

PACS numbers: 72.10. – d, 72.15.Qm, 72.20. – i

## STUDY OF CHARGE TRANSFER IN SEMICONDUCTING RARE EARTH CHALCOGENIDE THULIUM TELLURIDE (TmTe)

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*The study of charge transfer in rare earth chalcogenide semiconductor TmTe has been carried out by using experimental and theoretical X-ray powder diffraction (XRPD) data. The direction and amount of charge transfer are inferred by plotting and comparing the structure factor of the components. Thus, a charge transfer of 0.15 electrons is obtained in TmTe from Tm to Te.*

**Keywords:** TmTe, CHALCOGENIDE, CHARGE TRANSFER, VALENCE FLUCTUATION, XRPD.

*(Received 04 February 2011, in final form 18 June 2011)*

### 1. INTRODUCTION

The study of rare earth monochalcogenides have received much attention because of their important technological applications and interesting properties such as semiconductor to metallic transition, valence transition and structural phase transition under pressure, temperature and intrinsic stress. The transitions observed in rare earth chalcogenides find applications in pressure sensor or in a memory device triggered between a low resistance and high resistance state by external pressure [1]. The samarium monosulfide generates the electric voltage upon moderate heating to about 150 °C which leads to its use in thermo electric power converters [2]. New phenomenon of self heating upto 866 K and the EMF generation is observed in samarium monosulfides after termination of external heating. This effect finds promising applications of conversion of thermal energy into electricity [3-5]. The rare earth chalcogenide glasses finds applications in telecommunication devices, integrated optical systems, gas sensing and remote sensing devices [6-8]. These technologically fascinating applications kindle the interest on the study of rare earth monochalcogenides. They crystallize in the NaCl type structure and are semiconducting if the rare earth ion is in the divalent state and metallic if in trivalent state [9, 10]. The rare earth elements Sm, Eu, Yb and Tm have been proved to be existing in divalent semiconducting state. The valence fluctuation has been observed [11] 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 interconfiguration 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 [12]. Numerous experimental works have been

reported on the destabilization behavior of  $f$ -shell of these compounds. But, the theoretical description remains a challenging one [13]. Band theory and mean field theory are successful for explaining many kinds of materials. But they are not able to explain the properties of  $d$  or  $f$  electron systems in which the interactions among the electrons are strong. A wide variety of magnetic and transport properties such as metal-insulator transition, itinerant magnetism, valence fluctuation, Kondo effect, heavy fermions and superconductivity, and so on arises due to the correlations among  $d$  or  $f$  electrons and they are also called as strongly correlated electron systems [14]. The Tm monochalcogenides system is one such mysterious strongly correlated electron systems. Tm is found to have trivalent in TmS and fluctuating valence between 2 and 3 in TmSe and TmTe [15] at atmospheric condition. The physical mechanisms of these valence fluctuation phenomena have not been still well understood. Therefore, this paper deals with the presence of charge transfer in TmTe based on structure factor calculation and confirms the intermediate valence fluctuation and the results are presented in this paper.

## 2. X-RAY POWDER DIFFRACTION

The experimental X-ray powder diffraction data has shown that the TmTe has been crystallized in NaCl type structure with space group of Fm3m [15]. The theoretical XRPD pattern simulated by using Lazy Pulverx programme is compared with experimental XRPD [15] in Figure 1. And it has been observed that both are found to be in good agreement with each other. The Table 1 presents the experimental and theoretical XRPD data of indices of planes ( $hkl$ ), interplanar spacing ( $d$ ), and relative intensity ( $I/I_0$ ) of TmTe which agrees well with each other.

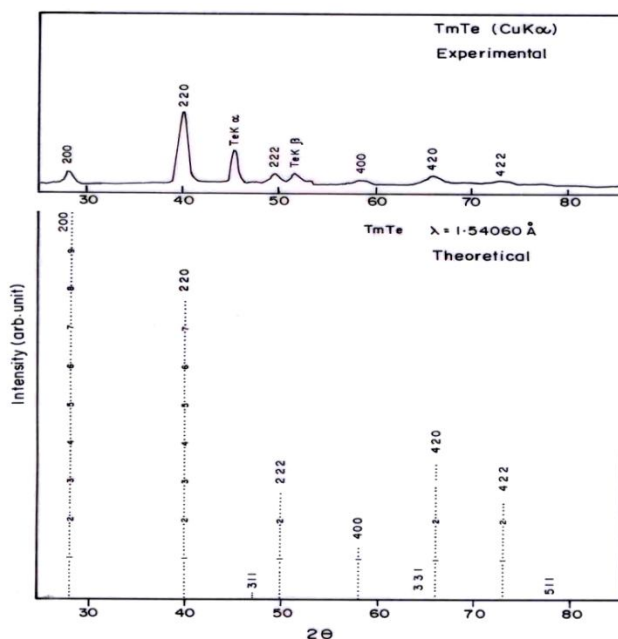


Fig. 1 – The experimental and simulated XRPD pattern of TmTe

### 3. THEORETICAL METHODOLOGY

The Magnetic properties of rare earth chalcogenides are determined by the occupancy of the strongly localized  $4f$  electron shells [16]. The rare earth metals have high magnetic moments and a diverse range of magnetic structure [17]. Most of the rare earth atoms are divalent in semiconducting state and trivalent in metallic state. The electronic structure factor calculations determine both the valence and lattice size [18] as a function of atomic number. All III-V compounds with zinc blende structure like GaAs and GaP involve

**Table 1** – The experimental and theoretical XRD data for  $TmTe$

| Sl. No | Experimental ASTM Values |        |         | Theoretical |        |         |           |
|--------|--------------------------|--------|---------|-------------|--------|---------|-----------|
|        | $hkl$                    | $d$    | $I/I_0$ | $hkl$       | $d$    | $I/I_0$ | $F_{hkl}$ |
| 1      | 200                      | 3.1908 | 70      | 200         | 3.1730 | 100.0   | 388.5     |
| 2      | 220                      | 2.2522 | 100     | 220         | 2.2436 | 76.8    | 354.8     |
| 3      | -                        | -      | -       | 311         | 1.9134 | 0.9     | 32.8      |
| 4      | 222                      | 1.8378 | 30      | 222         | 1.8319 | 27.4    | 330.0     |
| 5      | 400                      | 1.5829 | 10      | 400         | 1.5865 | 12.7    | 310.1     |
| 6      | -                        | -      | -       | 331         | 1.4559 | 0.3     | 27.4      |
| 7      | 420                      | 1.4193 | 40      | 420         | 1.4190 | 34.7    | 293.4     |
| 8      | 422                      | 1.2950 | 20      | 422         | 1.2954 | 25.4    | 279.2     |
| 9      | -                        | -      | -       | 511         | 1.2213 | 0.2     | 23.2      |
| 10     | -                        | -      | -       | 333         | 1.2213 | 0.1     | 23.2      |

a charge transfer between the nearest neighbors. Similarly, II-VI semiconductors like Zinc Selenide (ZnSe) involve charge transfer [19]. Though different techniques are available to determine the charge transfer, according to Cochran [20], only X-ray diffraction could give precisely the sign and magnitude of charge transfer. Therefore the presence of charge transfer in  $TmTe$  has been studied both theoretically and experimentally by using X-ray powder diffraction technique. For the present work, the X-ray diffraction data has been used [21]. Saravanan et al. [22-25] proposed a model for confirming the presence of charge transfer in the semiconductor compounds. 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 component of structure factors are plotted as a function of  $\sin\theta/\lambda$ . Then the form factor value 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 the charge transfer [26]. 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,

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

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

By suitable mathematical manipulations, the individual components of structure factor of Tm and Te are,

$$f_{\text{Tm}} = (F_1^0 + F_2^0) / 8$$

$$f_{\text{Te}} = (F_1^0 + F_2^0) / 8$$

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 factors [26]. Hence, the  $F_1^0$  and  $F_2^0$  values plotted against  $\sin\theta/\lambda$  and are interpolated for the same  $\sin\theta/\lambda$  values. The same procedure is adopted for the calculated structure factor also. The experimental and theoretical values of  $f_{\text{Tm}}$  and  $f_{\text{Te}}$  interpolated for the same  $\sin\theta/\lambda$  values after applying scaling correction are given in Table 2. These individual components are plotted against  $\sin\theta/\lambda$  in the range of 0.015 to 0.040  $\text{\AA}^{-1}$  in Figure 2. When charge transfer from Tm to Te,  $f_{\text{Tm}}^0$  should decrease and  $f_{\text{Te}}^0$  should increase. It is seen from Table 3 that  $f_{\text{Tm}}^0$  of Tm is less than atomic number of Tm by an amount equal to 0.15 indicating the charge transfer of 0.15 electron has taken place. Consequently,  $f_{\text{Te}}^0$  is larger than the atomic number of Te by the same. Thus, using the above formulations, the direction and amount of charge transfer in TmTe has been estimated.

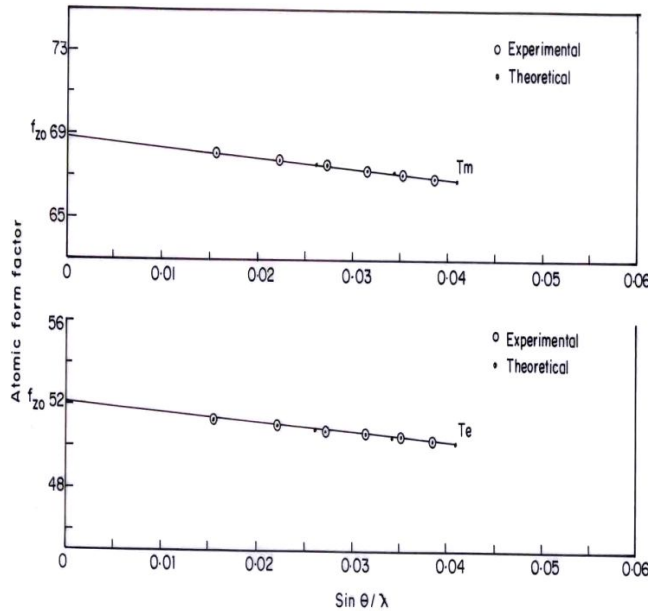
#### 4. RESULTS AND DISCUSSIONS

The Tm monochalcogenides display various physical properties depending upon the difference in chalcogen Te, Se or S. TmTe is a magnetic semiconductor. Its valence band is formed by a filled p band consisting of the 5p orbits of Te, while a vacant d band consisting of the 5d orbits of Tm becomes a conduction band, and the  $4f^{13}$  level exists in an energy gap between them [15]. The TmTe is crystallized in face centered cubic structure with lattice parameter of 6.346  $\text{\AA}$  and space group of Fm3m [27, 28]. It has four Tm atoms and four tellurium atoms per unit cell. The Figure 1 shows the well agreement of theoretical X-ray powder diffraction pattern simulated by Lazy-Pulverx programme with the experimental XRPD pattern. The Table 1 presents theoretical and experimental XRPD data which are found to be in good agreement with each other. It also gives the structure factors of  $f_{hkl}$  of TmTe. The Table 2 gives the experimental and theoretical atomic form factors for different  $\sin\theta/\lambda$  after applying scaling correction and is plotted in Figure 2. The values of individual form factors  $f^0$  at  $\sin\theta/\lambda$  are given in Table 3. When charge is transferring from Tm to Te in TmTe,  $f_{\text{Tm}}^0$  should decrease and  $f_{\text{Te}}^0$  should increase. It is well known that the atomic form factor of neutral atom of Tm and Te are 69 and 52 indicated by  $f_{ZO}$  in Figure 2 which are the atomic number of Tm and Te respectively. It is well clear that  $f_{\text{Tm}}^0$  is smaller than the atomic number of Tm by 0.15. Consequently,  $f_{\text{Te}}^0$  is larger than the atomic number of Te by more or less the same amount. This indicates the transfer of 0.15 electrons from Tm to Te which infers the charge transfer. This gives the strong evidence for the presence of intermediate valence fluctuation in TmTe at atmospheric condition. It has been reported from X-ray photo emission spectroscopy that the spontaneous interconfiguration mixing or intermediate valence fluctuation [27] is present in TmTe at room temperature and atmospheric pressure. Iandelli and Palenzona [28, 29].

**Table 2** – The atomic form factors of TmTe

| Sl.No. | Experimental         |          |          | Theoretical          |          |          |
|--------|----------------------|----------|----------|----------------------|----------|----------|
|        | $\sin\theta/\lambda$ | $f_{Tm}$ | $f_{Te}$ | $\sin\theta/\lambda$ | $f_{Tm}$ | $f_{Te}$ |
| 1      | 0.01567              | 68.16457 | 51.27719 | 0.01576              | 68.14886 | 51.26148 |
| 2      | 0.02220              | 67.88183 | 51.02586 | 0.02229              | 67.83470 | 51.01015 |
| 3      | -                    | -        | -        | 0.02613              | 67.61479 | 50.82165 |
| 4      | 0.02721              | 67.61479 | 50.72740 | 0.02730              | 67.64621 | 50.82165 |
| 5      | 0.03159              | 67.36346 | 50.60174 | 0.03152              | 67.33204 | 50.60174 |
| 6      | -                    | -        | -        | 0.03434              | 67.28492 | 50.42895 |
| 7      | 0.03523              | 67.15926 | 50.47608 | 0.03524              | 67.15926 | 50.50749 |
| 8      | 0.03861              | 66.98647 | 50.28758 | 0.03860              | 66.98647 | 50.25616 |
| 9      | -                    | -        | -        | 0.04094              | 66.86080 | 50.16191 |
| 10     | -                    | -        | -        | 0.04094              | 66.86080 | 50.16191 |

first found evidence for the polyvalent behaviour of Tm in TmTe from magnetic measurements. Resonant photo emission study reported [30] the evidence for the existence of trivalent 4f electrons in TmTe. Optical and photoemission studies [31] supported the fluctuating valence between 2 and 3 present in TmTe at atmospheric conditions. Thus, the present study of charge transfer in TmTe agrees well with the experimental results.



**Fig. 2** – The experimental and theoretical atomic form factor for TmTe

**Table 3** – The values of elemental structure factor components at  $\sin\theta/\lambda = 0$  for TmTe

| Elements | Experimental ( $f^0$ ) | Theoretical ( $f^0$ ) | Charge Transfer |
|----------|------------------------|-----------------------|-----------------|
| Tm       | 68.75                  | 68.75                 |                 |
| Te       | 52.15                  | 52.15                 | 0.15            |

## 5. CONCLUSIONS

The TmTe is crystallized in face centered cubic structure. The theoretical XRPD pattern is simulated and it is found to be in good agreement with experimental XRPD pattern. The structure factor of TmTe and the atomic form factors are calculated from XRPD data. The charge transfer of 0.15 electrons is deduced from Tm to Te in TmTe. It confirms the intermediate valence fluctuation in TmTe which agrees well with the experimentally reported result [27-30].

## REFERENCES

1. [http://en.wikipedia.org/wiki/Samarium\\_monochalcogenides](http://en.wikipedia.org/wiki/Samarium_monochalcogenides).
2. V.V. Kaminskii, S.M. Solov'ev, A.V. Golubkov, *Tech. Phys. Lett.* **28**, 229 (2002).
3. M.M. Kazanin, V.V. Kaminskii, S.M. Solov'ev, *Tech. Phys.* **45**, 659 (2000).
4. V.V. Kaminskii, S.M. Solov'ev, *Phys. Solid State* **43**, 439 (2001).
5. V.V. Kaminskii, L.N. Vasil'ev, M.V. Romanova, S.M. Solov'ev, *Phys. Solid State* **43**, 1030 (2001).
6. <http://eprints.esc.soton.ac.uk/4710/1/1740.pdf>.
7. S.A. Kozyukhin, A.R. Fairushin, E.N. Voronkov, *J. Optoelectron. Adv. M.* **7**, 1457 (2005).
8. S.A. Kozyukhin, E.N. Voronkov, N.P. Kuz'mina, *J. Non-Cryst. Solids* **352**, 1547 (2006).
9. S. Aripnammal, S. Natarajan, *Mod. Phys. Lett. B* **11**, 1189 (1997).
10. S. Aripnammal, R. Jayavel, S. Natarajan, *Int. J. Mod. Phys. B* **15**, 3465 (2001).
11. K. Hanzawa, *J. Phys. Soc. Jpn.* **71**, 1481 (2002).
12. C.M. Varma, *Rev. Mod. Phys.* **48**, 219 (1976).
13. T. Matsumura, T. Kosaka, J. Tang, T. Matsumoto, H. Takahashi, N. Mori, T. Suzuki, *Phys. Rev. Lett.* **78**, 1138 (1997).
14. D. Debray, A. Werner, D.L. Decker, M. Loewenhaupt, E. Holland-Moritz, *Phys. Rev. B* **25**, 3841 (1982).
15. T. Matsumoto, J. Tang, N. Mori, *The Rigagu Journal* **15**, 25 (1998).
16. W. Cochran, *Nature* **191**, 60 (1961).
17. P. Strange, A. Svane, W.M. Temmerman, Z. Szotek, H. Winter, *Nature* **399**, 756 (1999).
18. B. Johansson, *Phys. Rev. B* **20**, 1315 (1979).
19. H. Skriver, *Systematics and Properties of Lanthanides*, (Reidel – Dordrecht: 1983).
20. B.D. Cullity, *Elements of X-ray Powder Diffraction*, 2<sup>nd</sup> ed., (Addison – Wesley Publishing Company, Inc.: USA: 1978).
21. N. Srinivasan, R. Saravanan, S. Israel, S.K. Mohanlal, *Cryst. Res. Technol.* **31**, K6 (1996).
22. R. Saravanan, S.K. Mohanlal, K.S. Chandrasekaran, *J. Phys. Chem. Solids* **52**, 879 (1991).
23. R. Saravanan, S.K. Mohanlal, K.S. Chandrasekaran, *Acta Cryst. A* **48**, 4 (1992).
24. R. Saravanan, S.K. Mohanlal, K.S. Chandrasekaran, *Z. Kristallogr.* **200**, 7 (1992).
25. R. Saravanan, S. Israel, N. Srinivasan and S.K. Mohanlal, *phys. status sol. B* **194**, 435 (1996).
26. A. Svane, P. Strange, W.M. Temmerman, Z. Szotek, H. Winter, L. Petit, *phys. status solidi B* **223**, 105 (2001).
27. M. Compagna, E. Bucher, G.K. Wertheim, D.N.E. Buchanan, L.D. Longinotti, *Phys. Rev. Lett.* **32**, 885 (1974).
28. E. Bucher, V. Narayanamurti, A. Jayaraman, *J. Appl. Phys.* **42**, 1741 (1971).
29. A. Iandelli, A. Palenzona, *Colloq. Intern. Centre Natl. Rech. Sci. (Paris)* **157**, 397 (1967).
30. Y. Ufuktepe, Sh. Kimura, T. Kinoshita, Kr.G. Nath, H. Kumigashira, T. Takahashi, T. Matsumara, T. Suzuki, H. Ogasawara, Ak. Kotani, *J. Phys. Soc. Jpn.* **67**, 2018 (1998).
31. R. Suryanarayanan, G. Guntherodt, J.L. Freeouf, F. Holtzberg, *Phys. Rev. B* **12**, 4215 (1975).