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A photoemission investigation of the valence band electronic structure of Pd₂TiIn and Pd₂TiSn

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Abstract. The valence bands of the intermetallic compounds Pd₂TiIn and Pd₂TiSn have been investigated by ultraviolet photoemission utilizing synchrotron radiation. The valence bands of both alloys have a width of 7–8 eV with a prominent peak at a binding energy of 2.6 eV and a shoulder extending to the Fermi edge. Measurements obtained at the Pd 4d Cooper minimum and at the Ti 3p threshold indicate that the feature at 2.6 eV is largely composed of contributions from Pd 4d states, whereas the Ti 3d states contribute most strongly immediately below the Fermi level. Experimental photoemission spectra show good agreement with theoretical calculations.

1. Introduction

Ternary alloys of the composition Pd₂TiX (X = Al, In or Sn) are recent additions to the family of intermetallic compounds possessing the face-centred-cubic Heusler L2₁ structure [1]. These alloys are of particular interest since magnetic ground states have been reported, despite the fact that none of the constituent elements has a spontaneous moment [2–4]. Pd₂TiAl and Pd₂TiSn have been reported to order ferromagnetically with moments of 0.21 and 0.005 μ_B /formula unit respectively. Pd₂TiIn is reported to be an antiferromagnet with an effective paramagnetic moment of 4.9 μ_B /formula unit. Although band-structure calculations are available for these materials, they do not reveal the origin of the magnetic behaviour [5–7].

As calculations of the electronic structure appear to contradict the magnetic measurements, it is desirable to experimentally probe the valence bands of these alloys. Ultraviolet photoemission is an obvious technique to employ, as it has been widely used in the investigation of the electronic structure of metals and their alloys [8]. By utilizing tunable radiation associated with a synchrotron source, it is also possible to investigate the contribution of constituent elements to the valence band by means of Cooper minima [9] and 3p to 3d resonances [10]. These techniques have already been employed to experimentally determine the Pd 4d and Ti 3d contributions to the density of states for Pd₂TiAl [11]. The aim of the research described in this paper was to extend this analysis to an investigation of the valence bands of the related alloys Pd₂TiIn and Pd₂TiSn and to investigate the validity of existing band-structure calculations.

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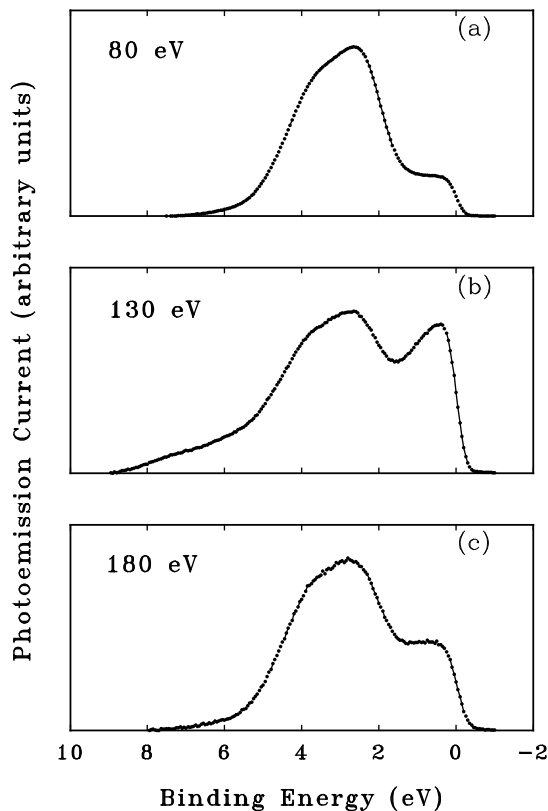


Figure 1. Electron energy distribution curves for Pd₂TiIn obtained at photon energies of (a) 80, (b) 130 and (c) 180 eV. Spectra have been flux normalized and the inelastic background has been removed.

2. Experimental procedure

Ingots of Pd₂TiIn and Pd₂TiSn were manufactured by repeatedly melting stoichiometric proportions of the high-purity constituent elements in an argon arc furnace. The loss of weight recorded after this process was <0.1% in each case. The ingots were annealed at 1073 K for 24 hours in evacuated quartz ampoules and then quench cooled. Samples to be used for photoemission measurements were spark eroded to approximate dimensions of 15 × 10 × 2 mm and the front faces polished to a 1 μm finish. Each sample was secured to a stainless steel platen by means of spot-welded tabs and, following degreasing, the assembly was attached to an ultra-high-vacuum sample manipulator.

Ultraviolet photoemission measurements were performed on stations 6.1 and 6.2 at the Daresbury synchrotron radiation source. These beamlines have been described briefly in a previous paper [11] and a more detailed description can be found elsewhere [12, 13]. Base pressures of 1 × 10⁻¹⁰ mbar (station 6.1) and 5 × 10⁻¹¹ mbar (station 6.2) were achieved following a 453 K bake-out for 36 hours. The alloys were cleaned *in situ* by mechanical abrasion of the surface using a diamond file mounted on a wobble stick. Sample cleanliness and surface stoichiometry were verified by Auger electron spectroscopy. Emitted electrons were energy analysed using a double-pass cylindrical mirror analyser aligned at 90° to the photon beam and operated with a pass energy of 10 eV. The photon flux was monitored by

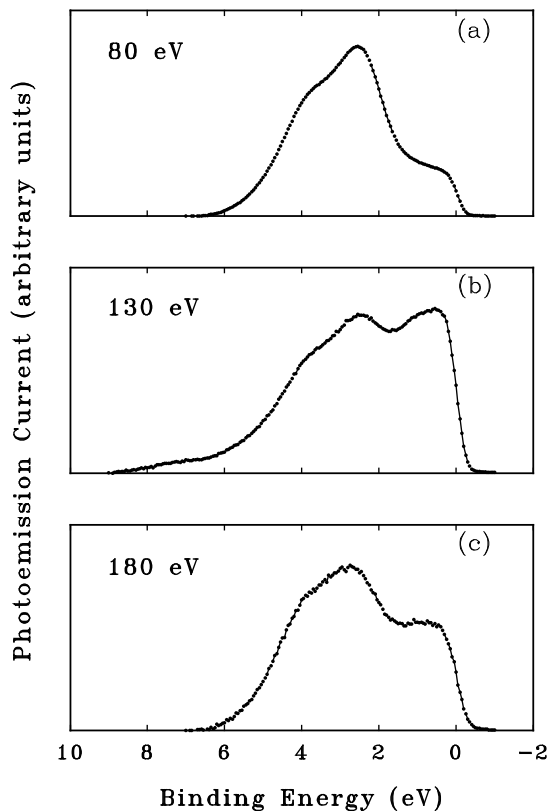


Figure 2. Electron energy distribution curves for Pd_2TiSn obtained at photon energies of (a) 80, (b) 130 and (c) 180 eV. Spectra have been flux normalized and the inelastic background has been removed.

measurement of the drain current from a tungsten grid and all of the photoemission spectra were normalized to this flux.

3. Results and discussion

Photoemission spectra were obtained for each sample in the photon energy range 20–180 eV. Measurements were initially taken from different regions of each ingot employing a range of take-off angles. However, no discernible differences in spectral shape were observed and all subsequent spectra were recorded with the sample surface at an angle of 45° to both the photon beam and energy analyser. Figures 1 and 2 show electron energy distribution curves (EDCs) at selected photon energies for Pd_2TiIn and Pd_2TiSn respectively. In each case, the inelastic background has been removed by means of a Shirley algorithm with three iterations [14]. Binding energies have been referenced to the Fermi level, which was arbitrarily assigned a value of zero. Since the photoionization cross-sections for s and p states are comparatively low, the valence band spectra will be dominated by transitions from the Pd and Ti d bands [15]. The valence band for each alloy can be seen to extend to approximately 7–8 eV below the Fermi level. At 80 and 180 eV, both sets of spectra exhibit a prominent peak at about 2.6 eV binding energy with a shoulder extending to the Fermi

edge. At 130 eV, however, the shape of the spectra changes markedly. The photoemission intensity of the feature at 2.6 eV passes through a minimum and the shoulder at the Fermi edge becomes resolved into a well defined peak at a binding energy of approximately 0.5 eV. Since a photon energy of 130 eV corresponds to the Cooper minimum for Pd 4d photoemission [16], it would be reasonable to assume that the feature at 2.6 eV is dominated by transitions from Pd 4d-derived states. Also, since the relative contribution from Ti 3d states will be enhanced at 130 eV, this suggests that the emerging peak immediately below the Fermi level is associated with Ti 3d electrons.

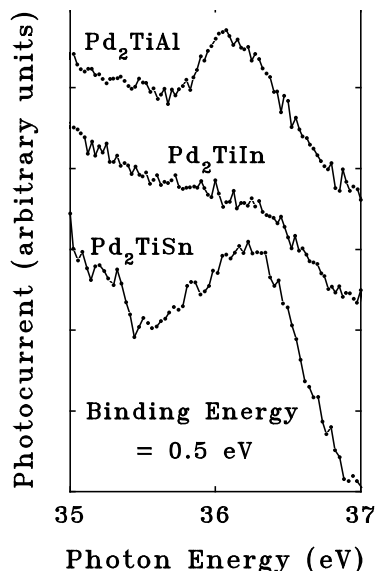


Figure 3. Constant-initial-state spectra obtained at a binding energy of 0.5 eV for Pd₂TiX alloys in the region of the Ti 3p threshold. The spectra have been displaced along the ordinate for clarity.

In order to confirm the participation of Ti 3d electrons at the Fermi edge, constant-initial-state (CIS) spectra were recorded at a binding energy of 0.5 eV across the region of the Ti 3p threshold for each alloy. The results are shown in figure 3, together with a similar spectrum for Pd₂TiAl included for comparison. An enhancement in photocurrent is observed in the CIS spectra with a maximum at about 36.2 eV photon energy. Since the binding energy of the 3p state in metallic Ti is at 32.7 eV [17], the enhancement is consistent with a 3p-to-3d resonance. This confirms the involvement of electrons from Ti 3d-derived states close to the Fermi edge. Resonance effects of reduced intensity were also observed in CIS spectra obtained at higher binding energies for each alloy. This suggests that, although the Ti 3d states contribute across the full width of the valence band, the strongest contribution is just below the Fermi edge. This supports the evidence for a strong Ti contribution at 0.5 eV obtained from the spectra at the Pd 4d Cooper minimum. Differences in the magnitude of the resonant enhancement between the alloys may reflect changes in localization of the Ti 3d states, since the shape and intensity of a resonance is known to be strongly influenced by initial-state hybridization [18]. The resonance is relatively much weaker for the Pd₂TiIn sample than for the Al- and Sn-containing samples. A possible explanation, therefore, could be increased delocalization of the Ti 3d electrons in the In alloy, although the reason for this apparent difference is not clear.

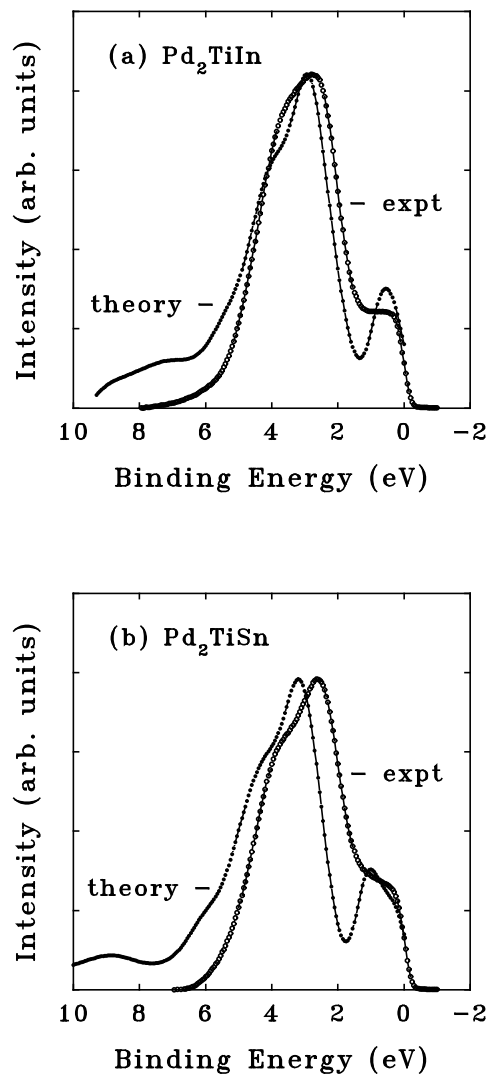


Figure 4. Comparison of a background-subtracted photoemission spectrum of (a) Pd_2TiIn and (b) Pd_2TiSn obtained at a photon energy of 90 eV with the respective calculated density of states based on the LMTO method [6, 7] (reproduced with permission). The calculated densities of states have been broadened by convolution with Lorentzian and Gaussian functions to represent lifetime effects and the effect of finite instrumental resolution. Details are described in the text. The experimental spectra have been arbitrarily normalized to be on approximately the same scale as the calculations.

In figure 4, the experimental photoemission spectra for the alloys are compared with band structures calculated by Jezierski and co-workers using the linear muffin-tin orbital (LMTO) method [6, 7]. The calculated density of states for each alloy has been convoluted with Lorentzian functions of half-width at half-maximum (HWHM) decreasing, in proportion with the square of the binding energy, from 1.0 eV at the bottom of the band to 0.0 eV at the Fermi level. The same functions have been used to model intrinsic broadening in Cu_3Pd alloys [19]. To model the broadening effects due to finite instrumental resolution, the

density of states have been further convoluted with a Gaussian function of 0.3 eV HWHM. For ease of comparison, the secondary-electron contribution has been removed from the experimental EDCs and each spectrum arbitrarily normalized to be on approximately the same scale as the corresponding calculated density of states. EDCs obtained at 90 eV were used since, at this photon energy, the Pd 4d and Ti 3d cross-sections are comparable and the spectra should broadly represent the shape of the density of states. However, variations in the cross-sections across the valence band depending upon the bonding or antibonding nature of the states involved has not been considered [16]. Self-energy effects have also been neglected. Features at approximately 7 eV and 9 eV in the calculated curves for Pd₂TiIn and Pd₂TiSn respectively are due to the s states of In and Sn in each alloy. These features are not observed in the experimental curves due to low cross-sections. Despite the above factors, there remains good agreement between experiment and theory in terms of the width and shape of the valence band. In addition, the calculations predict that the main peak in the density of states is dominated by contributions from the Pd 4d band, whilst the highest occupied density of states for the Ti 3d band is just below the Fermi level. This also agrees very well with the photoemission results. However, despite this agreement, the failure of the LMTO method to adequately account for the magnetic behaviour remains a cause for concern.

4. Conclusion

The electronic structures of the Heusler alloys Pd₂TiIn and Pd₂TiSn have been studied by means of ultraviolet photoemission spectroscopy with tunable synchrotron radiation. The valence band photoemission spectra for the two alloys are very similar. The valence band extends to approximately 7–8 eV below the Fermi level in each case and is characterized by a high density of states at 2.6 eV and a shoulder extending to the Fermi edge. The Cooper minimum in the photoionization cross-section of the Pd 4d states and resonant enhancement in the region of the Ti 3p threshold have both been utilized to probe the contribution of the constituent elements to the valence band. For each alloy, the main peak in the density of states is dominated by contributions from Pd 4d-derived states. Ti 3d states contribute most strongly at the Fermi level. These conclusions are consistent with an earlier photoemission study of Pd₂TiAl and theoretical calculations of the band structures.

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