

Study on Intermediate Valence Fluctuation in Samarium Telluride (SmTe)

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Intermediate valence fluctuation of samarium telluride (SmTe) is analyzed by charge transfer calculation using experimental and theoretical X-ray powder diffraction (XRPD) data. The direction and amount of charge transfer are determined by plotting and comparing the structure factor components. The charge transfer thus obtained for SmTe is 0.11 electrons from Sm to Te.

Key words: SmTe; Valence Fluctuation; Charge Transfer; XRD.

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1. Introduction

In the past few years a great deal of research has been done on the properties of rare earth metals and their compounds. A subclass of these materials is referred to as intermediate valence fluctuating or inter-configuration fluctuating compounds and sometimes as mixed valence or mixed configuration compounds [1]. The mixed valence phenomena are expected to arise in systems where two electron configurations corresponding to 4f occupation numbers n and $n - 1$ have nearly degenerate energies. So the ground state of a mixed valence compound is a quantum mechanical mixture of both the $4f^n$ and $4f^{n-1}d$ configuration on each rare earth ion [2]. Therefore, rare earth compounds received considerable interest due to the intricate electronic properties relating to highly correlated f-electrons. Although numerous experimental works have been reported on the destabilization behaviour of f shell of these compounds, the theoretical description of these valence fluctuations remains a challenging one till now [3]. This paper deals with studying the intermediate valence fluctuation by determining the charge transfer in SmTe based on structure factor calculation. All III-V compounds with zinc blende structure involve a charge transfer between the nearest neighbours. Similarly, II-VI semiconductors like zinc selenide (ZnSe) involve charge transfer [4]. Though different techniques are available to determine the charge transfer, according to Cochran [5] only X-ray powder diffraction (XRPD) and piezoelectric studies could give precisely the sign and magnitude of charge trans-

fer. Therefore, the intermediate valence fluctuation in SmTe is studied both theoretically and experimentally by charge transfer calculation using X-ray diffraction technique. The results are presented in this paper.

2. Theory

The rare earth metals have high magnetic moments and a diverse range of magnetic structures [6]. Their magnetic properties are determined by the occupancy of the strongly localized 4f electronic shells while the outer s- and d-electrons determine the bonding and other electronic properties [7]. Most of the rare earth atoms are divalent but generally become trivalent in the metallic state. In some materials, the energy difference between these valence states is small and, by changing some external parameters such as pressure, a transition from one to another occurs. The mechanism underlying this valence transition and the reason for the differing valence states are not well understood. It has been reported that electronic structure calculations determine both the valency and the lattice size as a function of atomic number and hence understand the valence transition [8].

Saravanan et al. [9–12] have conducted X-ray diffraction studies on III-V semiconductors such as GaAs, InSb, GaP and InP over the entire reciprocal space. The model proposed by Saravanan et al. has been used for confirming the presence of charge transfer in these semiconductor compounds [9–12]. In this paper, the JCPDS XRPD data [13] has been used for determining the experimental and theoretical

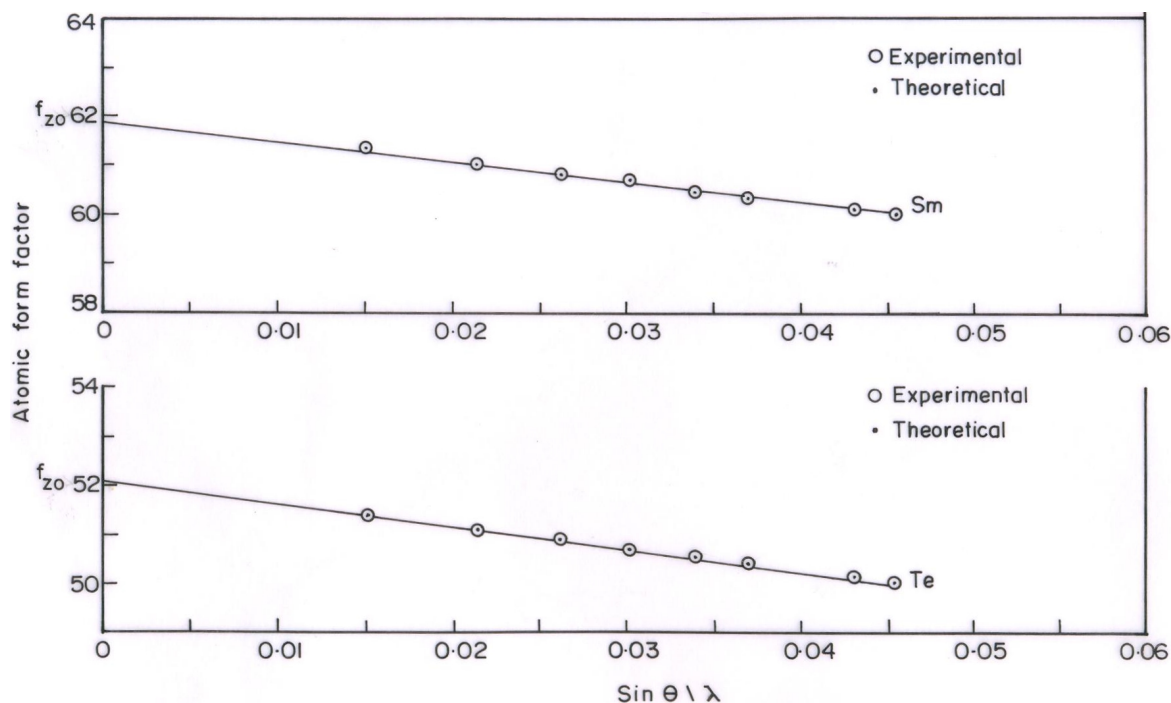


Fig. 1. Plot of experimental and theoretical atomic form factors versus $\sin \theta/\lambda$ for SmTe.

atomic form factors of SmTe for different $\sin \theta/\lambda$ values. The principal involved in the present method is to plot the elemental components of structure factors versus $\sin \theta/\lambda$. Then, the form factor at $\sin \theta/\lambda = 0$ will be equal to the atomic number (Z) of the element. Any deviation from the value of Z can be attributed to charge transfer [4]. 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

$$F_1^0 = 4(f_{\text{Sm}} + f_{\text{Te}}) \text{ for } h + k + l = 4n,$$

$$F_2^0 = 4(f_{\text{Sm}} - f_{\text{Te}}) \text{ for } h + k + l = 4n + 2.$$

By suitable mathematical manipulations, the individual components of the structure factors of Sm and Te are

$$F_{\text{Sm}} = (F_1^0 + F_2^0)/8, \quad F_{\text{Te}} = (F_1^0 - F_2^0)/8,$$

respectively. But, the F_1^0 and F_2^0 values are at different $\sin \theta/\lambda$ values. So, one cannot add or subtract these quantities to get the component structure factor [14]. Hence, the F_1^0 and F_2^0 values are plotted against $\sin \theta/\lambda$ and are interpolated for the same $\sin \theta/\lambda$ values. The same procedure is adopted for

Table 1. Atomic form factors of SmTe.

Sl. No.	Experimental			Theoretical		
	$\sin \theta/\lambda$	f_{Sm}	f_{Te}	$\sin \theta/\lambda$	f_{Sm}	f_{Te}
1	0.01515	61.31419	51.37003	0.01517	61.29388	51.37003
2	0.02146	60.94865	51.09661	0.02145	60.95880	51.12489
3	0.02632	60.73542	50.90804	0.02627	60.73542	50.87975
4	0.03030	60.60342	50.70061	0.03033	60.60342	50.71004
5	0.03401	60.33943	50.57804	0.03391	60.40035	50.58747
6	0.03704	60.20743	50.45547	0.03715	60.22773	50.46490
7	0.04310	59.93328	50.16319	0.04289	60.01451	50.15376
8	0.04546	59.86220	50.03119	0.04550	59.88251	50.04062

the calculated structure factor. The experimental and theoretical values of f_{Sm} and f_{Te} interpolated for the same $\sin \theta/\lambda$ after applying scaling correction are given in Table 1. The individual components are plotted against $\sin \theta/\lambda$ in the range of 0.015 to 0.045 \AA^{-1} and are given in Figure 1. When charge is transferring from Sm to Te in SmTe, f_{Sm}^0 should decrease and f_{Te}^0 should increase. Using the above formulations, the direction and magnitude of charge transfer in SmTe have been estimated.

3. X-Ray Powder Diffraction (XRPD)

The experimental JCPDS XRPD data has shown that SmTe has crystallized in a NaCl-type structure

Table 2. Experimental and theoretical XRPD data of plane indices (hkl), interplanar spacing (d), relative intensity (I/I_0) and structure factors (F_{hkl}) of SmTe.

Sl. No.	Experimental [13]			Theoretical			
	hkl	d	I/I_0	hkl	d	I/I_0	F_{hkl}
1	–	–	–	111	3.8070	0.7	21.9
2	200	3.30	75	200	3.2970	100.0	354.0
3	220	2.33	100	220	2.3313	73.6	321.6
4	–	–	–	311	1.9882	0.4	21.5
5	222	1.90	50	222	1.9035	25.6	298.1
6	400	1.65	25	400	1.6485	12.0	279.5
7	–	–	–	331	1.5128	0.2	21.3
8	420	1.47	100	420	1.4745	34.2	264.3
9	422	1.35	100	422	1.3460	27.5	251.3
10	–	–	–	511	1.2690	0.2	21.5
11	–	–	–	333	1.2690	0.1	21.5
12	440	1.16	50	440	1.1657	12.4	230.4
13	–	–	–	531	1.1146	0.5	21.8
14	442	1.10	125	442	1.0990	27.3	221.7
15	600	1.10	125	600	1.0990	6.8	221.7

Table 3. Elemental structure factor components at $\sin \theta/\lambda = 0$.

Element	Experimental f^0	Theoretical f^0
Sm	61.89	61.89
Te	52.11	52.13

with space group $Fm\bar{3}m$ [13]. The theoretical XRPD data simulated by the Lazy-Pulverix programme has been compared with the experimental XRPD data in Table 2 which gives the plane indices (hkl), interplanar spacing (d) and relative intensity (I/I_0) of SmTe. The theoretical deduced structure factor (F_{hkl}) of SmTe is also presented in Table 2. We are not able to compare this calculated structure with the observed data because observed single crystal data are not available. However, it has been observed that both the theoretical and experimental values of hkl , d and I/I_0 are in good agreement with each other. The experimental and theoretical atomic form factors of SmTe deduced from XRPD data for $\sin \theta/\lambda$ (after applying scaling correction) are presented in Table 1 and plotted in Figure 1.

4. Results and Discussion

SmTe has crystallized in a face centered cubic structure with the lattice parameter 6.594 Å and the space group $Fm\bar{3}m$. It has four Sm atoms and four Te atoms per unit cell. The experimental atomic form factors have been calculated from the XRPD data. The theoretical simulated XRPD data obtained by the Lazy-Pulverix programme is compared with experimental JCPDS XRPD data in Table 2. They are found to be in good agreement Table 2 also gives the structure factors F_{hkl} of SmTe. The experimental and theoretical atomic form factors for different $\sin \theta/\lambda$ after applying scaling correction are reported in Table 1 and plotted in Figure 1. The values of individual form factors f^0 at $\sin \theta/\lambda$ are given in Table 3. When charge is transferring from Sm to Te in SmTe, f_{Sm}^0 should decrease and f_{Te}^0 should increase. The atomic number of Sm is 62 and of Te it is 52. Therefore, the atomic form factor f_{zo} of the neutral atoms Sm and Te are indicated by f_{zo} in Figure 1. It makes clear that f_{Sm}^0 is smaller than the atomic number of Sm by an amount of 0.11. Consequently, f_{Te}^0 is larger than the atomic number of Te by more or less the same amount. This indicates the transfer of 0.11 electron from Sm to Te which confirms the presence of charge transfer. It has been reported [15] that SmTe is a semiconducting material in which the samarium ions have valence 2+ or at most a very small deviation. This gives favourable support for the presence of charge transfer of 0.11 electron in SmTe. Moreover, the presence of intermediate valence fluctuation in SmTe inferred from the present study is agreed with experimental reports [16–20].

5. Conclusions

The simulated theoretical XRPD pattern agrees well with the experimental XRPD data. The structure factor of SmTe is calculated and the atomic form factors are calculated. Charge transfer of 0.11 electron from Sm to Te is observed which confirms the intermediate valence fluctuation experimentally determined [16–20].

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