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Copper K-Edge and Pauling's Effective Charge in Some Systems: A Correlation Between them

Rakesh Kumar Ranjan[1], R.N. Sinha[2], K.K. Dubey[3]
PG Dept. of Physics Veer Kunwar Singh University, Ara, Bihar, India[1]
PG Dept.of Physics V. B. University , Hazaribag, Jharkhand, India[2]
Dept.of Applied Physics, Cambridge Institute of Technology, Ranchi, Jharkhand[3]
sonuranjan_ara@yahoo.co.in[1], rajendra_sinha@yahoo.com[2]

Abstract: *For structural information around the X-ray absorbing atom XANES is considered to be an appropriate tool. But XANES is still passing through developing stage leaving wide area for developing analytical method for quantitative analysis. Inverse correlation* $ER^2 = c$ *has been widely used for the determination of inter atomic distances in several model systems, where E is the energy of a XANES peak, R is the inter-atomic distance and c is a parameter whose nature has not been fully understood. We in the present paper have correlated c with effective-charge on the K-edge of X-ray absorbing Copper atom in* La_2CuO_4, $CuCl_2$, *Cu (acetate)* $_2$, Cu_2O, *CuO*, $CuSO_4$**.**

1. INTRODUCTION

For probing the local structure in a wide variety of materials XAS (X-ray absorption spectroscopy) has achieved a fast momentum during the past few decades. XAS has been divided into two regions: the X-ray absorption near edge structure (XANES) and the X-ray absorption fine structure (EXAFS). XANES lies upto approximately 50 eV above the threshold and EXAFS lies beyond 50 eV above the threshold1, 2. XANES passes through a number of factors, such as, multiple scattering, chemical effects and the curvature of the outgoing photo-electrons etc while these factors are relatively insignificant in the EXAFS region. For this reason XANES become important for local structural analysis in materials. But the complexity of these phenomena makes the analysis of XANES more difficult. Several workers attempted to explain XANES but the theoretical understanding of the phenomena, in the right direction was probably initiated by Natoli3, 5 in the eighties.

The kinetic energy of the ejected photo-electron is small near the absorption edge. The scattering processes (or resonances) are influenced by (1) the core potentials of central absorbing atom and its neighbors and (2) by the valence electron charge distribution in the inter-molecular region. This resonance is due to scattering process where the photo-electron is resonantly scattered back and forth along the internuclear axis between the absorbing atom and its neighbours. Therefore the continuum peaks should be sensitive to co-ordination geometry and intermolecular distances.

An inverse correlation exists between shape resonance peak energy and the first co-ordination shell-distances(R)according to Kutzler at al6.They demonstrated that the molecular potential due to the molecular cage defined by the first-shell ligands has an overall qualitative effect on the observed spectral features by using multiple scattered wave SCF X-alpha calculations on transition metal K-edges.Natoli3, 5 deduced a relation by using his multiple scattering theory of XANES as given by

$$(E_r - V_O)R^2 = C_r \qquad \text{.................... (1)}$$

and $$(E_b - V_o)R^2 = C_b \qquad \text{…………….. (2)}$$

where E_r and E_b are continuum and bound resonance energies respectively, V_o is the average interstitial potential and C_r and C_b correspond to the continuum and bound state resonances respectively. Since V_o is not an experimentally accessible quantity, Natoli modified equations (1) and (2) as

$$(E_r - E_b) R^2 = C_r - C_b \qquad \text{……………… (3)}$$

Although this modification eliminates V_o but C_r and C_b are still unknown. This process of bond-distance determination using this equation is very complicated. Bianconi[1-2] has suggested the following equation

$(E_r - E_b) R^2 = C =$ Constant ……………….. (4)

This relation applies for the bound states (Pre-peaks) at the K -edge of Transition elements in insulators with tetrahedral coordination but with small variation (~2o%) of R. The effects of variation of phase-shift of different elements were neglected which greatly reduce the practical utility of equations (3) & (4) for the measurement of nearest neighbor distances in model systems. But till date nature and value of C_r and C_b or C has not been clearly understood. We in this present paper have attempted to correlate this constant with Pauling,s effective charge[7] (q) on the absorber in K-edges of Copper in La_2CuO_4, $CuCl_2$, Cu (acetate) $_2$, Cu_2O, CuO , $CuSO_4$.

2. EXPERIMENTAL METHOD

The experimental method and spectra have been given elsewhere[11-12].

Method of Calculation and Discussion:

An energy reference is essential for the analysis of XAS. After making some approximations this reference energy has been defined by different workers in different ways[1-2] for XANES region. Most common among them are (i) the first inflection point of the X-ray absorption edge(ii) the middle of the sharp rising part of the absorption edge(iii) the first or second peak of the derivative spectra(iv) the beginning of the continuum etc. But these methods cannot be unambiguously applied in case of high resolution XAS. In defining the reference energy the effect of the thickness of the absorber on XAS or the area covered by XANES spectra has not been taken under consideration. Caphart et al[10] attempted to include the area of XANES spectra for defining the edge-shift but their method does not eliminate the thickness effect of the absorber. Alp et al[8, 9] have defined the characteristic energy(S)of XAS using energy moments taking into account the thickness effect of the absorber and area of XANES spectra but they failed to establish any definite correlation between the characteristic energy(reference energy) and the formal valance of copper in some systems of its compounds. By Alp et al the n^{th} moment of energy $M^{(n)}$ with respect to the absorption coefficient,μ(E), in the energy range L_0 to L_1 is defined as:

$$M^{(n)} = \int_{L0}^{L1} E^{(n)} \mu(E) dE$$

Where L_0 and L_1 are the lower and upper limits of integration respectively. The mean energy of this region is given as

$$<E> = \frac{M^{(1)}}{M^{(0)}}$$

And the characteristic energy is given as

$$S = 2<E> - L_1$$

In the present work we have taken L_0 =0eV (the first inflection point) and L_1 =35 eV i.e. nearly the full area of XANES spectra for each system under study and then S has been calculated. The values thus obtained have been given in table-1.

The fact that the chemical-shift in XAS provides information about the charge density on the X-ray absorbing atom, the characteristic energy(S) and the nearest neighbor distance (R) must have some relation with effective-charge,(q), on the X-ray absorbing atom. In the present work the effective charge (q), on the X-ray absorbing Copper atom(S) have been calculated using Pauling formulas. Of different functional relations an exponential curve fit given as

$SR^2 = ae^{bq}$ ………………………………………(6)

was found to be the best fit for SR^2 and effective charge,q, where a and b are least squire fit parameters(values of a and b given in table-1),graph shown in figure 1.

Table-1: Correlation between SR^2 and q

Values of ($S \times R^2$)calculated for some Cu K-edge system at different energy modes.

Name of the absorber	**Effective Charge (q) el.per atom**	**Crystallographic value of R in Ā**	**characteristic energy(S)**	**(SR^2)**
La_2CuO_4	1.666	1.86	6.65	12.36
$CuCl_2$	1.9489	2.30+0.01	6.81	15.67
$Cu(acetate)_2$	1.1104	1.947	6.18	12.04
Cu_2O	0.86	1.849	5.45	10.08
CuO	1.4473	1.96	6.05	11.86
$CuSO_4$	1.5766	2.10+_0.02	5.88	12.36

Equation of graph: $SR^2=ae^{bq}$

Value of least sq. parameter

$a = 7.737901997$

$b = 0.3224264863$

correlation coefficient: $r = 0.88847$

Table 1

Correlation between SR^2 and the effective charge (q) in **copper system** at 35 eV. in exponential mode($SR^2=ae^{bq}$)

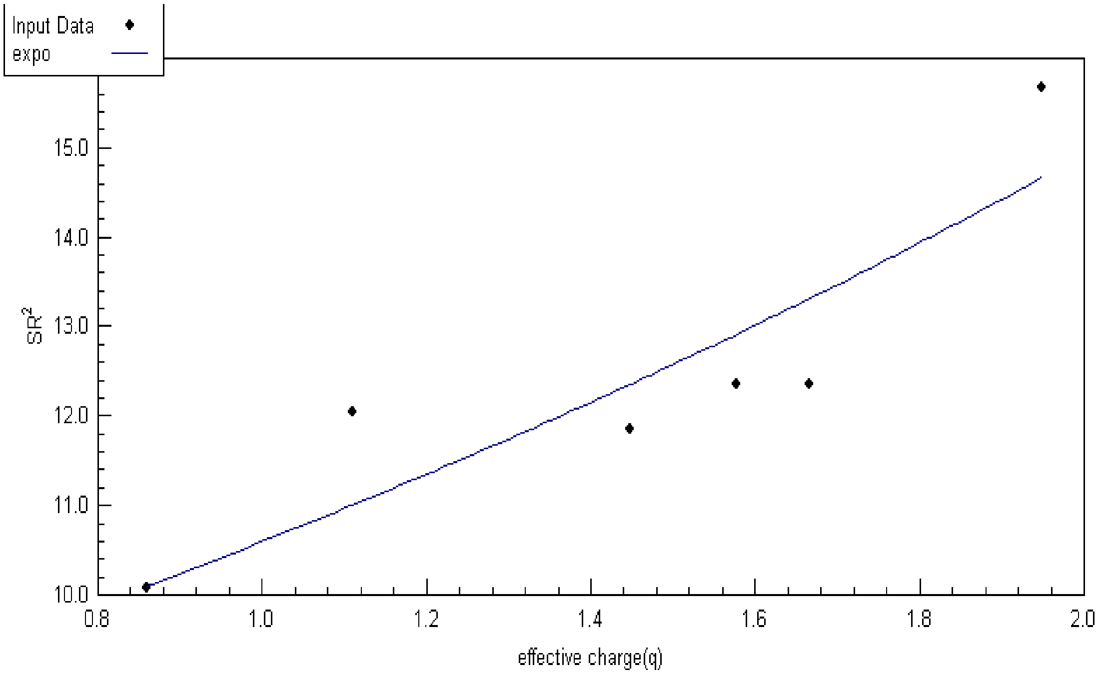

Fig.1: Exponential curve fit showing correlation between (SR^2) and (q) of Copper System at 35 eV. of energy.

The high degree of correlation coefficient $(r)\sim 89\%$ between SR^2 and q suggests that C_r, C_b or C depends upon the chemical environment around the X-ray absorbing atom defined by effective charge on the atom.

3. CONCLUSION

The high degree of correlation obtained in the present work suggests that the Energy Moments criterion for the determination of the edge – energy in a very good method as it taken into account. The effect of the absorber and area of the XANES Spectra. This approach seens to be a better method for the analysis of XANES features.

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