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Photoemission study of the electronic structure of praseodymium filled skutterudite ($PrOs_4Sb_{12}$)

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Abstract. Here we report the electronic structure of praseodymium filled skutterudite compound $PrOs_4Sb_{12}$. The theoretical photoemission spectrum (PES) at $\hbar\omega = 21.2$ eV shows four distinct structures peaking at about –0.2, –7.7, –13.7 and –18.2 eV. But on increasing the photon energy to 40.8 eV, the peak at –0.2 eV becomes a prominent or pronounced peak, the peak at –7.7 eV decreases in intensity, the peak at –13.7 eV increases intensity, the peak at –18.2 eV reduces in intensity and another peak emerges. These structures are interpreted to be associated with the density-of-states features on the basis of the results of band structure calculation. Hence, the peak at –0.2 eV arises from the symmetry point P at –11.61 eV, the peak at –7.7 eV comes from the symmetry point P at –11.62 eV, the peak at –13.7 eV arises from the symmetry point P at –11.88 eV and the peak at –18.2 eV arises from the symmetry point P at –11.88 eV. The PES energy level difference for $PrOs_4Sb_{12}$ fell within the range –0.5 to –7.5 eV indicating that it can be used in designing electronic devices. The energies of specific electronic states in the band structure of $PrOs_4Sb_{12}$ showed that it could be used for the development of solid-state devices.

Keywords: photoemission spectroscopy, electronic structure, energy level difference, superconductor.

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1. Introduction

Praseodymium filled skutterudite compound $PrOs_4Sb_{12}$ is related to ternary transition metal pnictide compounds with the general structural formula RT_4X_{12} (where R – Pr, Ca, Sr, Ba, La – Eu, Yb, Th, U; T – Fe, Ru, Os; X – pnictogen: P, As, Sb). Some of the variety of interesting physical properties displayed by filled skutterudite compound includes superconductivity [1, 2], magnetic order [3, 4], heavy fermion behaviour [5-8], non-Fermi liquid behaviour [9] and metal-insulator transition [10]. Heavy fermion superconductivity have been observed in $PrOs_4Sb_{12}$ with an electronic specific heat coefficient $\gamma = 350$ mJ/mol·K^2 and a superconducting transition temperature $T_c = 1.85$ K. Hence, $PrOs_4Sb_{12}$ is a superconductor. One of the most important fundamental properties of this compound is its electronic structure. The electronic structure of $PrOs_4Sb_{12}$ could be investigated using optical measurements and photoemission spectroscopy (PES). PES has been established as one of the most important methods to study the electronic structure of solids [11, 12]. Other forms of photoemission spectroscopy used to study the electronic structure of solids includes X-ray photoelectron spectroscopy (XPS), electron spectroscopy for chemical analysis (ESCA), inverse photoemission spectroscopy (IPES) and electron energy loss spectroscopy (EELS). Among these methods, only the photoemission spectroscopy method allows determination of absolute binding energies for electrons in solids. Furthermore, PES has widespread practical implications in various fields like surface chemistry or materials science and has significantly contributed to understanding the fundamental principles in solid state physics.

The field of photoemission was pioneered in the early 1960's by several groups, in particular by the group of Spicer (Stanford) who measured the first UPS valence band spectrum in copper [13] and developed the three-step model [14], the group of Turner, who performed UPS on gases [15] using a novel type of vacuum ultraviolet (VUV) excitation source, namely: the differentially pumped gas discharge lamp [16] that is still common in UPS setups today, and the group of Siegbahn in Uppsala, who

developed a high-resolution XPS analyzer that allowed the detailed study of core-level binding energies of solids [17].

The crystal structure of $PrOs_4Sb_{12}$ calculated by D.H. Galvan and C. Samaniego [18] is shown in Fig. 1. It is characterized by the space group: Im–3–T_h^5NO 204, $Z = 2$, cubic lattice parameter $a = 0.93068$ nm, with the Pr atoms located in the position (2a), the Os atoms located at (8c), and the Sb atoms located at (24g) with $y = 0.15603$ and $z = 0.34035$.

In this work, we have investigated theoretically ultraviolet photoemission spectrum of the electronic structure of $PrOs_4Sb_{12}$. We also calculate the density of states for this compound. We compare the density of states with our photoemission spectrum.

2. Method of calculation

We used the three-step model [19] (or formulation) of photoemission to obtain the photoemission spectrum. In this model, photoemission is treated as a sequence of (1) optical excitation of an electron, (2) its transport through the solid which includes the possibility of inelastic scattering by other electrons, and finally, (3) the escape through the sample surface into vacuum. The energy distribution curve (EDC) of photoemitted electrons $I(E, \hbar\omega)$ is consequently a sum of a primary distribution of electrons $I_p(E, \hbar\omega)$ that have not suffered an inelastic collision and a background of secondary electrons $I_s(E, \hbar\omega)$, which have suffered an energy loss in one or more collisions

$$I(E, \hbar\omega) = I_p(E, \hbar\omega) + I_s(E, \hbar\omega). \quad (1)$$

The primary distribution is factorized according to the three-step model into a distribution of photoexcited electrons $D(E, \hbar\omega)$, a transmission function $T(E)$, and an escape function $C(E)$.

$$I_p(E, \hbar\omega) = D(E, \hbar\omega) \times T(E) \times C(E). \quad (2)$$

$I_p(E, \hbar\omega)$ is thus the fraction of electrons that escapes from the solid without energy loss.

The energy distribution of the joint density of states (EDJDOS) which is defined by

$$D(E, \hbar\omega) = (2\pi)^{-3} \times \times \sum_E \int_k d^3k\, \delta\left(E_f(k) - E_i(k) - \hbar\omega\right) \delta\left(E - E_i(k)\right) \quad (3)$$

was obtained numerically using Simpson's rule. The values of wave vector k from the symmetry points in the band structure of these materials were used as input in the equation. The k values were used to obtain the energy (E) of each electronic state. The energy in k-space is given by $E(k) = \frac{\hbar^2}{2m}(k - K)^2$ where k is the wave vector, and K is the reciprocal lattice vector.

In a constant-matrix-element approximation, the energy distribution of the EDJDOS represents the energy distribution of photoexcited electrons referred to initial-state energy.

The energy distribution of the EDJDOS obtained was multiplied by appropriate transmission function and escape factors in order to obtain the photoemission intensity $I(E, \hbar\omega)$.

$$I(E, \hbar\omega) = D(E, \hbar\omega) \times T(E) \times C(E), \quad (4)$$

where $D(E, \hbar\omega)$ = energy distribution of joint density of states already given above; $T(E)$ = threshold factor and $T(E)$ is a slowly varying function of E with a value of the order of 0.1 for a metal at photon energies of ~15 eV; $C(E)$ is the escape factor.

We also make use of the energy band structure of $PrOs_4Sb_{12}$ in obtaining the theoretical photoemission spectrum. The energy band structure of $PrOs_4Sb_{12}$ was calculated using 51k points by D.H. Galvan and C. Samaniego [89]. Energies are referred to the valence-band maximum (VBM).

From Fig. 2, at the symmetry point Γ, the minimum of the valence state is the Γ_1 symmetry point at –12.0 eV. At the symmetry point P, the occupied states are at –11.9, –11.6, –1.4 and –11.3 eV. The symmetry points at –11.9, –11.6, –11.4 and –11.3 eV are maxima of the valence state. At the symmetry points H and N, the occupied states are at –11.7 and –11.85, –11.58 and –11.68, –11.5 and –11.4 eV, respectively.

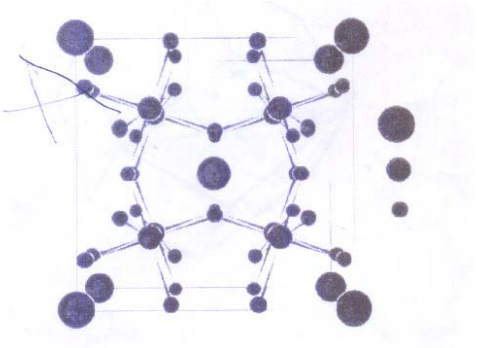

Fig. 1. Crystal structure of $PrOs_4Sb_{12}$.

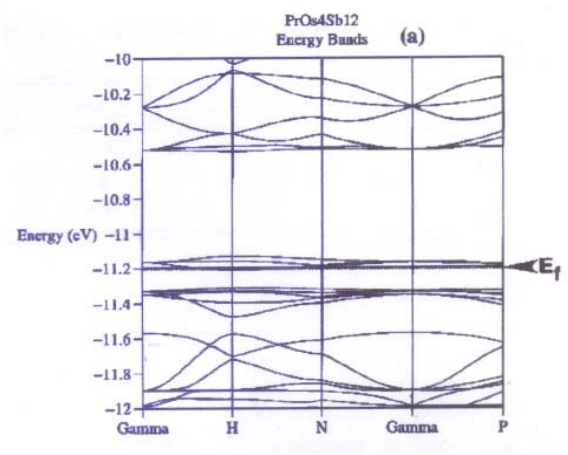

Fig. 2. Band structure of $PrOs_4Sb_{12}$.

The minimum of the valence state does not contribute to the peaks of density of states in the valence bands. Only the symmetry points that are maximum contribute significantly to the peaks of the density of states in the valence bands. So, the symmetry points P at –11.9, –11.6, –11.4, –11.3 eV, the symmetry points H at –11.7, –11.58, –11.5 eV and the symmetry point N at –11.85, –11.68, and –11.4 eV are maxima of the valence states. Hence, they contribute significantly to the peaks of the density of states in the valence bands.

3. Results and discussion

The relevant property of the band structure for our present purpose is the energy distribution of the EDJDOS defined by the equation (3). In a constant-matrix-element approximation, the EDJDOS represents the energy distribution of photoexcited electrons referred to the initial-state energy.

The EDJDOS has been evaluated numerically for praseodymium filled skutterudite from the equation (3). The band structure used here was that of D.H. Galvan and C. Samaniego [18]. The EDJDOS was then converted to an EDC by multiplying by appropriate threshold and escape factors.

The theoretical EDC's calculated in this way for photon energy 21.2 eV is shown in Fig. 3, which is the theoretical photoemission spectrum for praseodymium filled skutterudite under the photon energy $\hbar\omega =$ 21.2 eV. The theoretical photoemission spectrum at 21.2 eV shows four distinct structures peaking at about –0.2 eV indicated as A, –7.7 eV indicated as B, –13.7 eV indicated as C, and –18.2 eV indicated as D. On increasing the photon energy to 40.8 eV, the structure A at –0.2 eV becomes a prominent or pronounced peak, structure B decreases in intensity, structure C increases intensity, structure D reduces in intensity and another structure E emerges. The photoemission spectra are photon energy dependent, and this is explained by the photoionization cross-section of the valence electron orbitals.

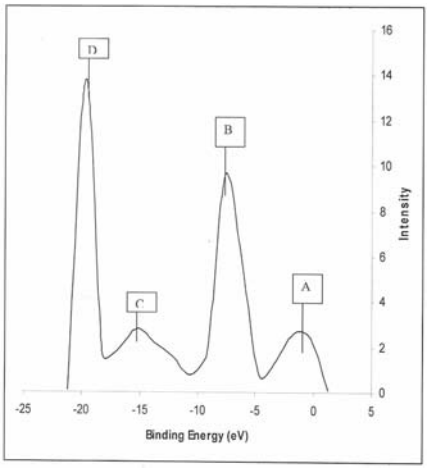

Fig. 3. Theoretical photoemission spectrum for $PrOs_4Sb_{12}$ measured at $\hbar\omega$ = 21.2 eV.

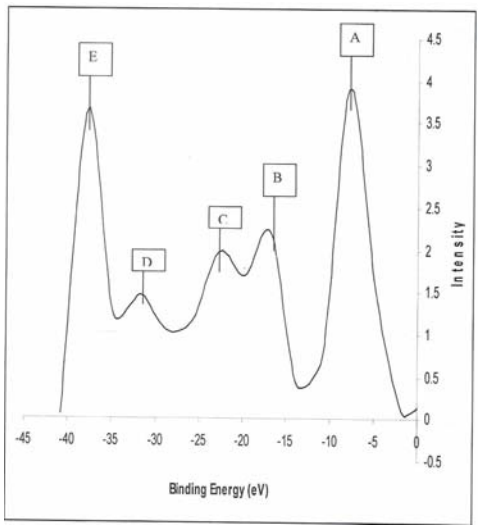

Fig. 4. Theoretical photoemission spectrum for $PrOs_4Sb_{12}$ measured at $\hbar\omega$ = 40.8 eV.

The density of states of praseodymium filled skutterudite obtained from the band structure is shown in Fig. 5. The density of states shows three distinct peaks. The first peak that is the most pronounced one is around –3.2 eV. The second peak is around –10.7 eV and the third peak is near –16.7 eV.

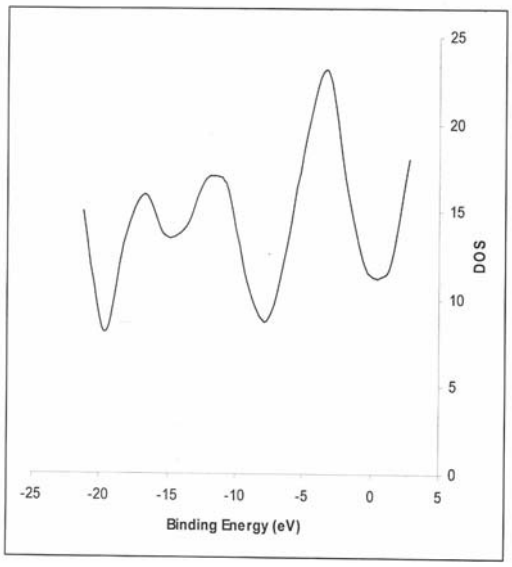

Fig. 5. Density of states (DOS) for $PrOs_4Sb_{12}$.

In Fig. 6, the calculated density of states was compared with the theoretical photoemission spectroscopy result. The threshold of the valence-band contribution to the density of states for $PrOs_4Sb_{12}$ is –12.0 eV, and it occurs at Γ_1. There is a transition from Γ_1 to the symmetry point P at –11.9 eV, so the peak D at –18.2 eV in the theoretical photoemission spectrum arises from the symmetry point P at –11.9 eV. There is also a transition from the Γ symmetry point at –11.9 eV to the symmetry point P at –11.88 eV. Likewise, there is

transition from the Γ symmetry point at –11.9 eV to the symmetry point P at –11.62 eV, so the peak B at –7.7 eV in the theoretical photoemission spectrum arises from the symmetry point P at –11.62 eV and finally, there is transition from the Γ symmetry point at –11.58 eV to the symmetry point P at –11.61 eV, thus, the peak A at –0.2 eV in the theoretical photoemission spectrum arises from the symmetry point P at –11.61 eV.

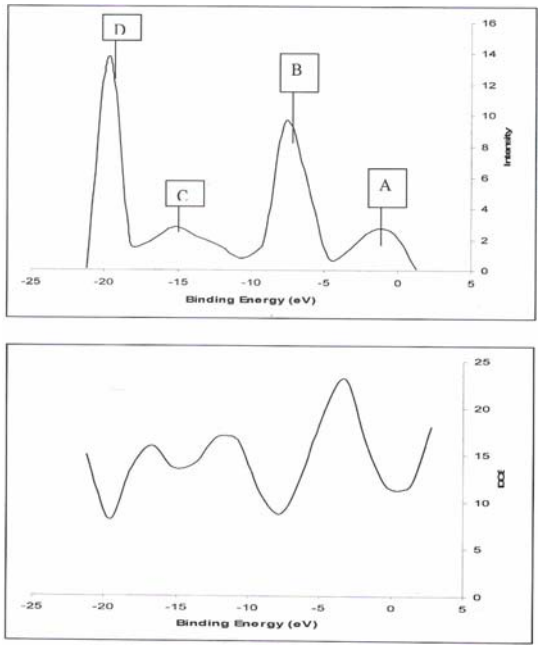

Fig. 6. Density of states of $PrOs_4Sb_{12}$ and the photoemission spectrum.

The photoemission spectrum obtained for $PrOs_4Sb_{12}$ showed four peaks which are labeled A, B, C, and D in order of the increasing binding energy. The peaks A and B, B and C, C and D are separated by the energy gaps (or distance between energy level) 7.5, 6.0, and 4.5 eV, respectively.

4. Conclusion

We have investigated theoretically the electronic structure of $PrOs_4Sb_{12}$ by using photoemission spectroscopy.

The theoretical photoemission spectrum obtained for $PrOs_4Sb_{12}$ at $\hbar\omega = 21.2$ eV shows four distinct structures at –0.2, –7.7, –13.7, and –18.2 eV. On the basis of the results obtained from our band structure calculations, these structures are interpreted as those associated with the density-of-states features. The peak A at –0.2 eV arises from the symmetry point P at –11.61 eV, the peak B at –7.7 eV comes from the symmetry point P at –11.62 eV, the peak C at –13.7 eV from the symmetry point P at –11.88 eV and the peak D at –18.2 eV – from the symmetry point P at –11.88 eV.

Finally, the energy gap or energy level difference between two peaks for $PrOs_4Sb_{12}$ fell within the range –0.5 to –7.5 eV indicating that it could be used for development of solid-state devices such as blue light-emitting diodes, lasers, solar cells and microwave devices.

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