

Electronic structure and optical properties of thorium monopnictides

S KUMAR* and S AULUCK†

Physics Department, Institute of Engineering and Technology, M.J.P. Rohilkhand University, Bareilly 243 006, India

†Department of Physics, Indian Institute of Technology, Roorkee 247 667, India

Abstract. We have calculated the electronic density of states (DOS) and dielectric function for the ThX (X = P, As and Sb) using the linear muffin tin orbital method within atomic sphere approximation (LMTO–ASA) including the combined correction terms. The calculated electronic DOS of ThSb has been compared with the available experimental data and we find a good agreement. The calculated optical conductivity for ThP and ThAs is increasing monotonically, while for ThSb a sharp peak has been found at 6.5 eV. Unfortunately there are no experimental data to compare with calculated optical properties, we hope our calculations will motivate some experimentalists.

Keywords. *Ab initio* calculation; electronic structure; optical properties.

1. Introduction

The electronic structure of the actinide compounds have been of good interest to the researcher in the condensed matter theory because of the low α radioactivity of thorium as compared to other actinide elements and important technological applications. So far their basic electronic properties have been studied in a few articles. Therefore, investigation of thorium monopnictides in light of development of predicting the electronic and other properties using the *ab initio* calculation becomes important. The X-ray diffraction investigation had been carried out by Olsen *et al* (1989) of the B1 (NaCl structure) and B2 (CsCl structure) phases. Very recently, a band structure calculation has been carried out by using tight binding linear muffin tin orbital method within atomic sphere approximation (TBLMTO–ASA) for the different phases of B1 and B2 of all the three monopnictides by Trinadh (1997). Reihl *et al* (1982b) have studied *f* and *d* electrons in actinide compounds and concluded that the measured spectra are dominated by localized 5*f* states in all compounds. There have been reports in the literature regarding the high resolution ($\Delta E < 150$ meV) photoemission with the synchrotron radiation of ThSb by Reihl *et al* (1982a). Davis *et al* (1994) had studied a band structure of ThAs at ambient pressure by using Kohn–Korringa–Rostokker (KKR) method. On the other hand, different investigators have conducted intense study of Th as a metal. Johansson *et al* (1995) studied anomalous behaviour of thorium crystal structure by using full-potential linear muffin–tin orbital (FPLMTO) method. Skriver (1984) studied electronic properties of thorium at pressure up to 400 kbar by using LMTO–ASA. No report

about the optical properties of the above family of compounds is available.

With this in mind we have performed calculation of the electronic density of states and dielectric function. Our calculations have been performed using LMTO–ASA, (Andersen 1975; Skriver 1984). The optical matrix elements are explicitly calculated as they are expected to play a significant role in the frequency dependence of the dielectric function. We also compare our calculated electronic density of state with available experimental data and theoretical investigations.

2. Method and details of calculation

We have used LMTO–ASA method (Andersen 1975) including combined correction term which is the linearized version of the highly accurate KKR band structure method. A LMTO is defined as Hankel function of kinetic energy, k^2 times a spherical harmonic in the interstitial region, and linear combination of radial Schrödinger solutions inside the muffin tin (MT) sphere. In conventional LMTO method, the interstitial region and the higher partial waves can be dispensed with if one uses the simplifying atomic sphere approximation (ASA), which form a single- k basis with $k^2 = 0$. In LMTO–ASA method, space is divided into overlapping atomic (Wigner–Seitz) sphere at various atomic sites, R , within which the potential and charge densities are spheridized. Matching at sphere boundary is continuous and once differentiable. The most attractive features of the LMTO formalism are the following: (i) metals, semiconductors and insulators involving any element of the periodic table are described on equal footing, (ii) LMTO basis set is minimal, with only 9 and 16 orbitals for *spd* and *spdf* elements, respectively and (iii) within ASA the secular

*Author for correspondence

equation can be separated into the structure dependent and the potential dependent parts. A comparative study of the LMTO methods have been discussed by Das (2001).

The calculation is performed for the measured lattice constant by Pearsons (1985) of $a = 5.8329 \text{ \AA}$, 5.9637 \AA and 3.8380 \AA for the ThP, ThAs and ThSb, respectively. The calculations are performed with equal sphere radii and a basis consisting of s , p , d and f LMTOs at each sites. The reliability of band structure methods based on the muffin tin approximation is best for closely packed structures. Since Th monopnictides are loosely packed crystals and hence they are not directly suitable for the conventional (LMTO-ASA) calculation. Therefore, two empty spheres have been introduced at appropriate chosen interstitial sites (Svane and Gunnarsson 1990; Kubler and Williams 1986). Scalar relativistic corrections are included but spin orbit coupling is neglected in the calculations. We have used the Barth-Hedin (1972) exchange correlation potential. Since f level in the Th is unoccupied therefore, the compound, ThX ($X = \text{P, As, Sb}$), is not magnetic. Although f orbital plays an important role as discussed by Gupta and Loucks (1971), the positions (0, 0, 0) for Th and (0.5, 0.5, 0.5) for X atom were used. In order to have close packing, two empty spheres (ES) were placed in the interstitial positions (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) along body diagonal of the unit cell. The one electron self-consistent potential are obtained by performing iterations on a mesh of $252 \vec{k}$ points in the irreducible Brillouin zone (IBZ). We have used a tetrahedron method proposed by Svane and Gunnarsson (1990) for the density of states (DOS) and optical properties.

3. Density of states

The density of states are depicted in figures 1, 2 and 3 for the ThP, ThAs and ThSb, respectively. In all the figures Fermi level is shifted to 0 eV. We show here total DOS (sum of all basis which is considered in both atoms) and partial DOS of only those sub-orbital of each atoms that has considerable contribution towards total density of states. Calculated DOS are similar to the one obtained by Trinadh (1997), although he has not depicted the partial density of states for any system. The main structure in the DOS are dominated by $-p$, $-d$ and $-p$ sub orbital of the Th and $-p$, $-d$ and $-p$ sub orbital of P, Sb and As of the ThP, ThAs and ThSb systems, respectively. There is small contribution coming from f -sub orbital but it is quite important because this part is dominant near the Fermi level shown for the ThP in 1 which is in agreement with the earlier calculation performed by Gupta and Loucks (1971). Our calculations for the total DOS of ThP yield main structure at -11.7 , -10.2 , -8.2 , and -5.3 eV below the Fermi level and 3.6 and 6.8 eV above the Fermi level. The above structure arises mainly from the

bonding $\text{Th}(6p)\text{-P}(3p, 3d, 3s)$ and $\text{Th}(6p, sd, 5f)\text{-P}(3p, 3s)$ below the Fermi level and $\text{Th}(6d, 5f)\text{-P}(3d, 3p)$ anti-bonding above the Fermi level. The calculated DOS is in agreement with the TBLMTO-ASA calculation by Trinadh (1997). Calculated total DOS for ThAs shows main structure are at -11.6 , -9.6 , -7.6 and -4.9 eV below the Fermi level and 2.9 and 4.4 eV above the Fermi level arises mainly from the bonding $\text{Th}(6p, 5d)\text{-As}(4s, 3d)$ and $\text{Th}(6p, 5d)\text{-As}(4p, 4s)$ below the Fermi level and $\text{Th}(6d, 5f)\text{-As}(4s, 3d)$ antibonding above the Fermi level. In case of ThSb total density of states have main structures at -5.6 , -4.9 , -3.9 and -0.1 eV below the Fermi level and 1.6 and 2.7 eV above the Fermi level, which arises mainly from the bonding $\text{Th}(6d, 7s)\text{-Sb}(4d, 6s, 5p)$ and $\text{Th}(6d, 7s, 6p)\text{-Sb}(5s, 5p, 4d)$ below the Fermi level and $\text{Th}(6d, 7s, 6p, 5f)\text{-Sb}(5s, 5p, 4d)$ antibonding above the Fermi level. The calculated DOS is compared with the

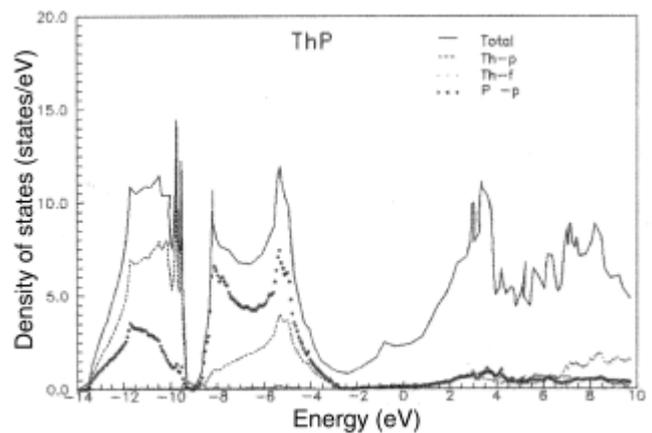


Figure 1. Calculated electronic density of states for ThP system. Full line, dashed line, dots and small circle for total, Th- p , Th- f and P- p parts, respectively.

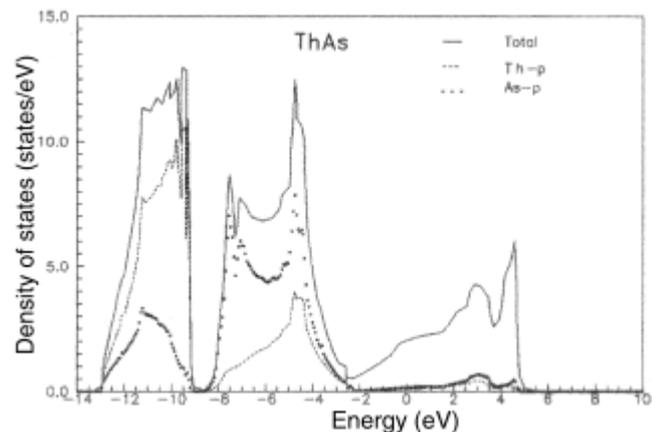


Figure 2. Calculated electronic density of states for ThAs system. Full line, dashed line and points for total, Th- p part and As- p part, respectively.

only available photoemission data by Reihl *et al* (1982a) which is in good agreement with our calculated total density of states. A broad peak has been seen at -3.8 eV in calculated and observed photoemission data. Shoulders at -0.1 eV are also observed in calculated and observed photoemission data.

4. Optical properties

The calculation of the optical properties of the solids is beset with numerous problems. The dielectric function is the central importance quantity which has to be calculated. For cubic system there is only one component to be calculated i.e. ϵ_{xx} . For hexagonal/tetragonal systems one has to calculate two components, ϵ_{\parallel} and ϵ_{\perp} , corresponding to electric field parallel and perpendicular to the c -axis. Calculations of the dielectric function involve the energy eigenvalues and the electron wave functions. These are the natural output of the *ab initio* band structure calculation which are usually performed under local density approximation (LDA) (Koenig *et al* 1983; Alouani *et al* 1986). Empirical scaling of optical conduction was proposed by Janak *et al* (1975) but we are not aware of any similar detailed work. We have thus performed calculation of the dielectric function using the standard expression (Alouani *et al* 1986)

$$\epsilon(\omega) = \frac{8}{3\pi\omega^2} \sum_n \sum_{n'} \int_{\text{BZ}} |P_{nn'}(\bar{k})|^2 \frac{dS_{\bar{k}}}{\nabla \mathbf{w}_{m'}(\bar{k})}.$$

The above expression is written in atomic units with $e^2 = 1/m = 2$ and $\hbar = 1$. Here ω is the photon energy (Ry) and $P_{nn'}(\bar{k})$ the dipolar matrix element between initial $|n(\bar{k})\rangle$ and final $|n'(\bar{k})\rangle$ states with their eigenvalues $E_n(\bar{k})$ and $E_{n'}(\bar{k})$, respectively

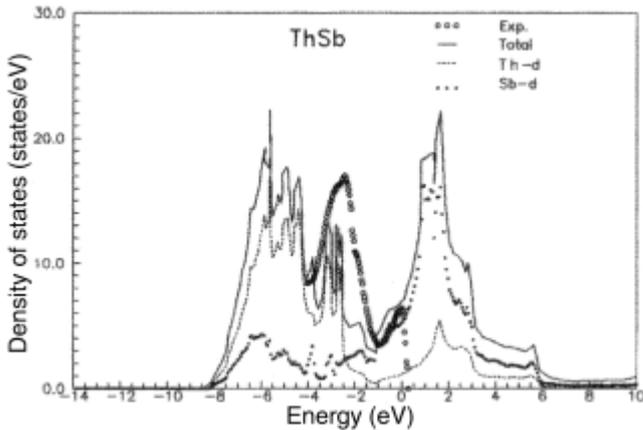


Figure 3. Calculated electronic density of states for ThSb system. Circle, full line, dashed line and points for photoemission data, total density of states, Th- p part and Sb- d part, respectively.

$$\mathbf{w}_{m'}(\bar{k}) = E_{n'}(\bar{k}) - E_n(\bar{k}) = \omega$$

and the constant surface energy

$$S_k = \{\bar{k}; \mathbf{w}_{m'}(\bar{k}) = \omega\}.$$

In the LMTO-ASA, $P_{nn'}(\bar{k})$, can be easily calculated (Koenig and Khan 1983; Alouani *et al* 1986). We have calculated the frequency dependent dielectric function, $\epsilon(\omega)$ and optical conductivity, $\mathcal{S}(\omega)$, using LMTO-ASA method based on the theory discussed in the preceding section. Optical matrix elements are explicitly calculated within LMTO-ASA and then $\mathcal{S}(\omega)$ is calculated. Calculation for all the three systems ThP, ThAs and ThSb are done at 252 K points in the Brillouin zone (BZ) summation. The effects of using K points in the BZ has already been discussed in the earlier work by Khan *et al* (1993). The calculated results i.e. optical conductivity, $\mathcal{S}(\omega)$ and total imaginary dielectric function, $\epsilon''(\omega)$ are depicted in figures 4 and 5 of panels a , b and c for ThP, ThAs and ThSb systems, respectively. The calculated optical conductivity, $\mathcal{S}(\omega)$, increases monotonically for the ThP and ThAs, a broad structure at 6.5 eV has been observed in the case of ThSb. The calculated total imaginary dielec-

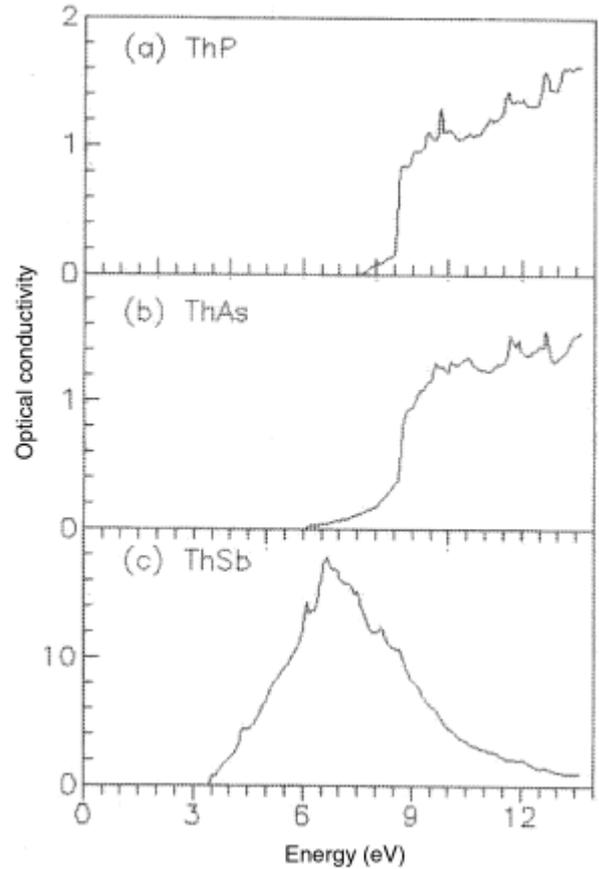


Figure 4. Calculated frequency dependent optical conductivity, $\mathcal{S}(\omega)$, for ThP, ThAs and ThSb are shown in panels a , b and c , respectively.

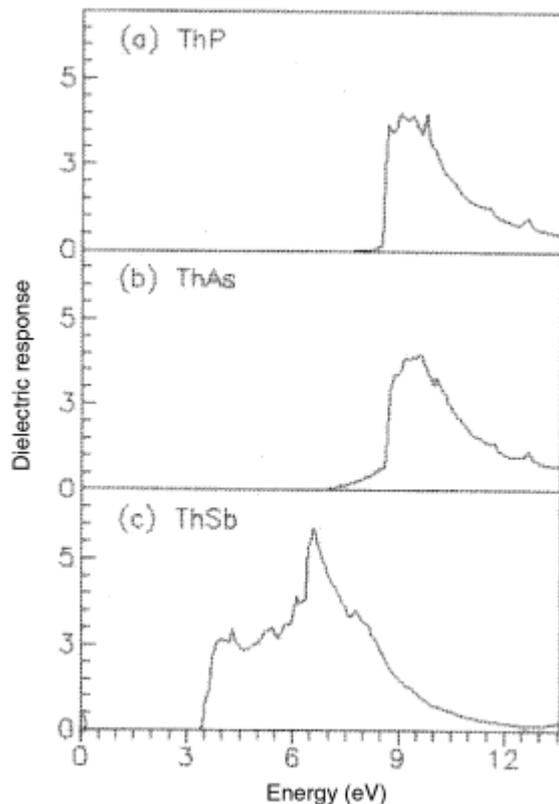


Figure 5. Calculated frequency dependent dielectric function, $\epsilon(\omega)$, for ThP, ThAs and ThSb, are shown in panels *a*, *b* and *c*, respectively.

tric function, $\epsilon(\omega)$, for ThSb that is depicted in figure 5 of panel *c* show a sharp structure at 6.8 eV. In order to identify the origin of structure in $\epsilon(\omega)$ we have decided to take simple approach and i.e. that structure in $\epsilon(\omega)$ usually arises from a set of parallel bands over a sufficient region in k space. Our band structure is very similar to the previously calculated band of Trinadh (1997). Thus looking at the band structure (Trinadh 1997) one could try to identify the origin of structure in $\epsilon(\omega)$. The peak has been identified as arising from parallel set of bands along $L\Gamma$ and around Γ .

5. Conclusions

In this article we have presented the results of the electronic density of states and optical properties of thorium monpnictides using LMTO-ASA (Andersen 1975). The calculations demonstrate the importance of including correction terms which lead to a good improvement in

the electronic DOS. The calculated DOS for ThSb is in overall good agreement with the available photoemission data except that our calculated peaks shifted to lower energies by 0.5–1.0 eV. The calculated dielectric function and optical conductivity for ThSb shows a broad peak at ≈ 6.5 eV. In the absence of experimental data, it has not been compared.

Acknowledgements

One of the authors (SK) wishes to thank the Indian National Science Academy and the All India Council for Technical Education, New Delhi, for financial support. He is also thankful to Prof. Z H Zaidi and Prof. P N Ram for their constant interest and encouragement. Part of this calculation was done at Computer Centre, IIT, Roorkee.

References

- Alouani M, Koch J M and Khan M A 1986 *J. Phys.* **F16** 437
- Andersen O K 1975 *Phys. Rev.* **B12** 3060
- Das G P 2001 in *Electronic structure of alloys, surfaces and clusters* (eds) A Mookerjee and D D Sarma (London: Taylor and Francis) and references therein
- Davis H L 1994 *Electronic structure and related properties* (eds) A J Freeman and J Darby (New York: Academic Press) Vol. II, pp 1–49
- Gupta R P and Loucks T L 1971 *Phys. Rev.* **B3** 1834
- Janak J F, Williams A R and Moruzzi V L 1975 *Phys. Rev.* **B11** 1522
- Johansson B, Ahuja R, Eriksson O and Wills J M 1995 *Phys. Rev. Lett.* **75** 280
- Khan M A, Kashyap A, Solanki A K, Nautiyal T and Auluck S 1993 *Phys. Rev.* **B48** 16947
- Koenig C and Khan M A 1983 *Phys. Rev.* **B17** 6129
- Kubler J and Williams A R 1986 *J. Magn. Magn. Mater.* **54–57** 603
- Lehmann G and Taut M 1972 *Phys. Status Solidi* **B54** 469
- Olsen J S, Gerward L, Benedict V and Luo H 1989 *J. Appl. Crystal.* **22** 63
- Reihl B, Martensson N, Eastman D E, Arko A J and Vogt O 1982a *J. Appl. Phys.* **53** 2008
- Reihl B, Martensson N, Eastman D E and Vogt O 1982b *Phys. Rev.* **B26** 1842
- Skriver H L 1980 *Phys. Rev.* **B21** 1489
- Skriver H L 1984 *The LMTO method* (Berlin: Springer Verlag)
- Svane A and Gunnarsson O 1990 *Phys. Rev. Lett.* **65** 1148
- Trinadh 1997 *Electronic structure and phase stability studies of some monpnictides and monochalcogenides under pressure*, D Phil Thesis, Anna University, Madras
- Von Barth U and Hedin L 1972 *J. Phys.* **C5** 1629