Estimation of Phase Parameters in some Cobalt Compounds using X-ray Absorption Data

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Abstract— Extended X-ray absorption fine structure data at the K-edge for three cobalt compounds viz., cobalt sulphate(I), cobalt nitrate(II) and cobalt chloride(III) have been analyzed for the estimation of phase parameters alpha1, beta1 and delta1. On the basis of our studies it may be concluded that backscattering phase shift and the total phase shift varies with the change in ligands. The total phase shift values for the presently studied compounds exhibit a linear variation with wave vector k. Average bond distances have been obtained for the samples studied using Levy's and Lytle, Stern, Sayers (LSS) method. The present method of determination of phase parameters using the graphical technique is simple and comparable to the other theoretical methods.

Keywords — _Cobalt compounds, Phase parameters, EXAFS, Bond lengths_

I. INTRODUCTION

An important feature of the X-ray absorption spectrum is the fluctuations in intensity observed on the high energy side of the X-ray absorption edge. The fine structure near the absorption edge covering the energy range upto nearly 50 eV is called X-ray absorption near edge structure (XANES). From 50eV onwards upto several hundred eV the structure is called extended X-ray absorption fine structure (EXAFS). X-ray absorption spectroscopic studies have been recently reported for copper (II) Micro cyclic carbamide complexes by Bhalse and coworkers [1], in which they have reported bond lengths using Levy's method, Lytle's method, LSS method and FT method. These graphical methods provide estimation of various phase parameters involved in the X-ray absorption process. These parameter include α_1 (bonding parameter), β_1 (backscattering phase shift) and δ_1 (total phase shift). Apart from bond length determination, these graphical methods allow us to estimate phase parameters and they provide an incite in the physical process involved. There for in the present communication we have reported the estimation of phase parameters in some cobalt compounds using the X-ray absorption data previously reported [2,3].

II. EXPERIMENTAL

The arrangement utilized for recording the spectra experimentally have been given in an earlier publication. [4]

III. RESULTS AND DISCUSSION

In the X-ray absorption process the outgoing wave interacts with the nearest neighbours and the backscattered wave undergoes phase change. The changes of the phase with the wavelength of the photoelectron mainly depend on the distance between the central metal ion and the atom doing backscattering. The variation of the backscattering strength as a function of energy of the photoelectron depends on the type of atom doing the back scattering. Thus EXAFS provides information on the atomic surroundings of the central atom.

In Table 1 the values of maxima and minima of EXAFS have been reported for the three cobalt compounds. The _k_ values have been determined using the relation $k = (0.263E)^{1/2}$, where E is the energy (in eV) of the peaks in the EXAFS measured from the inflection point of the component K_1 on the absorption curves as determined from the derivative spectra.

Table 1 – Position of maxima and minima and the values of wave vector _k_ for cobalt compounds.

Structure	n	Compound		
		Cobalt Sulphate $k(\text{Å}^{-1})$	_Cobalt Nitrate_ $k(\text{Å}^{-1})$	_Cobalt Chloride_ $k(\text{Å}^{-1})$

A	0	1.48	1.47	1.52
α	1	2.95	2.85	2.76
B	2	3.67	3.70	3.87
β	3	4.86	4.89	5.05
C	4	6.02	6.15	5.73
γ	5	7.75	7.37	6.54
D	6	8.03	8.29	7.23
δ	7	-	-	7.81
A	0	1.48	1.47	1.52

In equation (1) n is the order of the position of EXAFS maxima and minima and R_1 represents radius of the first coordination sphere. This equation was used to determination of β_1 and R_1.

$$(\tfrac{1}{2} + n)\pi = 2k(R_1-\alpha_1) + 2\beta_1 - \pi \qquad (1)$$

In the above equation n=0,2,4,.... for maxima and n=1,3,5,.... for minima. Table 2 gives the average bond lengths for the cobalt compounds as estimated by Levy's method [5]. The bond lengths have also been obtained by modified Lytle, Stern and Sayers (LSS) graphical method [6,7].

Table 2 – The estimated average bond distance (Å), bonding parameter (α_1) and phase parameter (β_1) for cobalt compounds.

Compounds	R (Levy's method)	Slope	α_1 Central atom phase shift	β_1 Back scattering phase shift	R_1 (LSS method)
Cobalt Sulphate	1.99	0.89	0.31	1.29	1.96
Cobalt Nitrate	1.97	0.88	0.31	1.41	1.93
Cobalt Chloride	1.94	1.00	0.31	2.33	1.93

By plotting n *vs* k as depicted in Fig. 1, we have determined the slopes of the straight lines which give the values of (R_1-α_1) as seen from equation (1). Using α_1 = 0.31 Å [1] for each of the samples, R_1 (the average bond lengths) have been determined. *Lytle et al.*[6] have mentioned that the parameter α_1 depends to a large extent on the central absorbing atom and for chemically similar systems the value of α_1 remain more or less the same. The phase parameter β_1 was also estimated from the straight line graphs. Table 2, gives the values of R_1 and β_1 as determined by us for the three compounds. The values of bond lengths as obtained by LSS

method are also given in Table 2. Finally, the total phase shift (δ_1) were estimated from the following expression

$$\delta_1= - \alpha_1 k+ \beta_1 -\pi/2 \qquad (2)$$
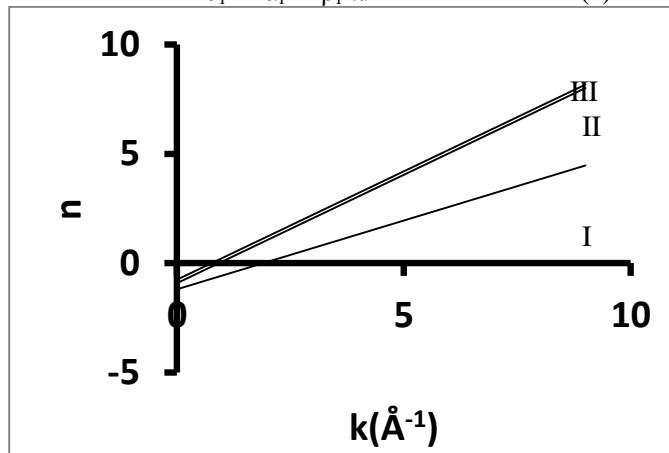

Figure 1- n vs k plot for cobalt compounds.

The values of δ_1 are given in Table 3. In Fig. 2, the values of δ_1 have been plotted against the wave vector k. The sine term in the EXAFS equation determines its periodicity. Several attempts [8, 9, 10] have been made to determine phase shifts theoretically. A comparison of total phase shift expressed by equation (2) may be done with the theoretical phase shifts given by Teo and Co-workers [8, 9].

$$Q_{ab}= Q_a (k)+ Q_b (k) -\pi \qquad (3)$$

Table 3 – The estimated total phase shift (δ_1) for cobalt compounds.

Structure	Compound		
	Cobalt Sulphate	Cobalt Nitrate	Cobalt Chloride
A	-0.07	-0.05	-0.26
α	0.64	0.73	0.45
B	1.79	1.81	1.25
β	2.67	2.70	2.01
C	3.57	3.55	3.11
γ	4.14	4.43	4.12
D	5.54	5.47	5.21
δ	-	-	6.38

The phase parameter $2k\alpha_1$ resembles Q_a , the phase shift due to the central atom, while $2\beta_1$ resembles Q_b , the back scattering phase shift. The values of δ_1 when plotted against k give a curve similar in character to the theoretical curves obtained by Mckale *et al* [10]. Generally it is observed that the total phase shift for compounds belonging to a given system should be more or less have the same values. However, this is not the case. We have found that the curves δ_1 *vs* k (Fig. 2) are different for the three compounds. If we plot δ_1 *vs* k, we get straight lines nearly parallel to each other that indicates a linear variation between the total phase shift δ_1 and k. The sequence of β_1 amongst the presently studied compounds is

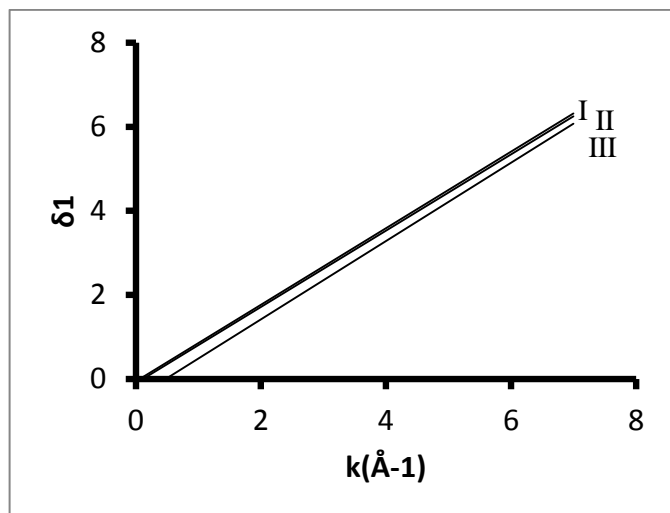Cobalt-chloride (2.33) > Cobalt-nitrate (1.41) > Cobalt-sulphate (1.29)   (4)

Figure 2 – Variation of total phase shift δ_1 with wave vector k for cobalt compounds.

Our β_1 values also indicate that a systematic change in the environment around central metal ion is responsible for the different values of β_1. Further the magnitude of these shifts depends on the nature and distance of the scatterer from the central metal ion. The variation in the average metal-ligand bond distances as seen in Table 2, for the different compounds is small and this indicates that around the central metal cobalt ion, the variation in the backscattering contribution from the nearest neighbours follows the sequence as mentioned in Eq.(4) above. It is obvious from the values obtained for β_1, and average bond distances as reported in table (2), that the sequence of variation is reversed in the case of two parameters. The order is reversed in the average bond distance viz.,

Cobalt- sulphate (1.99) > Cobalt-nitrate (1.97) > Cobalt-chloride (1.94)

This also shows that the nearest neighbour contribution towards backscattering parameter is more pronounced. Stearns and Stearns [11], using the Fourier transformation method, observed that the parameter α_1 can be interpreted as corresponding to the scattering size of the atoms, whereas the parameter β_1 is associated with the depth of the potential well in which the absorbing atom is placed. They further showed that an atom pair in any condensed material has a unique linear phase function in the operating *k* rang.

IV.   CONCLUSION

The present method of phase shift determination using the graphical technique is simple and comparable to the other theoretical methods [12, 13, 14, 15, 16, 17]. Previous workers [18] studied the effect of counter ions on X-ray absorption parameters utilizing phase shifts. The above analysis provides a physical picture of the X-ray absorption process. Further this procedure for estimating phase shifts may be utilized in various substances, e.g. amorphous materials, metallic glasses and bio molecules.

V.   REFERENCES

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