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HAL Id: jpa-00247040
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Submitted on 1 Jan 1994

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Electronic structures and optical properties of some fluorite structured intermetallics

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(Received 28 January 1994, revised 30 June 1994, accepted 24 August 1994)

Abstract. — The electronic energy band structures of three intermetallic compounds have been studied using the composite wave variational version of the APW method. The band structure results of PtIn2 and IrSn2 are compatible with other noble metal intermetallics. The densely populated valence band region of AuSb2 largely differs from that of PtIn2 and other intermetallics, but resemble those of AuGa2 and provides an important basis for interpreting various physical observables. The DOS, JDOS, ε(ω) spectra and Fermi surfaces of the compounds calculated from the respective band structure data are different. The difference is attributed to the dissimilar nature and position of the bands immediately above and below the Fermi level.

1. Introduction.

The growing interest in the physical properties of the intermetallics and their technological importance [1-7] basically motivated us to study the electronic properties of a series of Au and Pt binary intermetallic compounds [8, 9]. In this paper we present the electronic band structure results of three isostructural compounds, namely, IrSn2, PtIn2 and AuSb2. The compounds remain unexplored to this date, except for the few physico-chemical studies that have been made presently. In recent times an estimation of the heat capacity of AuSb2 based on contribution of the core atoms in the compound has been performed [10]. The systems AuSb2 and PtIn2 have also been thermodynamically assessed in order to provide thermodynamic data bases for performing calculations on multicomponent systems [11]. Chemical studies like the interaction of aurostibite with chloride solution has been studied as a possible mechanism for the preparation of mustard gold [12]. Moreover, the grain size of PtIn2 is important for its workability and hence has several applications. Theoretical work whose predictive capability and understanding can guide further experiments, has also not yet been done on these compounds. The detail electronic energy band calculations, which are reported here for the first time will surely serve this purpose and provide a framework for the analysis of d-band intermetallics. The band structure calculations have been performed using the composite wave
variational version [13] of the APW method [14]. Despite its limitations, the method has already been applied to a series of compounds [15, 16] with great success. The potential here is constructed by superposition of the free atom solution of Herman and Skillman [17].

2. Results and discussion.

IrSn₂, PtIn₂ and AuSb₂ belong to the cubic fluorite structure of the type AX₂, where A stands for a noble metal and X represents a Gr. III/IV or V metal. The lattice constants used in the calculation are 11.977 a.u. for IrSn₂, 12.005 a.u. for PtIn₂ and 12.578 a.u. for AuSb₂ [18].

In figures 1, 2 and 3 we exhibit the electronic energy bands for IrSn₂, PtIn₂ and AuSb₂ respectively. Our discussion is concerned mainly with the bands immediately above and below the Fermi level, as the other ones are not so critical in describing the physical observables. The band structure results are quite similar to those for other Au and Pt intermetallics [8, 9, 19-21] and we can indicate some salient features of these intermetallics as:

1. The lowest lying band, situated well below the Fermi energy is best described as a bonding combination between nearest neighbour X atoms, has also a significant admixture of s character of the noble metal.

2. The next two completely filled bands above the s band originate from the 5d orbitals of the noble metal. These narrow d bands split nearly identically at the Γ point, as for the respective elemental metals, despite the large difference in their band width. The broadening of d-bands in the case of pure metals, reflects the stronger d-d overlap interaction between noble metal atoms as a result of smaller interatomic distances as compared to those for the compounds.

The d-band width as estimated from the measurement of the energy separation between the d-bands at the Γ point for these intermetallic compounds provide interesting information about d-d interaction as a function of primary interatomic distance. A marked decrease in the 5d band

![Fig. 1 — Band structure of IrSn₂ along the symmetry points and axes.](image-url)
Fig. 2. — Band structure of PtIn₂ along the symmetry points and axes.

Fig. 3. — Band structure of AuSb₂ along the symmetry points and axes.
width in Au and Pt series [8, 9] with the increase of lattice parameter indicates the decrease of strength of interaction between 5d orbitals on the neighbouring noble metal atoms.

(3) The antibonding states $X_3 - \Gamma'_{25} - L_1 - W'_{2} - K_3 - \Gamma'_{2}$ arise mostly from the s states of the X-atoms. However, there lies a pronounced difference regarding the position of this state in different intermetallics.

In the case of IrSn$_2$, the antibonding band lies partly above $E_F$ in the $\Gamma - X$ region and is situated completely below Fermi energy in all the other symmetry directions. The band is therefore almost completely filled up, having a small hole surface around $\Gamma$, and thus contributing insignificantly to the Fermi surface.

In the case of PtIn$_2$, the band is located completely above $E_F$ along $W - X$ and $\Gamma - X$ directions, and is partially filled along $\Gamma - L$ and $\Gamma - K$ directions, whereas, in AuSb$_2$ it is completely filled throughout the BZ and lies well below the Fermi energy. This feature of a completely filled antibonding state is also observed in another Au intermetallic, namely, AuGa$_2$ [19-21], which is found to behave quite differently from the other Au intermetallics.

(4) The remaining bands near the Fermi energy are primarily composed of X-atoms together with a small contribution of the noble metal. The positions of these bands, namely, $\Gamma'_{25}$ and $\Gamma'_{15}$ are quite different for the different compounds. In AuSb$_2$, the two bands lie below or just on the Fermi energy, whereas, in PtIn$_2$, the bands are completely vacant. In addition to this, the relative order of the two bands at $\Gamma$ is inverted. Apart from the ordering of the levels, the nature and the shape of other bands in the conduction band region are quite similar in all the three compounds.

The density of states (DOS) and the joint density of states (JDOS) of the compounds have been calculated by the linear energy tetrahedron method. Here 1/48th part of the Brillouin zone is divided into a mesh of 215 points. Calculations are done for all the symmetry points and axes and at all general points on the surface of the three tetrahedra. The energies for the rest of the points are calculated by quadratic interpolation.

The calculated DOS of IrSn$_2$, depicted in figure 4, is characterized by six different structures of various sizes, shapes and nature. The first four lie in the valence band region whereas the last two are situated in the conduction band region. The first small structure lying between $-0.96$ and $-0.91$ Ryd. originates from the lowest bonding band. The next two peaks, a small but sharp structure at $-0.69$ Ryd. and a large but prominent peak at $-0.635$ Ryd., owe their origin to the closely spaced flat Ir d-bands in the $\Delta$ and $\Sigma$ region. The small structure at $-0.58$ Ryd. originates from the two bands, namely, the $Z_1$ band in the $X - W$ region and the flat $L'_{2} - K_3$ band in the $L - K$ direction. The first small structure centred at $-0.16$ Ryd. in the conduction band region arises due to (i) the crossing of degenerate and nondegenerate $\Delta$ bands of p character in the $X - \Gamma$ region and (ii) overlap of $\Sigma$ bands of p-d character in the $K - \Gamma$ region. The last small sharp peak centred at $-0.075$ Ryd. is attributed to a large number of closely spaced bands originating from $\Gamma'_{25}$ and $\Gamma'_{15}$ (near $\Gamma$) in $\Sigma$ region and the crossing of degenerate band $\Lambda_3(\Gamma'_{25} - L'_{2})$ and nearly flat band $\Lambda_1(\Gamma'_{15} - L_1)$.

In the next two figures 5 and 6, the density of states for PtIn$_2$ and AuSb$_2$ are shown. In the DOS of PtIn$_2$, the first small peak at about $-0.885$ Ryd. arises from the flat portion of the lowest bonding band. This band is also responsible for the formation of the next two small structures. The large peak centred at $-0.5$ Ryd. along with the prominent structures lying between $-0.55$ Ryd. to $-0.65$ Ryd. are attributed to the comparatively less dispersed 5d band of the noble metal. In the conduction band region, near the Fermi level, a small peak centred at $-0.145$ Ryd. is observed, which comes mainly from the flat portion of the bands $\Gamma'_{2} - X_3$ and $\Gamma'_{15} - X_1$ about $X$. A small contribution also comes from the band $\Gamma'_{25} - K_1$ around $K$ and the flat portion of $\Gamma'_{15} - L_3$ around $L$. The next small structure at $0.015$ Ryd. chiefly arises from a number of closely spaced bands around $\Gamma'_{15}$ and $\Gamma'_{25}$ in the
Fig. 4. — Density of states of IrSn$_2$ as a function of energy.

Fig. 5. — Density of states of PtIn$_2$ as a function of energy.

Fig. 6. — Density of states of AuSb$_2$ as a function of energy.

Fig. 7. — $\epsilon_2(\omega)$ spectra of IrSn$_2$ calculated from the JDOS value by assuming constant matrix elements.

$\Gamma$ – K region and the flat band along $\Gamma_1$ – L$_1$. The structure at 0.105 Ryd. results from the crossing of a few bands around the symmetry point $\Gamma_1$ and $W_2$ in the respective energy region. The valence band region of AuSb$_2$ is largely populated as is reflected in the occurrence of a number of peaks and structures in the DOS. The first small peak centred at – 0.97 Ryd. along
with the two structures at $-0.82$ Ryd. and $-0.775$ Ryd. originate from the bonding band. The pronounced peak at $-0.675$ Ryd. associated with a small structure at $-0.725$ Ryd., originating from the d-band or Au-metal, is characteristic of noble metal intermetallics. Besides these, unlike PtIn$_2$, there arises a number of structures before the Fermi energy. The two structures at $-0.5$ Ryd. and $-0.4$ Ryd. arise due to the filled flat antibonding band and the degenerate $\Delta_4$ band at $\Gamma_{25}$. The partially filled $\Delta_1(X_1 - \Gamma_{15})$ and the crossing of two filled flat bands starting from $\Gamma_{15}$ to L$_3$ through L, are responsible for the formation of the peak at $-0.27$ Ryd. near $E_F$. In the conduction band region, the first small structure close to $E_F$ is contributed by a number of bands crossing the Fermi level in the $\Gamma - K$ and $\Gamma - L$ regions.

The complex dielectric function, which can be obtained experimentally from optical spectroscopic studies, reveals the character of the electronic band structure. Thus structures in the dielectric function can be related to $k$ conserving electric dipole transitions from an initial state $|i\rangle$ to a final state $|f\rangle$ separated by an energy $\hbar \omega$. For this purpose $\varepsilon_2(\omega)$, the imaginary part of the dielectric function calculated directly from JDOS results, has been presented in figures 7, 8 and 9, so that, it can be used as a guide for assigning optical structures to specific regions of the BZ directly.

In the $\varepsilon_2$ spectra of IrSn$_2$ (Fig. 7), the first two small structures at 1.1 and 1.4 eV result due to transitions from $z_4(X_3 - W_3)$ to $z_1(W_2' - X_1)$ around X, and from $Q_1(L_1 - W_3)$ to $Q_2(L_3' - W_2')$ about L respectively. The large peak centred at 1.75 eV reflects the presence of parallel bands in the energy band picture and is attributed to transitions between the bands $\Delta_2(X_2 - \Gamma_{21})$ and $\Delta_1(X_1 - \Gamma_1)$. Contribution to the peak also results from the transition between a small portion of degenerate band $\Delta_3(\Gamma_{15} - L_3)$ lying just below the Fermi level to the degenerate $\Delta_3(\Gamma_{25} - L_3)$ band and non-degenerate $\Delta_1(\Gamma_{15} - L_1)$ band around L. The next structure at 2.0 eV arises due to transition from the crossing of three bands, namely,
\( \Delta_5 \), \( \Delta_1 \) and \( \Delta'_1 \) to the upper \( \Delta_1 \) band. Transition from \( \Delta_3(\Gamma_{15} - L_3) \) to parallel \( \Lambda_1(\Gamma_1 - L'_2) \) band is responsible for the associated structure at 2.25 eV. The well defined broad structure at 3.5 eV results due to transition between the middle portion of overlapping \( \Sigma_2 \) and \( \Sigma_3 \) band to parallel \( \Sigma_4 \) and \( \Sigma_3 \) bands.

In AuSb\(_2\) (Fig. 8), the first small peak at 0.55 eV has originally been assigned to \( L'_9 \) – \( L'_2 \) transition. In addition to these well defined critical points, extended regions of the BZ also contribute to the peak. The next structure at 0.75 eV is ascribed to a transition from the partly filled degenerate band \( \Lambda_1 \) to the bottom of the conduction band \( \Lambda_1 \) around \( L \). In the formation of the remaining structures, significant contributions come from the \( \Gamma - K \) region.

In this region there are five parallel bands, among which the lowest one is \( \Sigma_3(\Gamma_{25} - K_3) \) which lies mostly in the valence band region, and the four other bands which have Au s-p and p-d character mixed with Sb p character lie in the conduction band region. Transitions between the \( \Sigma_3 \) band and the group of aforesaid four conduction bands (\( \Sigma_2 \), \( \Sigma_4 \), \( \Sigma_3 \) and \( \Sigma_1 \)) are responsible for the formation of the next four consecutive structures at or near 1.5, 2.2, 3.25 and 4.6 eV respectively. In addition to the primary contribution coming from the \( \Gamma - K \) region, the well defined structure at 2.2 eV is also caused by the transition between (i) the bands \( z_4(W_3 - X'_2) \) and \( z_1(W_1 - X_1) \) around \( W \) and (ii) degenerate band \( \Delta_3(\Gamma_{25} - X'_2) \) and \( \Delta_1(\Gamma_1 - X_1) \) around \( \Gamma \).

In the \( \varepsilon_2(\omega) \) spectra of PtIn\(_2\), \( \Gamma - X \) and \( \Gamma - K \) regions play a dominant role, where most of the transitions occur between the filled antibonding band and the unoccupied band having mostly s-p character. The first peak at 0.5 eV can be interpreted as due to transition from the antibonding band lying almost on the Fermi energy to the band \( \Delta_1(\Gamma_{15} - X_1) \) around \( X \). In the formation of the structure at 0.75 eV the largest contribution comes from the parallel bands \( Q_1 - Q_2 \) around \( L \). Transitions from the middle of \( \Delta_1 \) and \( \Delta_4 \) bands to \( \Delta'_1 \) band also take part in it. The next peak around 2.3 eV is associated with the transition from the degenerate band \( \Delta_3 \) together with \( \Delta_1 \) to the upper \( \Delta_1 \) band in the middle of \( \Gamma - X \) region, and from \( \Sigma_4 \) band to the \( \Sigma_1 \) band about \( K \). The structure alongside originates due to transition from the crossing of \( \Sigma_2 \) and \( \Sigma_3 \) bands to the parallel band \( \Sigma_4 \) near \( \Gamma \). Between 3 to 4 eV, a small structure is observed in \( \varepsilon_2 \) spectrum, whereas, a shoulder is seen in JDOS curve. Contributions to this shoulder/structure come from all of the irreducible wedge. The prominent structure at 4.25 eV can be ascribed as due to transition between the crossing of \( \Sigma_1 \) and \( \Sigma_3 \) bands and the higher \( \Sigma_1 \) band in \( \Gamma - K \) region.

The Fermi surface cross sections of a number of bands are shown in figures 10, 11 and 12, along two high symmetry planes for IrSn\(_2\), PtIn\(_2\) and AuSb\(_2\) respectively. The bands taking part in the formation of the Fermi surfaces are not similar in nature for the three intermetallics, due to which, the topology of the Fermi surfaces are quite different, as is evident from the figures. In AuSb\(_2\), the antibonding band connected to the s-like valence electrons of Sb-atom, lies entirely below the Fermi level, and hence does not contribute to the Fermi surface. However, a significant contribution comes from the intersection of the Fermi level with bands having s-p and p-d characters. In PtIn\(_2\), on the other hand, the antibonding band which is partially filled contributes considerably.

3. Conclusion.

The band structures of IrSn\(_2\), PtIn\(_2\) and AuSb\(_2\) have been reported in this paper for the first time. The energy band picture has strong resemblance with the band structure results of the fluorite structure binary intermetallics reported previously. The overall nature and ordering of the bands are in good agreement with those studied earlier. The DOS and \( \varepsilon_2(\omega) \) spectra along with the Fermi surfaces have been presented and analysed.
Fig. 10. — The Fermi surface cross-sections of IrSn₂. (a) plane ΓXL. (b) plane ΓXK. The hatched parts denote the occupied states.

Fig. 11. — The Fermi surface cross-sections of PtIn₂. Left hand parts. plane ΓXL, right hand parts. ΓXK. The hatched parts denote the occupied states.

The overall shape of the bands of the three compounds seems to encounter a reasonable agreement, with only minor differences in the relative order between levels, such as, \( \Gamma_{15} \) and \( \Gamma_{15} \) states lying at the top of the antibonding band. However, regarding the position of the bands, with respect to the Fermi energy, AuSb₂ exhibits a pronounced difference. The antibonding band which is made up mainly of s-electrons of Sb, lies well below the Fermi energy, and does not contribute to the Fermi surface. This second X-site s band is very important to the Knight shift, while making but a small contribution, when present, to the density of states at the Fermi level, and possibly to most other observables involving states at or near the Fermi surface. In the noble metal intermetallic AuGa₂, the strong temperature dependent susceptibility and Knight shift are found to differ anomalously from the other isoelectric and isostructural compounds AuIn₂ and AuAl₂ [22]. This unusual behaviour of
AuGa$_2$ was attributed to the position of the Gallium 4s antibonding band [19], which was found to lie entirely below the Fermi energy, thus contributing nothing to the Fermi surface. Hence it is expected that, AuSb$_2$, which has similar band structure results as AuGa$_2$, might exhibit interesting findings in the field of susceptibility, Knight shift and de Hass-van Alphen measurements. In addition to this antibonding band, bands having s-p and p-d characters lie partially or fully in the valence band region as is reflected by the occurrence of a number of peaks/structures below the Fermi energy in the DOS.

IrSn$_2$ and PtIn$_2$, which are less complicated reflect the characteristic band structure for the noble metal intermetallics. Besides the low lying valence band of essentially X-site $s$-character, and the $d$-band manifold of the noble metal, the presence of a distinct $s$-$p$ band crossing the Fermi level is observed. The contribution to the optical spectra coming from particular sets of valence and conduction bands are different for the three compounds. The largest contribution for PtIn$_2$ comes from the $\Gamma$ – X region, whereas for AuSb$_2$ it is from the $\Gamma$ – K and $\Gamma$ – L regions. The topology of the Fermi surfaces of AuSb$_2$ also have no resemblance as the shape and relative position of the bands around the Fermi level are dissimilar. Comparative study of experimental and theoretical findings is lacking as no experimental work in IrSn$_2$ has been reported till this date. In the coming years, this work should therefore assist researchers working in appropriate field.

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