0.6^j
Co	1
CoS	7	7.1972	7.41 ± 1.0^k
CoSe	7	7.3175	3.99 ± 1.0^k
Co ₂ O ₃	8	2.94	2.20 ± 0.3^l
CoCO ₃	11	6.33	7.34 ± 0.3^l
CoS ₂	13	7.92	8.99 ± 1.0^k
CoCl ₂	18.4	8.48	7.2^m
CoBr ₂	20.8	8.28	8.6 ± 0.3^n
Pb	4
PbSe	10	1.8	2.7 ± 0.7^o
PbS	10	2.59	4.0 ± 0.7^p
PbO	10	5.35	3.2 ± 0.7^p

Table 1. (Contd.)

Metal/ Compound	$Z^{a,b}$	Calculated ΔE_F in eV	Experimental C.S. ΔE_c in eV
PbCl ₂	18	4.2	3.0 ± 0.7 ^p
Pb ₂ O ₄	36	6.5	4.5 ^a
Pb(CH ₃ COO) ₂	50	6.99	5.2 ^a
Ga	3
Ga ₂ T ₃	12	-3.83	-3.4 ± 0.5 ^f
GaCl ₃	15.9	-0.87	-0.81 ± 0.5 ^g
Ga ₂ Se ₃	24	1.57	1.3 ± 0.5 ^f
Fe	1
FeS	7	6.74	6.5 ^t
FeO	7	10.54	9.2 ^d
Fe ₂ O ₃	20	12.61	12.1 ^d
Fe ₂ (SO ₄) ₃	92	13.72	13.9 ^t
Y	1
YCl ₃	22	7.98	9.85 ^u
Y ₂ O ₃	20	10.72	7.5 ^u
Y ₂ (SO ₄) ₃	92	12.26	13.14 ^u

a. (Srivastava et al 1979)

c. (Salem et al 1978)

e. (Salem et al J. Phys. 1978)

g. (Padalia et al 1973)

i. (Gupta and Nigam 1972)

k. (Kondawar and Mande 1976)

m. (Kondawar and Mande 1973)

o. (Vishnoi and Agarwal 1970)

q. (Vishnoi 1970)

s. (Verma and Agarwal 1967)

u. (Bhide and Bhat 1968).

b. (Srivastava and Kumar 1981)

d. (Sanner 1941)

f. (Kulkarni and Mande 1971)

h. (Kawata and Maeda 1973)

j. (Verma and Agarwal 1968)

l. (Nigam and Gupta 1973)

n. (Dey and Agarwal 1972)

p. (Dey and Agarwal 1971)

r. (Sapre and Mande 1973)

t. (Lindh 1925)

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 value of plasmon energy for dielectrics.

With the help of equation (4) the difference ΔE_F in the Fermi energy of a metal and its compounds has been calculated. It has been found that ΔE_F agrees fairly well with the experimentally observed chemical shift ΔE_c (see table 1)

$$\Delta E_C = \Delta E_F = (E_F)_{\text{comp}} - (E_F)_{\text{metal}} \quad (7)$$

ΔE_F may be positive or negative depending upon whether $(E_F)_c \geq (E_F)_m$. This explains the nature of chemical shift. On these lines one can correlate the chemical shift data and make predictions regarding the nature of the chemical shifts in various compounds of a metal with the help of their Fermi energies only. In case of some compounds the difference between our theoretical values and experimentally observed values may be due to the fact that (i) we have used an approximate but simple method for calculating Fermi energies ' E_F ' and we have not taken into account the effect of relaxation energy, screening effect, etc. as their contribution to chemical shift is small and complexities are involved for their calculations. (ii) experimental values of ΔE_c for the same compounds by different workers (Lindh 1925; Sanner 1941; Kulkarni and Mande 1971; Gupta and Nigam 1972; Saxena *et al* 1974; Salem *et al* 1978) vary as much as up to 40%. Thus within the limits of experimental errors and theoretical approximations the calculated values of ΔE_c and ΔE_F are in fair agreement with each other.

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