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The ordered Heusler alloy Pd₂MnIn investigated by photoelectron spectroscopy

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Abstract

The full, ordered, antiferromagnetic Heusler alloy Pd₂MnIn has been investigated using synchrotron radiation photoelectron spectroscopy. The Pd 4d Cooper minimum at 130 eV photon energy and the Mn 3p to 3d resonance at 49.5 eV photon energy have been used to determine the partial spectral weights of the Pd 4d and Mn 3d derived states. These partial spectral weights are consistent with published partial density of states calculated using the augmented spherical wave method. A quantitative fit of the resonant profile yielded an asymmetry parameter of 1.6 ± 0.4 , indicating delocalization of the filled Mn 3d states.

1. Introduction

Heusler alloys [1] have a long history of scientific investigation [2], motivated by their wide variety of magnetic and other properties. Contemporary interest in their fabrication and properties is very large and expanding, fuelled by the discovery of properties that have potentially valuable technological applications, including half-metallic behaviour [3] and ferromagnetic shape alloys [4]. The archetypal Heusler alloy is a structurally and chemically ordered compound of the form X₂MnZ comprising four interpenetrating face-centred cubic (fcc) lattices. The element X is usually a first row transition or noble metal such as Co, Ni, Cu, Pd or Pt, and element Z is usually a group IIIB or IVB element such as Al, In, Sn or Sb. They are generally considered to be ideal arrays of magnetic moments localized on the Mn atoms. However, despite this localized magnetic behaviour, there is strong evidence from band structure calculations [5, 6], supported by experimental evidence, that the occupied Mn 3d states are delocalized. Calculations by Kübler *et al* [6] using the augmented spherical wave method indicate that the Mn and X d electrons hybridize into a common band and that the localized moment is due to localization of the unoccupied minority Mn 3d states.

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Pd_2MnIn is a weakly antiferromagnetic Heusler alloy with a moment close to $4 \mu_B$ that is confined to the Mn atoms [7]. It has been the subject of several experimental investigations including, field- and temperature-dependent resistivity, Hall effect and magneto-resistance [8], and the influence of chemical order on the magnetization properties [7, 9]. The evidence is that magnetic order is strongly dependent on chemical order, since as the structure disorders into the B_2 structure, the minimum distance between Mn atoms decreases. The band structure of Pd_2MnIn has been calculated [6], but as yet there has been no direct experimental investigation of the band structure.

Synchrotron radiation excited ultraviolet photoemission spectroscopy has been widely used to probe the electronic structure of elements and alloys, and is a standard method for investigating the validity of band structure calculations [10]. In Pd_2MnIn , the valence band photoemission spectra will be dominated by transitions from the Mn 3d and Pd 4d states since the photoionization cross-sections for the s and p states are comparatively low. Hence, the valence band spectrum, $S(h\nu, E_B)$, can be described by

$$S(h\nu, E_B) = C(h\nu) [N_{\text{Pd}}\sigma_{\text{Pd}}(h\nu)D_{\text{Pd}}(E_B) + N_{\text{Mn}}\sigma_{\text{Mn}}(h\nu)D_{\text{Mn}}(E_B)] \quad (1)$$

where $h\nu$ is the photon energy, E_B is the binding energy of the initial state, and $C(h\nu)$ includes factors to account for the photon flux, escape depth, detector efficiency and reflection and refraction of the photon beam at the sample [11, 12]. The latter term is technically also a function of E_B , but the effect is weak and it will not significantly affect the shape of the valence band spectrum. N_{Pd} and N_{Mn} represent the fractional contribution of d electrons supplied by each element to the density of states, the quantities $D_{\text{Pd}}(E_B)$ and $D_{\text{Mn}}(E_B)$ are the normalized partial density of states of the Pd 4d and Mn 3d respectively, and $\sigma_{\text{Pd}}(h\nu)$ and $\sigma_{\text{Mn}}(h\nu)$ are the photoionization cross-sections neglecting variations across the band.

Identification of the partial density of states associated with each element in an alloy is facilitated by some important effects that utilize variable photon energy. Photoemission transitions from 4d or 5d metals such as Pd and Pt to particular final states produce a characteristic minimum in the cross-section, known as the Cooper minimum [13], which is due to the cancellation of matrix element integrals. In the Pd_2MnIn alloy, excitation energies corresponding to the region of the Pd 4d Cooper minimum will enhance relatively the contribution from transitions arising from Mn 3d derived states. In the case that the Pd 4d cross-section at the Cooper minimum can be considered negligible in comparison with that for Mn 3d, then σ_{Pd} in equation (1) can be taken as zero and the spectrum will reflect the shape of the Mn 3d partial density of states.

Resonant photoemission is a complementary technique that similarly utilizes the tunable radiation associated with a synchrotron source and that may be employed to investigate the contribution from Mn 3d derived states. At photon energies near the 3p threshold, photoemission from a 3d state can occur either directly, or via promotion of a p electron to an unoccupied d state followed by autoionization. The interference of the direct and indirect processes results in a characteristic modulation in photoemission intensity from regions of the valence band possessing Mn 3d character. The lineshape has been described by Fano [14], in which the modulated photocurrent, $I_{\text{mod}}(h\nu, E_B)$, can be expressed as

$$I_{\text{mod}}(h\nu, E_B) = I_r(h\nu, E_B) \left[\frac{\{q(E_B) + \varepsilon(h\nu, E_B)\}^2}{1 + \varepsilon(h\nu, E_B)^2} \right] + I_{\text{nr}}(h\nu, E_B) \quad (2a)$$

where

$$\varepsilon(h\nu, E_B) = \frac{2[h\nu - h\nu_0(E_B)]}{\Gamma(E_B)}. \quad (2b)$$

Here, $I_r(h\nu, E_B)$ and $I_{nr}(h\nu, E_B)$ represent the resonant and non-resonant photoemission intensities respectively. The parameters characterizing the lineshape are the resonance energy, $h\nu_0(E_B)$, the asymmetry parameter, $q(E_B)$, and the spectral width, $\Gamma(E_B)$. The shape and intensity of a resonance are influenced by the degree of initial state hybridization [15–17], and so quantitative analysis of resonant lineshapes can provide information on the localization of states.

The aim of the research described in this paper was to utilize the methods outlined above to provide information on the valence band electronic structure of the antiferromagnetic Heusler alloy Pd₂MnIn. In particular, the Pd 4d Cooper minimum and the Mn 3p to 3d resonance was employed to investigate the partial density of states for the Mn 3d band, as it is the Mn sites that carry the magnetic moment. The results are discussed in the context of earlier photoemission studies of Heusler alloys and available band structure calculations.

2. Experimental details

A slug of Pd₂MnIn was prepared by melting the appropriate quantities of the high-purity constituent elements in an argon arc furnace. It was then annealed in an evacuated quartz ampoule at 1000 K for 48 h, followed by cooling at 1 K h⁻¹ to below the order–disorder transition temperature of 880 K, and then finally it was cooled at 1 K min⁻¹ to room temperature; this is a recipe that had previously been shown to produce the *L2*₁ structure [7]. The structure was then verified by x-ray diffraction. The slug was machined by spark erosion to a useable shape and the front face was polished to a final finish of 1 μm using diamond paste. The sample was then cleaned by immersion in degreasing solvents. Cleaning *in situ* was effected by scraping the surface using a diamond file mounted on a wobble stick, to ensure that the oxidized layer was completely removed. The elemental composition of the surface was investigated by Auger electron spectroscopy before and after scraping, and it was found that the cleaning process had produced a surface that was close to stoichiometric.

Photoemission measurements were performed under conditions of ultrahigh vacuum on beamline 6 at the Synchrotron Radiation Source, Daresbury [18]. An angle-integrated, double-pass cylindrical mirror analyser was employed with a pass energy of 10 eV to detect and energy sort the emitted electrons. The detector was aligned at 90° to the incoming photon beam, and the photon flux was monitored by measuring the drain current from a tungsten mesh to enable spectrum normalization.

Electron energy distribution curves were obtained by detecting a range of electron kinetic energies at constant photon energy. Binding energies were then referenced to the Fermi level (E_F), which was assigned a value of zero. The experimental resolution in the photon energy range 40–70 eV was previously [19] estimated to be 0.2 eV HWHM (half width at half maximum). Two types of experiments were performed: in the first experiment the photoemission spectrum was collected at the Cooper minimum for Pd and at another photon energy well away from it. In the second, electron energy distribution curves were collected in small photon energy increments through the Mn 3p to 3d resonance.

3. Results and discussion

A typical electron energy distribution curve is shown in figure 1(a). It was collected at a photon energy of 80 eV, where the contributions from states derived from the Pd 4d and Mn 3d orbitals will dominate the other valence states by virtue of having a much larger cross-section [20]. The Fermi level is well replicated in the spectrum, but the region of highest density of states is to be found between 2 and 6 eV below the edge. At this energy, the spectrum will actually mostly

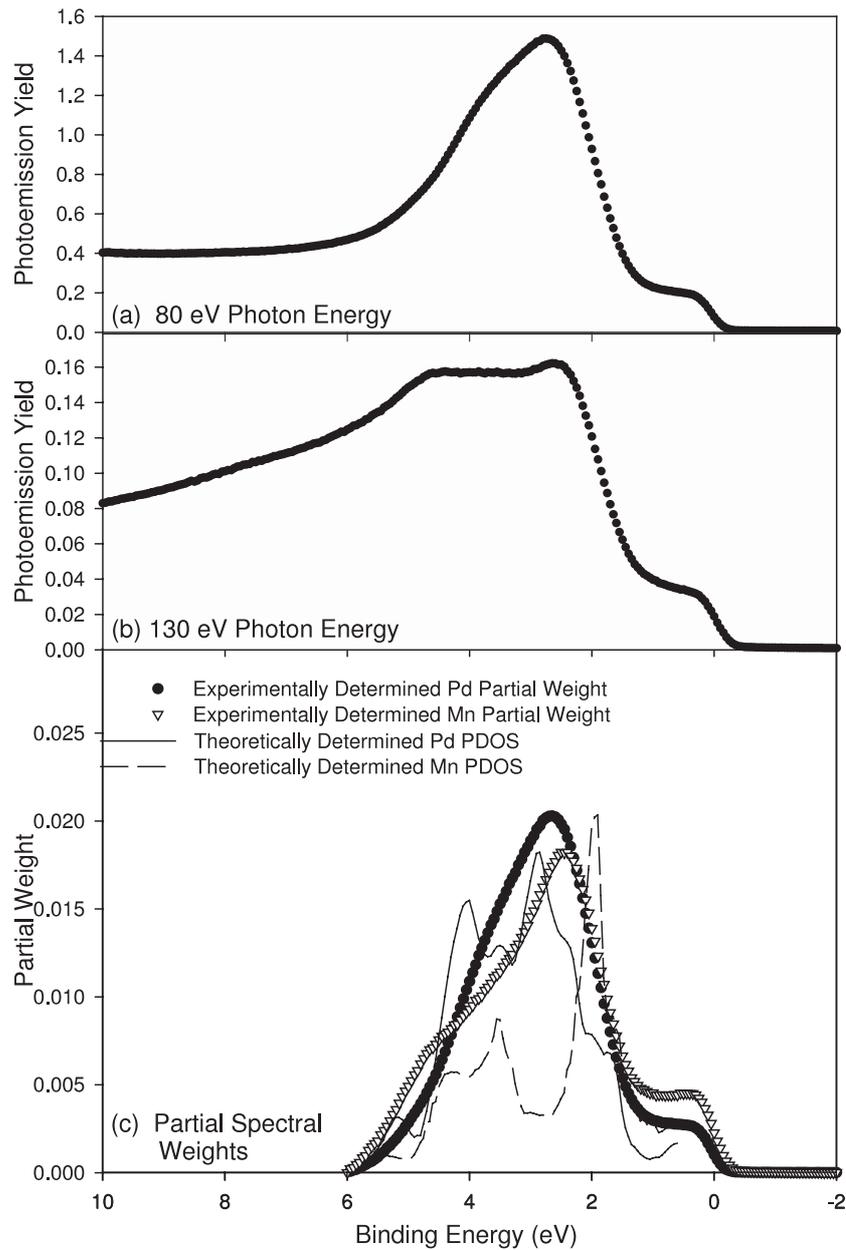


Figure 1. Photoemission from Pd₂MnIn. Part (a) shows the spectrum collected at 80 eV photon energy, well away from the Pd 4d Cooper minimum. Part (b) shows the spectrum collected at 130 eV photon energy, the Pd 4d Cooper minimum. Part (c) shows the partial spectral weights allocated to Pd 4d and Mn 3d determined using the method described in the text, and compared with the densities of states from [6] (Data excerpted with permission from Kübler *et al* [6], copyright 1983 by the American Physical Society).

reflect the full Pd 4d band as it contributes more d electrons per formula unit than the Mn 3d and it has a slightly larger cross-section.

Further information about the contributions of the Mn and Pd d electrons to the photoemission spectrum can be obtained by varying the photon energy. Figure 1(b) shows the spectrum obtained utilizing a photon energy of 130 eV, which is close to the Cooper minimum [21] for the Pd 4d. This spectrum will be dominated by the Mn 3d contribution as the cross-section for the Pd 4d is very low at this energy. The spectrum is clearly different in shape with a prominent feature emerging at a binding energy of 4.7 eV, which must correspond to a Mn 3d derived state.

To facilitate comparison of the data with the calculations of Kübler *et al* [6], we have used a procedure to extract the partial spectral weights that has been used previously [21]. Taking the spectrum at 130 eV energy to represent the partial density of states of Mn 3d, we have normalized it and subtracted it from the normalized spectrum collected using a photon energy of 80 eV. This relatively simple procedure is complicated by two factors. The first is that the photoemission cross-sections will differ between 130 and 80 eV, and this has been corrected using the calculations of Yeh and Lindau [20]. The second complication is that the yield from the W grid that is used to normalize the photoemission current varies with photon energy in a way that is not well known. The correct scaling factor was determined by applying the constraint that there are 20 d electrons associated with the Pd 4d and five associated with the Mn 3d. The precise details of this constraint only weakly affect the resulting spectral weights.

To remove the contribution arising from inelastic processes the two spectra had their background removed using the Shirley algorithm [22]. The procedure outlined in the last paragraph was then used to determine the partial spectral weights. The partial spectral weights associated with Pd 4d and Mn 3d derived states are shown in figure 1(c): the Mn contribution is indicated by open triangles and the Pd contribution by filled circles. Both have been normalized to give an integral of unity. Also shown in figure 1(c) is the partial density of d states of both elements calculated by the augmented-spherical-wave formalism by Kübler *et al* [6], adapted with permission to show the sum of the two spin contributions. It can be seen that there are strong similarities in the shapes of the curves. Such comparisons of spectral weights and band structure calculations can be informative, but it must be borne in mind that this procedure does not include matrix element effects in the photoemission transition [23] or small variations in escape depth across the band. Note that the complete overlap of the Mn 3d and Pd 4d can be seen in both calculation and experiment. Features in the experimental data will be broadened relative to the calculation by both intrinsic lifetime effects and extrinsic experimental effects [19], giving an overall Gaussian half-width of around 0.5 eV. The experiment shows similar bandwidths to those in the calculation and has similar features. The Pd 4d contribution maximizes at 2.7 eV binding energy with a shoulder at 4 eV, both corresponding to similar features in the calculated partial density of states. The Mn 3d contribution differs in shape maximizing at 2.45 eV and showing a shoulder at 4.7 eV. Both of these features correspond to peaks that are visible in the calculation, but shifted to slightly higher binding energy. The relative intensities of calculated and empirical weights are in reasonably good agreement.

The reliability of the Cooper minimum method rests on the requirement for the photoemission from all the Pd 4d states to be suppressed. However, there are several solid-state effects that will inhibit this effect. Bonding and anti-bonding states in Pd may exhibit differing photon-energy-dependent emission intensities [11], resulting in a different depth of minimum depending on binding energy. The initial state hybridization indicated by calculations will also reduce the magnitude of the minimum. For this reason it is informative to support the conclusions of a Cooper minimum analysis by using resonant photoemission, so a series of electron energy distribution curves was collected in the vicinity of the Mn 3p to 3d resonance. When the photon energy is equal to the difference between the binding energies of the 3p and the empty 3d states there is an enhancement of photoemission from filled 3d states. Figure 2

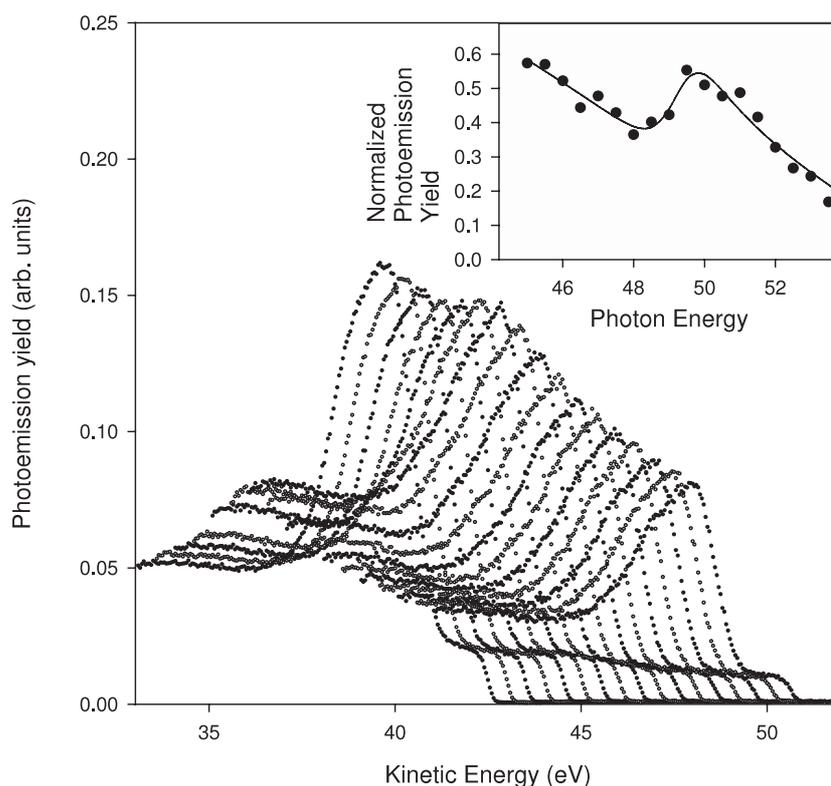


Figure 2. Photoemission from Pd_2MnIn for photon energies in the vicinity of the Mn 3p to 3d resonance. The inset shows the background-subtracted and normalized photoemission intensity at 4.7 eV binding energy with a Fano profile fitted to the data.

shows the raw curves collected for photon energies between 47 and 55 eV. The envelope of the curves clearly demonstrates the resonant enhancement at around 50 eV, which indicates that significant Mn 3d nature is retained in the alloy: the stronger the resonance the more localized and atomic-like the initial state.

It is useful to compare the curve obtained at the resonance maximum with that in the minimum before the resonance ('on' and 'off' resonance). As the resonant photoemission pathway decays into the inelastic background, causing it to exhibit the same variation in intensity, it is necessary to first remove this background using the Shirley method referred to above. To make a good comparison, it is also necessary to adjust the intensity to account for variations in photoemission cross-section and yield from the W grid. This was done by recording the In 4d levels within the same spectra and adjusting the intensity of these to fit the calculated variation in cross-section [20] with photon energy. This procedure is slightly complicated by the maximization in the In cross-section at around 50 eV, but it appears to be reliable. The on- and off-resonance spectra are shown together in figure 3 in comparison with the calculated Mn 3d partial density of states. It can be seen that there is a difference in shape between the two spectra, with the on-resonance peak showing enhancement near both of the main features in the calculated curve, at 2.5 and 4.7 eV binding energies. Both of these are entirely consistent with the Mn partial spectral weight as determined using the Cooper minimum method.

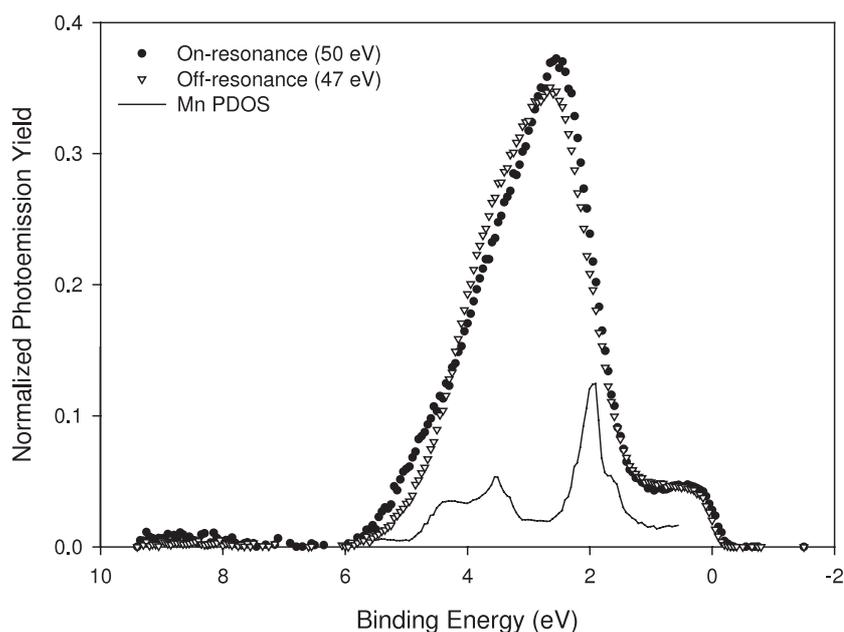


Figure 3. Background-subtracted photoemission from Pd₂MnIn showing both the on-resonance (filled circles) and off-resonance (open triangles) photon energies. The data are compared with the Mn 3d density of states adapted from [6] (Data excerpted with permission from Kübler *et al* [6], copyright 1983 by the American Physical Society).

The measured intensity of the Mn 3p to 3d resonance can be related to the degree of localization of the Mn 3d states. Quantitative analysis of resonances in similar compounds has been used to infer atomic-like or hybridized nature of the states. For example, Robey *et al* [24] analysed Ni₂MnSb by resonant photoemission, and associated relatively strong resonant features with weakly hybridized states. In the limit of no hybridization, resonances associated with Mn 3d derived states were stated to be characterized by q -values in the range 2.2–2.5, as found for atomic Mn [25]. More strongly hybridized states were associated with weaker resonances, and gave q -values that were significantly lower.

To investigate the resonance in Pd₂MnIn more quantitatively, a Fano analysis was performed on the resonant lineshape of the feature at 4.7 eV binding energy. Prior to fitting, the data were carefully prepared by removing the inelastic background. The intensity from the 4.7 eV feature was then extracted and is shown in the inset to figure 2. The fit to the data was then performed using equation (2) with a linear non-resonant contribution. The Fano parameters that were extracted are listed in table 1. The resonance energy, $h\nu_0$, of 49.3 ± 0.2 eV is typical of such compounds. The asymmetry parameter, q , which has a value of 1.6 ± 0.4 , suggests that there is a good deal of hybridization between the bands as indicated by the calculations of Kübler [6]. Thus, although Heusler alloys are often quoted as model examples of systems with localized moments, the occupied Mn 3d states cannot be described as localized.

4. Conclusions

The full, ordered, antiferromagnetic Heusler alloy Pd₂MnIn has been investigated using photoelectron spectroscopy. The shape of the photoelectron spectrum is consistent with the

Table 1. Parameters obtained from the fit to Pd₂MnIn photoemission data at the Mn 3p to 3d resonance.

Fano parameters	Value
$h\nu_0$ (eV)	49.3 ± 0.2 eV
q	1.6 ± 0.4
Γ (eV)	2.1 ± 0.5 eV

density of states calculated by Kübler *et al* [6]. The partial spectral weights of both the Pd 4d and Mn 3d derived states have been investigated using both the Copper minimum effect and resonant photoemission, and both methods have been shown to be both self-consistent and consistent with the published calculations. Finally, a fit to the Mn 3p to 3d resonance profile has shown that the occupied Mn 3d states are relatively delocalized.

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