A CORRELATION BETWEEN CHEMICAL SHIFT AND PAULING'S EFFECTIVE CHARGE IN SOME COPPER SYSTEMS

RAKESH KUMAR RANJAN[*], SUSHMA KUMARI [**] AND R.N.SINHA[***]

1.Department of Physics,V.K.S.University, Ara, Bihar, India.

2. Department of Chemistry,V.K.S.University, Ara, Bihar, India.

3. University Department of Physics,V.B.University, Hazaribag,Jharkhand India.

Abstract

Though XAS has emerged as an appropriate tool for obtaining structural information around the X – ray absorbing atom, it's Theoretical analysis has remained very difficult till date, We in the present paper have defined the Chemical – shift in terms of the position of the Main peak appearing in the X- ray absorption spectra and have Correlated the same with Pauling's effective charge. The high degree of correlation shows that the position of the main peak in the spectra can be very well utilised for obtaining physico – chemical properties of the System.

Introduction

X-ray absorption Spectra (XAS) is sensitive to the valence state and neighboring atoms of the absorbing elements. K-edge x-ray absorption reflects the transition probability from a is orbital to the unfilled conduction band. The effect of oxidation state on chemical shift is significant. Therefore the chemical shift[1] of x-ray absorption edge structure provides information from which

the oxidation state can be obtained. The chemical shift of absorption edge can be used for chemical state analysis. X-ray absorption near-edge structure (XANES) spectroscopy is a technique that can be used to determine oxidation states and optionally derive other information on the chemical environment of chemical elements in various materials. This information is extracted from the shape and chemical shift of the absorption edge of the element of interest. To record the absorption edge profile with a sufficient degree of detail, materials under investigation are irradiated with a beam of highly monochromatic tunable synchrotron radiation[1]. The energy of the primary beam is scanned over the desired absorption edge. The position of the absorption edge of the absorbing atom changes due to the change in the chemical environment around the absorbing atom. This change in the position of the absorption edge due to the chemical environment (around the absorbing atom) is called the chemical shift.

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon :

1.   The formal oxidation state of the atom.

2.   The local chemical and physical environment.

Changes in either (1) or (2) give rise to small shifts in the peak positions in the spectrum, the so-called chemical shifts.

An element forming a compound in a chemical combination suffers through a change in the energy of the absorption edge of the metal. It is due to the change in the potential causing a change in the binding energy of the electron (to be ejected as photon) of the photo-absorbing atom. This shift in the energy of the X-ray absorption edge is known as chemical shift. It is equal

to the difference of energy of the absorption edge of the metal in compound (E_c) and in pure elemental state (E_m), i.e., chemical shift ΔE, (in eV) is given by,

$$\Delta E = E_c - E_m \tag{1}$$

The extensive studies made by Cauchois[2], Meisel[3], Azaroff and Pease[4], Nagel and Baun[5], Srivastava and Nigam[6], Mande[7] suggested that the chemical shift is governed by the several physico-chemical parameters such as effective charge, valence, ionicity, co-ordination number, number of electrons taking part in the bond formation etc. The observed high energy shifts of the X-ray absorption edges are attributed by the following two factors :

(i)   The participation of the valence electrons in the chemical bond   formation causes the tighter binding of the core level because of the change of effective charge (or screening) of the nucleus.

(ii)   Appearance of energy gap due to transition from a metal (or element) to a compound.

The photo-electron spectroscopy provides the direct evidence of the first factor. The second factor is believed to be related to various parameters such as covalence, effective charge, coordination number, crystal structure etc.

Various attempts have been made by the several workers to correlate the chemical shift with valency, ionicity and coordination number, Sapre and Mande[8] and with the effective charge [9,10,11] Siegbahn et.al.[12] have shown using photoelectron spectroscopy that the chemical-shifts are due to change in local potential set up by the differences in charge distribution among atoms in molecule. The first potential is assumed to be approximately proportional to the charge on the atom. It is generally dominant. The second potential is called the molecular potential. This is set

up by the charge distribution in the rest of the molecule. The nature of this local potential is very complicated as it is anisotropic and having a three dimensional character. The shape of the local potential depends upon different molecular parameters such as coordination number, bond length, valence of the absorbing atom, electronegativity of the atoms in the molecule, molecular geometry etc. and the core hole depth. The photoelectron eventually tunnels [13,14] the potential barrier where it is resonantly trapped.

A satisfactory and general theory of chemical shift connecting the other physico-chemical parameters is very difficult to propose due to the complex and anisotropic nature of the molecular potential and perhaps this is the reason why most of the relationship between chemical shift and other physico-chemical parameters proposed by various workers have been empirical in nature. The effective charge on the absorbing atom develops due to different factors such as coordination number, valency, bond length, nature of bonding (covalency), electronegativity etc. The effective charge on the absorbing atom is a measure of the charge transfer from the absorber to the neighbouring atom. Therefore in most of the studies on chemical shift attempts have been made to correlate the chemical-shift with the effective charge.

According to the empirical formula of Agarwal and Verma[15] the chemical shift is towards the high energy side of the metal edge. It increases progressively with the increase of the valence of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding.

2. Experimental Method

The experimental method and spectra have been given elsewhere[16,17]

3. Method of Calculation and Discussion

In terms of XANES features as the XANES features are affected by the physico -chemical environment of the system, We have tried to correlate the shift of the main peak ΔS of XANES with effective change, q calculated using Pauling's method. Instead of calculating the chemical shift of the edge, we have calculated the shift of main peak in a compound with respect to the position of the corresponding position in the metal, i.e for a given system,

$$E_{compound} \, (\, main - peak) - E_{metal} \, (\, main - peak) = \Delta E \qquad (2)$$

Of the different correlations tried we have found that the correlation

$$q = a \, \Delta E^3 + b \, \Delta E^2 + c \, \Delta E + d \qquad (3)$$

given the best result.

The result for the system has been shown in tables 1 and, Corresponding Graphs in Fig.1.

CONCULTION

From the results we find that the shift ΔE exhibits polynomial correlation of high degree with corresponding change q of the system. Hence instead of searching the edge position by different methods (as proposed by different workers) the prominent XANES features obtained from the experimental curve can be directly utilized for study of chemical shift and other correlated physico- chemical parameters.

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Table 1 : Correlation between chemical shift for each peak and effective charge for in some Copper Systems.

Absorber	E_C in eV*	q	ΔE_C eV
Cu (Acetate)$_2$	27.82	1.71	3.04
CuCl$_2$	21.30	1.95	3.48
CuF$_2$	26.08	1.66	1.3
CuSO$_4$	26.95	1.58	2.17
Cu(NO$_3$)$_2$	26.52	1.6	1.74
La$_2$CuO$_4$	23.04	1.65	1.74
CuO	28.26	1.45	3.48
Cu	24.78	———	———

(*Value taken from Ref. No. 16,17)

Fig 1: Correlation between q and $\triangle$E in Copper systems in Polynomial Curve Fit.
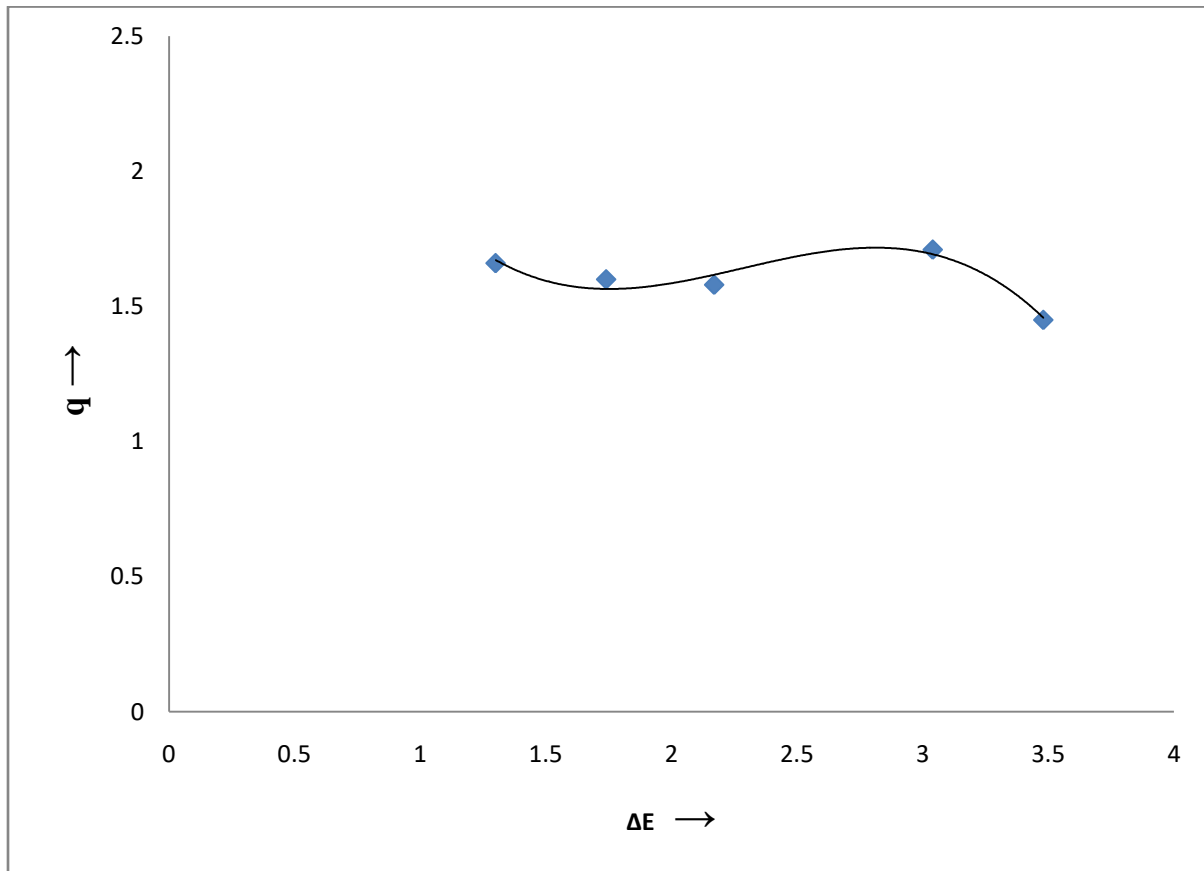
$$q = a \triangle E^3 + b \triangle E^2 + c \triangle E + d$$

Coefficient Value   **Correlation Coefficient**

$$a = 0.256, \quad b = 1.758 \qquad R^2 = 0.919$$
$$c = 3.795, \quad d = 4.197$$