Chalcogenide Letters Vol. 8, No. 2, February 2011, p. 139 – 146

STUDY OF CHARGE TRANSFER AND STRUCTURE FACTOR CALCULATION IN YbS

S.ARIPONNAMMAL* ,S.K.RATHIKA
Department of Physics, Gandhigram Rural Institute (Deemed University)
Gandhigram -624302, Dindigul District, Tamil Nadu, India

Ytterbium chalcogenides receive greater interest because of their interesting properties such as valence transition, semiconductor to metallic transition and structural phase transition etc. In this paper, the presence of charge transfer in Ytterbium Sulphide(YbS) is analysed by experimental and theoretical X-ray diffraction data. The direction and amount of charge transfer are inferred by plotting and comparing the structure factor of the components. Thus, the charge transfer of 0.48 electron from Ytterbium(Yb) to Sulphur(S) is observed in YbS from the present study which confirms the intermediate valence fluctuation. Further, the charge transfer in YbS, YbSe and YbTe is found to be decreasing with the increase of lattice constant and energy gap which correlates the valency and lattice size.

(Received January 21, 2011; accepted February 6, 2011)

Keywords: YbS, Charge transfer, Valence fluctuation,XRD

1. Introduction

The rareearth compounds have increasingly been studied in the last decades and much valuable information on magnetism, crystal fields and related phenomena have been obtained from these materials. The growing interest in rareearth compounds is activated by the unique physical properties associated with the localized character of the 4f levels of the rareearth ions[1]. The valence fluctuation phenomena have been reported[2] to occur in rare earth compounds containing the beginning (Ce), near the middle (Sm and Eu) and near the end (Tm and Yb) members of the rare earth elements in the periodic table. The terms intermediate valence fluctuation and inter configuration fluctuation are used for manifesting the characteristics of these systems. If the configuration $4f^n$ of rare earth ions is nearly degenerate with $4f^{n-1}$ plus a surplus conduction electron, the 4f state will fluctuate between those adjacent valence states[3]. The mixed valence phenomena occurring in rare earth compounds receives a great deal of interest in the 1970s and early 1980s. Although the burst of activity dealing with mixed valence materials in 1970s has been superseded by the subsequent shift of interest towards other strongly correlated electron systems such as heavy fermions, high temperature superconductors etc., some questions regarding the fundamental mechanism involved in valence fluctuation were left unsettled. In recent years these questions are being revisited as a result of the insight gained in studying related systems[4]. The Ytterbium chalcogenides are ferro magnetic semiconductors and offer unique possibility to study the magnetic properties[5]. Although numerous experimental works have been reported on the destabilization behaviour of f-shell of these compounds, the theoretical description remains a challenging one[6]. In this paper, the presence of intermediate valence fluctuation is reported by deducing the charge transfer in YbS based on structure factor calculations.

*Corresponding author: ariponnammal@yahoo.co.in

2. X-ray diffraction

The experimental x-ray diffraction data has shown that the YbS has been crystallized in NaCl type structure with space group of Fm3m[7] . The theoretical x-ray powder diffraction pattern has been simulated by using Lazy-Pulverx programme and is shown in Figure 1. The theoretical XRD data has been compared with the experimental XRD data in table1 and both are found to be in good agreement with each other. The table1 gives the plane indices (hkl), interplanar spacing (d), relative intensity (I/I_0) and the deduced structure factor (F_{hkl}) of YbS.

3. Theory

All III – V compounds like GaAs, InSb, GaP and InP with zinc blende structure involve a charge transfer between the nearest neighbours. Similarly II – VI compounds semiconductors like Zinc Selenide (ZnSe) involve a charge transfer[8]. Though different techniques are available to determine the charge transfer, according to Cochran[8], only x –ray diffraction could give precisely the sign and magnitude of charge transfer. For the present work, the x-ray diffraction data has been used[7]. Saravanan et al[9-12] proposed a model for confirming the presence of charge transfer in these semiconductor compounds. It has been reported that the electronic structure factor calculations determine both the valency and the lattice size as a function of atomic number[9] and hence understand the valence transition.

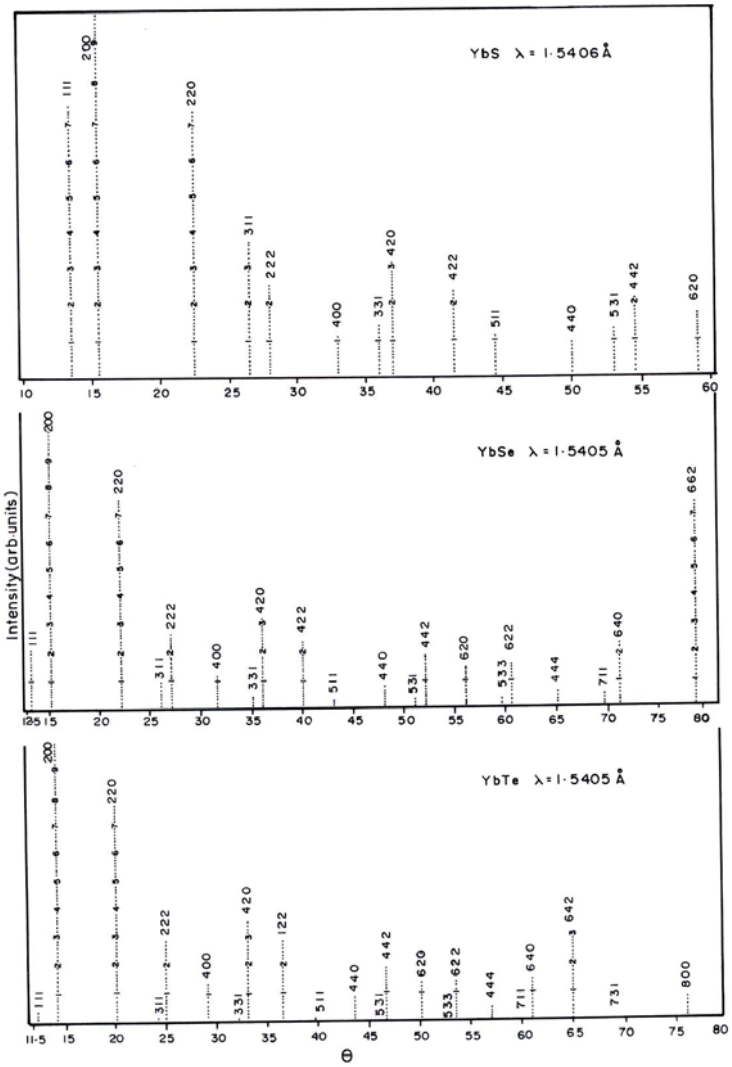

Fig. 1. The simulated XRD patterns of YbS, YbSe and YbTe

Table 1. The experimental and theoretical XRD data of plane indices(hkl), interplanar spacing(d),relative intensity(I/I_0) and structural factors of YbS

Sl. No	Experimental [7]			Theoretical			
	hkl	**d**	**I/I_0**	**hkl**	**d**	**I/I_0**	**F_{hkl}**
1	111	3.290	70	111	3.2869	75.5	168.7
2	200	2.848	100	200	2.8465	100.0	262.4
3	220	2.014	70	220	2.0128	72.8	235.3
4	311	1.717	40	311	1.7165	37.2	144.4
5	222	1.644	25	222	1.6434	25.0	216.0
6	400	1.425	12	400	1.4233	11.4	201.1
7	331	1.306	12	331	1.3061	14.4	125.0
8	420	1.273	25	420	1.2730	31.1	189.0
9	422	1.162	16	422	1.1621	23.4	178.9
10	511	1.096	8	511	1.0956	8.3	110.7
11	333	1.096	8	333	1.0956	2.8	110.7
12	440	1.006	5	440	1.0064	8.6	162.7
13	531	0.962	6	531	0.9623	13.3	100.0
14	442	0.949	10	442	0.9488	16.5	155.9
15	600	0.949	10	600	0.9488	4.1	155.9
16	620	0.900	10	620	0.9001	17.1	149.8

The principle involved in the present method is to deduce the charge transfer by structure factor calculations and thereby infer the intermediate valence fluctuation. The elemental components of structure factors are plotted as a function of $\text{Sin}\theta/\lambda$. Then, the form factor value at $\text{Sin}\theta/\lambda = 0$ will be equal to the atomic number (z) of the element. Any deviation from the value of z can be attributed to the charge transfer[13]. The splitting of total structure factors into individual components is accomplished by exploiting the structure factor expressions of h+k+l = 4n and 4n +2 type reflection. That is

$$F_1^o = 4\,(f_{Yb} + f_S) \quad \text{for} \quad h+k+l = 4n$$
$$F_2^o = 4\,(f_{Yb} - f_S) \quad \text{for} \quad h+k+l = 4n+2$$

The individual components of structure factor of Yb and S are

$$F_{Yb} = (F_1^o + F_2^o)/8$$
$$f_S = (F_1^o - F_2^o)/8$$

respectively. But the F_1^o and F_2^o values are at different $\text{Sin}\theta/\lambda$ values. So, one cannot add or subtract these quantities to get the component structure factors[11]. Hence, the F_1^o and F_2^o values are plotted against $\text{Sin}\theta/\lambda$ and are interpolated for the same $\text{Sin}\theta/\lambda$ values. The same procedure is adopted for the calculated structure factor also. The experimental and theoretical values of f_{Yb} and f_S interpolated for the same $\text{Sin}\theta/\lambda$ values after applying scaling correction are given in Table 2. These individual components are plotted against $\text{Sin}\theta/\lambda$ in the range of 0.015to 0.055$Å^{-1}$ in Figure 2. When charge is transferring from Yb to S in YbS, f^0_{Yb} should decrease and f^0_S should increase which estimates the direction and amount of charge transfer in YbS.

Table 2. Atomic form factors of YbS

Sl. No	Experimental			Theoretical		
	Sin θ/λ	f_{Yb}	f_S	Sin θ/λ	f_{Yb}	f_S
1	0.01520	69.24526	15.64788	0.01521	69.21898	15.64788
2	0.01756	69.04818	15.56438	0.01757	69.04818	15.56438
3	0.02483	68.70657	15.38131	0.02484	68.70657	15.39737
4	0.02912	68.49635	15.29781	0.02913	68.49635	15.29460
5	0.03041	68.41752	15.27533	0.03042	68.41752	15.25285
6	0.03509	68.22044	15.15971	0.03513	68.22044	15.16934
7	0.03828	68.03650	15.07299	0.03828	68.03650	15.06978
8	0.03928	67.91825	15.04730	0.03928	67.91825	15.05051
9	0.04303	67.74745	14.95095	0.04303	67.74745	14.96701
10	0.04562	67.65548	14.90918	0.04564	67.65548	14.91562
11	0.04970	67.47153	14.79358	0.04968	67.47153	14.79679
12	0.05195	67.30073	14.75183	0.05196	67.30073	14.75504
13	0.05269	67.28759	14.72613	0.05270	67.28759	14.72934
14	0.05554	67.11679	14.66190	0.05555	67.11679	14.66190

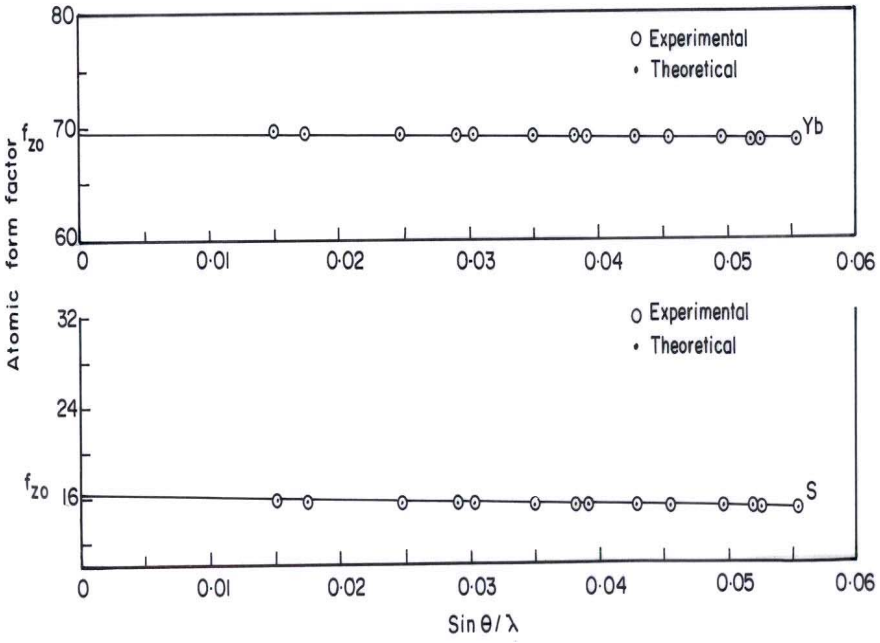

Fig. 2. The plot of experimental and theoretical atomic form factor versus Sinθ/λ for YbS

4. Results and discussion

The YbS has been crystallized with face centre cubic structure with lattice parameter of 5.693Å and space group of F_{m3m}. It has four Yb atoms and four sulphur atoms per unit cell. The experimental atomic form factors have been calculated from the XRD data. The theoretical simulated XRD pattern obtained by Lazy-Pulverx program is shown in figure1. Both the theoretical and experimental XRD data are found to be in good agreement as shown in table 1. It also gives the structure factors Fhkl of YbS. The reported theoretical simulated XRD patterns of

YbSe[14] and YbTe[15] are also shown in figure 1 for comparison.. The experimental and theoretical atomic form factors for different Sinθ/λ after applying scaling correction are reported in table 2 and plotted in figure 2. The values of individual form factors f^0 at Sinθ/λ are given in table 3. When charge is transferring from Yb to S in YbS, f_{Yb}^0 should decrease and f_S^0 should increase. It is well known that the atomic number of Ytterbium is 70 and for S is 16 . Therefore, the atomic form factors of neutral atoms Yb and S are indicated by f_{z0} in figure 1. It is clear from table 3 that f_{Yb}^0 is less than the atomic number of Ytterbium by an amount of about 0.48. Consequently, f_S^0 is larger than the atomic number of S by more or less the same amount. This indicates the transfer of 0.48 electron from Yb to S confirming the charge transfer. It has been reported[16,17] that the compound YbS is a semiconducting compound in which the Ytterbium ions have 2+ valence or at most a small deviation. This gives favourable support for the charge transfer in YbS and agrees well with the experimental report[12-19]. Moreover, similar studies on YbSe and YbTe have also been consolidated in order to make this study to

Table 3. Values of Elemental Structure Factor

Elements	Experimental f^0	Theoretical f^0	Charge transfer
Yb	69.52	69.52	0.48
S	16.43	16.43	

Components at Sin θ/λ = 0

be an interesting one. The atomic form factor curves of YbSe[14] and YbTe[15]have been shown in figure 3 and figure 4 respectively which clearly indicate the charge transfer. This infers the intermediate valence fluctuation from the present study and agrees with the experimental report[16-19]. The table 4 and figure 5 have shown the variation of lattice constant and energy gap[20,21] and amount charge transfer as a function of Ytterbium monochalcogenides YbS, YbSe and YbTe. The amount of charge transfer is found to be decreasing with the increase of lattice constant and energy gap which agrees with the experimental[17-18] correlation between the valence and lattice size.

5. Conclusions

The simulated theoretical XRD pattern (Figure 1) agrees well with the experimental XRD data[7] presented in table1. The atomic form factor curves (Figure 2) confirms the presence of charge transfer of 0.48 electron from Yb to S in YbS. . The reported[14,15] atomic form factor curves of YbSe and YbTe are also presented in figure 3 and figure 4 for understanding the mechanism involved in Ytterbium monochalcogenides. The decrease of charge transfer with increase of lattice constant and energy gap[20,21] has been observed in Figure 5 for YbS, YbSe and YbTe which highlights the correlation between valency and lattice size[17-18].

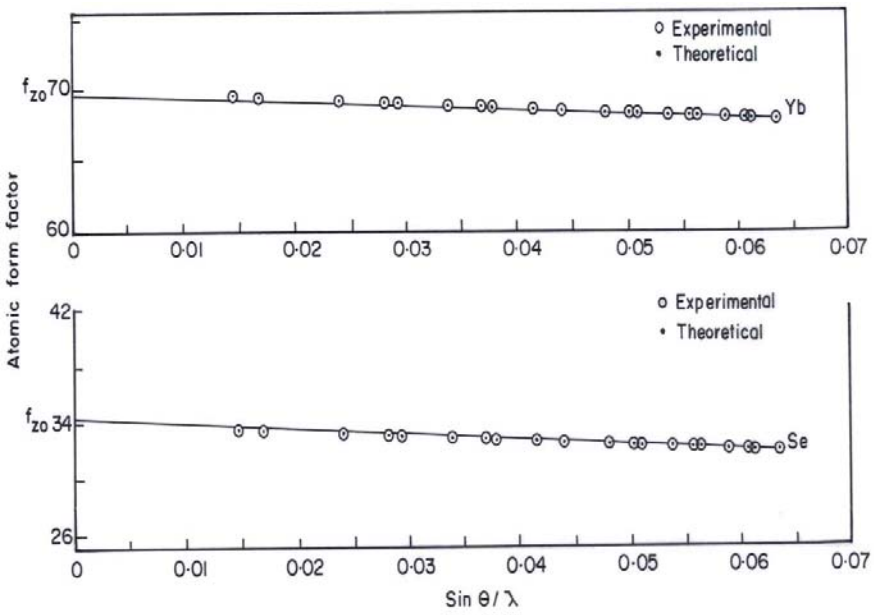

Fig. 3. The plot of experimental and theoretical atomic form factor versus Sinθ/λ for YbSe

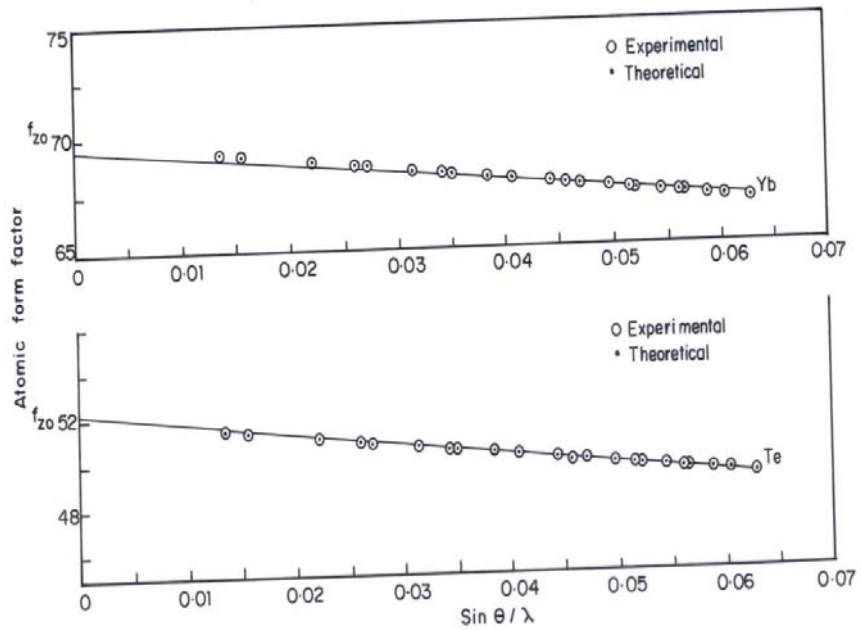

Fig. 4. The plot of Experimental and theoretical atomic form factor versus Sinθ/λ for YbTe.

Table 4 The lattice constant, energy gap and amount of charge transfer of Ytterbium monochalcogenides.

Compound	Lattice[21,22] constant (Å)	Energy Gap[21,22] (ev)	Charge transfer (electron)
YbS	5.693	1.1	0.48
YbSe	5.879	1.5	0.36
YbTe	6.353	1.8	0.20

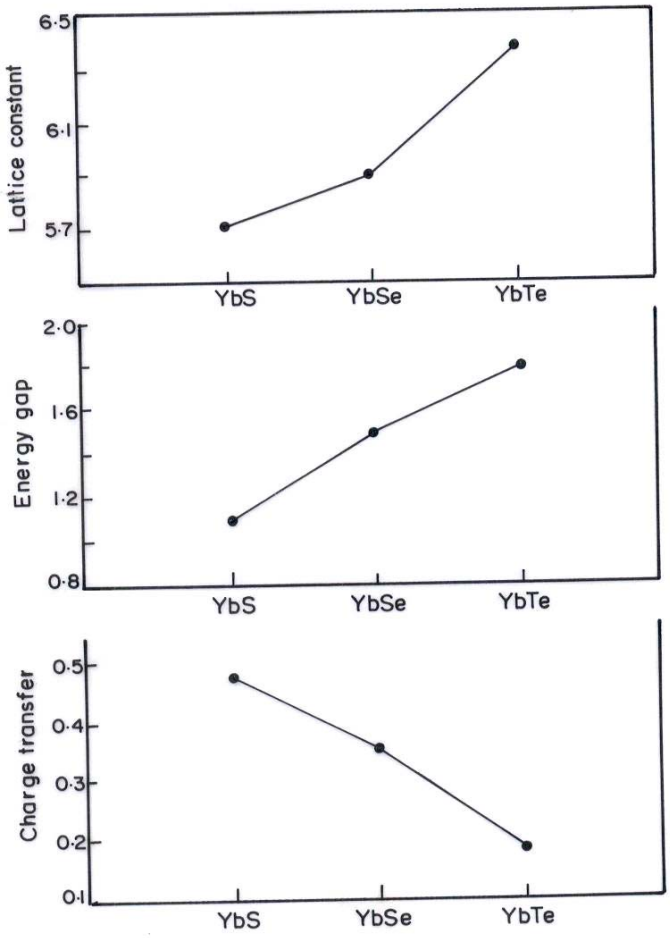

Figure 5 The plot of lattice constant, energy gap and charge transfer as a function of Yb monochalcogenides.

References

[1] J.Vitins, P.Wachter Physica **B86,** 213(1977).
[2] Katsurou Hanzawa Journal of Physical society of Japan **71** 1481 (2002).
[3] C.M.Varma Reviews of Modern physics **48** 219 (1976).
[4] V.N. Antonov, B.N.Harmon, A.N Yaresko, Phys. Rev. **B66** 165208-1 (2002).
[5] P.Wachter Solid state Communication **7** 693 (1969).
[6] A.Svane, P.Strange, W.M. Temmerman, Z.Szotek, H.Winter, L.Petit, Phys. Stat. Sol. **B223** 105 (2001).
[7] Selected powder diffraction data for metal and alloys , Published by JCPDS 314 (1974).
[8] W.Cochran Nature **191** 60 (1961).
[9] R.Saravanan, S.K.Mohanlal, K.S.Chandrasekaran, Acta Cryst. **A48** 4 (1992).
[10] R.Saravanan, S.K.Mohanlal, K.S.Chandrasekaran J. Phys. Chem. Solids **52** 879 (1991).
[11] B.D.Cullity, Elements of X-ray powder diffraction, Addison - Wesley publishing company Inc., (2nd Ed.) California., 140 (1978).
[12] R.Saravanan, S.K.Mohanlal, K.S.Chandrasekaran Z.Kristallogr. **200** 7 (1992).
[13] R.Saravanan, S.Israel, N.Srinivasan, S.K.Mohanlal Phys. Stat. Sol. **B194** 435 (1996).
[14] S.Ariponnammal, S.Radhika, P. Sivakumar International Journal of Modern Physics Letters B20 691 (2006).
[15] S.Ariponnammal, S.K.Rathiha Asian Journal of Spectroscopy 11 61 (2007).
[16] P.Strange, A.Svane, W.M.Temmerman, Z.Szotek, H.Winter Nature **399** 756 (1999).

[17] P.Wachter, Hand book of Physics and Chemistry of Rare earths, edited by K.A.Gschneidner, L.Eyring, S.Hufner (North Holland, Amsterdam) **19** 177 (1994).
[18] M.Campagna, E.Bucher, G.wertheim, L.D.Longinotti, Phys. Rev. Letters, **33** 165 (1974).
[19] D.B.Mcwhan, E.D.Isaacs, Polocarra, S.M.Shapira, B.T.Thole, S.Hoshino, Phys. Rev. **B47** 8630 (1993).
[20] A.Jayaraman, A.K.Singh, A.Chatterjee, S.Usha Devi, Phys. Rev. B9 2513 (1974).
[21] R.Lide David, CRC Hand Book of Chemistry and Physics,76th edition, CRC Press, Tokyo(1995).