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Correlation between x-ray absorption edge shift and Fermi energy

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Abstract. The chemical shift of x-ray absorption edges of various compounds of Co, Cu, Ga, As, Mo and W has been calculated using Fermi energy data. The calculated and experimentally observed values agree fairly well.

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1. Introduction

The x-ray absorption edge corresponds to a transition of a core electron to the first unoccupied level above the Fermi level. During chemical combination when metal forms a compound, the energy of x-ray absorption edge changes. The energy difference between the absorption edge of metal and its compound is called the chemical shift (ΔE_{C}).

Several workers [1–4] persued the research work on the chemical shifts of K or L absorption edges in the x-ray spectra of metals and their compounds. Various possible physico-chemical, both qualitative and quantitative explanations based on oxidation state [5], electronegativity [6,7], effective ionic charge [8–11], relaxation energy [12,13], ionicity [14] and coordination number [15,16] etc. have been put forward to account for these shifts, but without much success. Recently [17–20] Srivastava *et al.* have put forward two methods to calculate the chemical shifts of the x-ray absorption edges. The first method [19,20] is the Fermi energy shift method and the second method is the inner level [17,18] shift method. These methods do not give only the numerical order but also give the nature (*i.e.* sign) of the chemical shift.

In the present paper we have used the Fermi energy shift method for the calculation of the chemical shift and the calculated values agree fairly well with the observed values.

An x-ray K or L —absorption edge corresponds to the transition of K or L core— electrons to the lowest part of the conduction band (E_{C}) above the Fermi level (E_{F}). The energy difference between the edge for the compound and the metal is called the chemical shift (ΔE_{C}). In the x-ray absorption curve the edge corresponds to the first inflection point. Thus the chemical shift is a shift in the inflection points or shift in the bottom of the conduction bands of a metal and its compounds wher they undergo chemical combination. Thus the chemical shift can be defined as

$$\Delta E_{\mathrm{C}} = E_{\mathrm{C}}^{\mathrm{S}} - E_{\mathrm{C}}^{\mathrm{M}}, \tag{1}$$

where $E_{\mathrm{C}}^{\mathrm{S}}$ and $E_{\mathrm{C}}^{\mathrm{M}}$ are the energies at the bottom of the conduction bands of a semiconductor and metal respectively. However for metals, we know that

$$E_{\mathrm{C}}^{\mathrm{M}} = E_{\mathrm{F}}^{\mathrm{M}} \tag{2}$$

In the case of semiconductors the Fermi level is defined as

$$E_{\mathrm{F}} \approx \frac{E_{\mathrm{C}}^{\mathrm{S}} + E_{\mathrm{V}}^{\mathrm{S}}}{2} \tag{3}$$

where $E_{\mathrm{V}}^{\mathrm{S}}$ is the energy at the top of the valence band of a semiconductor. The energy gap ΔE_{G} between conduction band and valence band in case of semiconductors is given by

$$\Delta E_{\mathrm{G}} = E_{\mathrm{C}}^{\mathrm{S}} - E_{\mathrm{V}}^{\mathrm{S}}. \tag{4}$$

On combining equations (3) and (4) one can get the expression

$$E_{\mathrm{F}}^{\mathrm{S}} \approx E_{\mathrm{C}}^{\mathrm{S}} - \frac{\Delta E_{\mathrm{G}}}{2}. \tag{5}$$

For most of the semiconductors, ΔE_{G} is a small quantity and to a first approximation can be neglected. Thus equation (5) gives

$$E_{\mathrm{F}}^{\mathrm{S}} \approx E_{\mathrm{C}}^{\mathrm{S}}, \tag{6}$$

or using equations (1), (2) and (6), we can write

$$\Delta E_{\mathrm{C}} \approx E_{\mathrm{F}}^{\mathrm{S}} - E_{\mathrm{F}}^{\mathrm{M}}. \tag{7}$$

Thus, to the first approximation, the chemical shift can be calculated from the energy difference between the Fermi energy of a compound ($E_{\mathrm{F}}^{\mathrm{S}}$)and the metal ($E_{\mathrm{F}}^{\mathrm{M}}$). In other words, when a metal forms a compound its Fermi energy changes. As a result the x-ray absorption edge in the compound should be shifted with respect to its position in the metal. Appleton [21], Ulmer [22] and several other workers [23,29] reported this fact long ago.

The Fermi energy of a compound can be calculated by using the relation between Fermi energy and plasmon energy as defined by Pines [25],

$$E_{\mathrm{F}} = 0.29484\ (\hbar\omega_{\mathrm{p}})^{\frac{4}{3}}\ \mathrm{eV}. \tag{8}$$

where $\hbar\omega_\mathrm{p}$ is the plasmon energy, which is defined [26,27]

$$\hbar\omega_\mathrm{p} = 28.8\sqrt{\frac{Z\sigma}{W}}\ \mathrm{eV}, \tag{9}$$

where Z stands for the effective number of electrons taking part in plasma oscillations, σ is the density and W represents the molecular weight.

Equation (9) is valid only for the free electron gas model, but to a first approximation this can be used also for dielectrics [28]. According to Kittel [29], plasma oscillations in dielectrics and in metals are the same; Raether [30], Philipp and Ehrenreich [31] have given a relation for plasmon frequency of dielectrics as

$$w_\mathrm{pd}^2 = \frac{w_p^2}{(1-\delta\epsilon_0)}, \tag{10}$$

where $\delta\epsilon_0$, being a small quantity, can be neglected. Calculated values of $\hbar\omega_\mathrm{pd}$ and $\hbar\omega_\mathrm{p}$ are in fair agreement with the observed values of plasmon energy for dielectrics [31].

Blokhins [32], using Sommerfield formula for the Fermi energy

$$E_\mathrm{F} = \frac{h}{8m}\left(\frac{3n}{\pi}\right)^{2/3}, \tag{11}$$

has also shown that the chemical shift is directly proportional to the number of electrons in the Fermi level. Several workers [14,33–38] have reported this fact also.

Now, differentiating equation (11) we get

$$\Delta E_\mathrm{F} = \left[\frac{h}{12m}\left(\frac{3}{\pi}\right)^{2/3} n^{-1/3}\right]\Delta n \tag{12}$$

or $\Delta E_\mathrm{F} = \text{constant}\,\Delta n$.

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

$$\begin{aligned}\Delta E_\mathrm{F} = \Delta E_\mathrm{C} &= \text{constant}\,\Delta n\\ &= \text{constant}\,\Delta Z.\end{aligned}$$

Thus the chemical shift varies linearly with the change in the number of electrons (ΔZ) in the Fermi surface. This also substantiates our hypothesis mentioned above.

ΔE_F may be positive or negative depending upon whether $E_\mathrm{F}^\mathrm{S} < E_\mathrm{F}^\mathrm{M}$ or $E_\mathrm{F}^\mathrm{S} > E_\mathrm{F}^\mathrm{M}$. This explains the nature of the 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.

Compound/ Element	Z	σ	W	E_F	ΔE_C Cal. (eV)	ΔE_C Obs. (eV)	Ref.
Co	2	8.9	58.5	11.7747	—	—	—
Co_3Gd	7	9.15	334.5	8.6434	−3.1313	−3.6 + .5	[45]
Co_5Gd	11	8.80	451.7	9.3209	−2.4538	−2.79	[46]
Co_5Dy	11	9.05	457.0	9.4221	−2.3248	−2.31	[47]
Co_5Er	11	9.27	461.7	9.4621	−2.3125	−1.87	[47]
Co_5Ho	11	9.15	459.7	9.4542	−2.3205	−2.11	[47]
Co_5Tb	11	8.93	453.4	9.3880	−2.3867	−2.59	[47]
Co_5Nd	11	8.38	438.7	9.1983	−2.5487	−3.31	[48]
Co_5Pr	11	8.34	435.4	9.2153	−2.5594	−3.41	[46]
Co_5Sm	11	8.58	444.9	9.2571	−2.4829	−3.0	[49]
Cu	1	8.92	63.9	7.0325	—	—	—
$CuFeS_2$	11	4.40	183.8	10.6921	3.6596	2.6	[50]
CuGa	4	7.24	133.2	9.4097	2.3772	3.0	[51]
$CuGaS_2$	9	4.40	197.2	8.9246	1.8921	2.28	[50]
Cu_2GeSe_2	12	5.57	295.5	9.6618	2.6293	1.56	[50]
$CuInS_2$	8	4.71	178.3	9.2333	2.200	2.15	[50]
CuS	7	4.68	95.5	12.7592	5.723	3.5	[52]
Cu_2Te	4	7.27	254.6	6.1264	−0.9060	−1.0	[52]
Ga	3	5.904	69.7	10.535	—	—	—
Ga_2Se_2	10	4.92	297.2	7.8462	−2.6886	−1.5	[52]
Se	2	4.50	78.9	6.1219	—	—	—
SeO_2	14	3.95	110.7	16.3845	10.2635	11.8	[53]
Ge	4	5.35	72.5	11.5372	—	—	—
$GeSe_2$	16	4.68	230.3	12.3059	−0.7687	−0.6	[53]
As	3	5.727	74.9	9.7502	—	—	—
GaAs	6	3.69	144.6	7.4482	−2.302	−1.1	[54]
Nb	2	8.57	92.9	8.4342	—	—	—
$NbSe_2$	6	6.3	250.7	7.3724	−1.0617	−2.0	[52]
NbO	4	7.3	108.8	10.8281	2.3939	3.8	[52]
NbO_2	6	5.98	124.7	11.3424	2.9082	6.1	[52]
Mo	2	10.2	95.9	9.2738	—	—	—
$MoSe_2$	14	6.9	283.7	12.6900	3.4162	1.9	[52]
$MoTe_2$	14	7.681	351.1	11.8248	2.5510	1.6	[52]
Ni	1	8.90	58.71	7.3999	—	—	—
$NiSe_2$	13	6.79	216.5	14.3089	6.9089	6.7	[55]
W	2	19.35	83.8	9.2107	—	—	—
WO_3	8	7.29	231.5	10.3807	1.1700	2.7	[56]

TABLE I.

In case of some compounds the difference between our theoretical calculated values and experimentally observed values may be due to the following reasons:

i) An approximate but simple method for calculating Fermi energies E_F has been used, because we have neglected ΔE_G, we have also not taken into account the relaxation energy, screening effect etc. as their contribution to chemical shift is small and complexities are involved in their calculations.

ii) In some cases experimental values of the chemical shift (ΔE_C) for the same compounds observed by different workers [7,39–44] vary as much as upto 40%.

Using equation (7) authors have calculated the chemical shift for various compounds of Co, Cu, Ga, As, Mo etc. and compared it with the experimentally observed values of chemical shift. It has been found both agree fairly well (see Table I).

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Resumen. Se calcula el corrimiento químico de las bandas de absorción de rayos x para varios compuestos de Co, Cu, Ga, As, Mo y W, usando los datos existentes para la energía de Fermi. Se encuentra que los valores calculados y los experimentales coinciden satisfactoriamente.