

The experimental density of states of Pd 4d and Ti 3d in the intermetallic compound **Pd₂TiAl**

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 3955

(<http://iopscience.iop.org/0953-8984/8/21/020>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.206

The article was downloaded on 13/05/2010 at 18:23

Please note that [terms and conditions apply](#).

The experimental density of states of Pd 4d and Ti 3d in the intermetallic compound Pd₂TiAl

A J Liddiard, D Brown, M D Crapper†, M Petty, J G Smith, N D Telling, K H Bedwell, L B Flannery and P A Skull

Physics Department, University of Technology, Loughborough LE11 3TU, UK

Received 20 November 1995

Abstract. Photoemission measurements have been made of the intermetallic compound Pd₂TiAl utilizing synchrotron radiation in the energy range 40–180 eV. The valence band extends to a binding energy of 7 eV. Measurements made at the Cooper minimum for Pd 4d indicate that the highest density of states for Ti 3d is at the Fermi edge and that it decreases towards higher energy. Using this density of states and correcting for the photoemission cross-sections with energy, it has been possible to determine the density of states for Pd 4d which also contributes to the Fermi level. Resonance photoemission measurements are consistent with this conclusion and also indicate that the Pd 4d band is not completely full.

1. Introduction

The intermetallic compounds Pd₂TiZ have been the focus of a great deal of experimental and theoretical work recently [1–3] because magnetic ground states have been reported for compounds where Z = In, Sn or Al. In the case of Pd₂TiAl, ferromagnetic ordering with a moment of $(0.210 \pm 0.005) \mu_B$ per formula unit has been observed [2]. It is unusual, but not unknown, for compounds that do not contain a magnetic element to order ferromagnetically. Examples of such materials are Sc₃In [4], Au₄V [5] and ZrZn₂ [6], and these have been classified as weak itinerant ferromagnets. Such a classification is not appropriate to Pd₂TiAl as it appears to have a high Curie temperature. The origin of the reported magnetic behaviour of this new compound has been the subject of discussion, but as yet no definitive explanation has been forthcoming.

Pd₂TiAl forms a single-phase and highly ordered Heusler L2₁ structure with a lattice parameter of 6.322 Å. It has been the subject of studies using magnetometer measurements [1] and its band structure has been calculated using LMTO methods [3]. The calculations do not reveal the origin of the magnetic behaviour, but a model has been proposed recently [7] that suggests that a small moment may be carried by both the Pd and the Ti atoms, with the Pd possibly having a slightly unfilled 4d band (although still close to 4d¹⁰). It is clear that the origin of the reported magnetic behaviour must be in the detailed electronic structure, but to date no direct experimental investigation of this electronic structure has been carried out.

Ultraviolet photoemission spectroscopy (UPS) is a powerful method for the investigation of the electronic structure of metals [8]. It allows comparison to be made between calculated and experimental band structures and has been applied to many alloys and intermetallic

† To whom any correspondence should be addressed.

compounds. Two features of UPS, utilizing the variable photon energy available with synchrotron radiation, make it particularly useful for the study of 4d and 3d elements. The photoemission cross-sections of 4d elements show a pronounced minimum at photon energies around 100 eV. This is known as a Cooper minimum [9, 10]. Measurements at this minimum allow the contribution from other d states of the alloy to be investigated (the large cross-section of d states relative to s and p bands means that they dominate the photoemission spectrum). The other valuable feature is resonant enhancement of emission from a d band caused by a coherent p-to-d transition when the photon energy is equal to the binding energy of the p state [11, 12]. The resonant behaviour of 3p-to-3d excitations is particularly pronounced, but similar effects are also observed for 4p-to-4d excitations. Thus, UPS is particularly suited to the investigation of the Pd 4d and the Ti 3d states in Pd₂TiAl.

In this paper, we report the first photoemission investigation of the Pd₂TiAl intermetallic compound [13]. We have used Cooper minimum effects to identify the contributions of the Pd and Ti d bands to the density of states and resonant photoemission to verify these conclusions.

2. Experimental details

A specimen of Pd₂TiAl was prepared from rods of the constituent elements of better than 99.99% purity (Johnson–Matthey). The correct proportions of these elements were repeatedly melted in an argon arc furnace to produce an ingot with a mass of around 10 g. A loss of mass of less than 0.1% was recorded in this process. The ingot was then cut using spark erosion into a sample of dimensions 7 × 15 × 2 mm. The front face of this sample was polished using successive grades of diamond paste to a final finish of 0.1 μm. After this polishing, the sample was mounted securely onto a stainless-steel platen, which was then attached to a UHV sample manipulator.

The experiments were performed at the SRS Daresbury on stations 6.1 [14] and 6.2 [15], which are dedicated surface-science photoemission stations. Station 6.1 is equipped with a plane grating monochromator which provides a useful photon energy range of 40 to 180 eV. The resolution is determined by the monochromator exit slit and varies from a resolution of 100 meV at a photon energy of 80 eV, falling to around 300 meV at 140 eV. The base pressure throughout the measurements was 1×10^{-10} mbar. Station 6.2 is a two-level turbo-molecular pumped system with a base pressure of 5×10^{-11} mbar. Ultraviolet monochromatization is achieved using one of two toroidal gratings: 1800 lines mm⁻¹ or 700 lines mm⁻¹. The beamline has two Pt-coated SiC mirrors, and a Au-coated post-focusing mirror, and delivers around 10¹¹ photons per second. It has an energy resolution of 0.08 eV at low energy reducing to 0.24 eV at high energy. In both stations, the experiment was performed with an angle of incidence of 45°. Photoelectron energy analysis was performed using a Physical Electronics double-pass cylindrical-mirror analyser (CMA) that was aligned at 90° to the direction of the photon beam.

Mechanical *in situ* cleaning was used for all of the experiments reported here. For the measurements on station 6.1 a small brush with tungsten bristles was used, whilst for the 6.2 measurements files comprising diamond embedded in electro-deposited nickel were used. In each case the sample surface was mechanically abraded initially for around ten minutes to remove the surface oxide and then repeatedly every few hours for around thirty seconds to remove adsorbed contaminants. Surface cleanliness was monitored using Auger electron spectroscopy and no major contamination problems were found.

Following surface cleaning, photoemission spectra were collected for a variety of

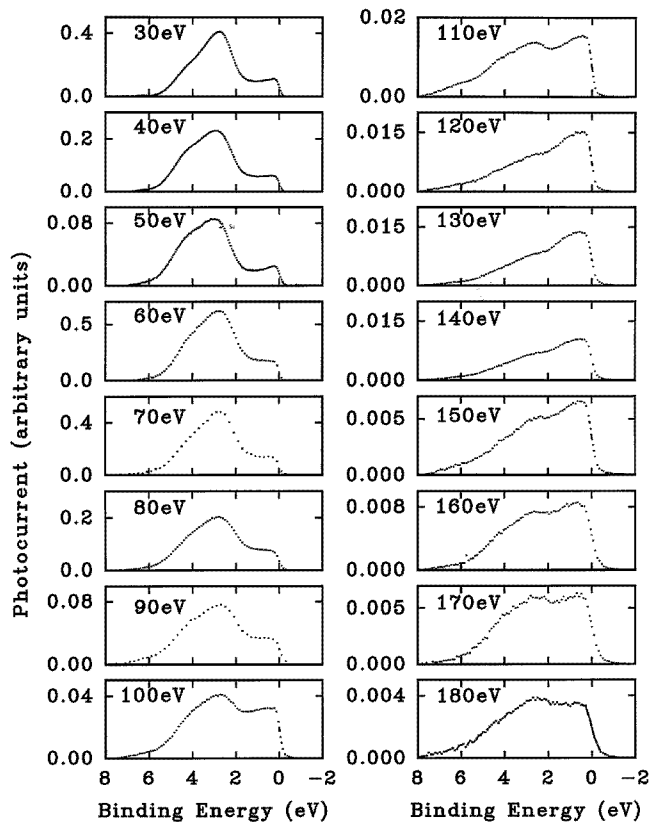


Figure 1. Electron energy distribution curves collected from Pd₂TiAl for photon energies between 30 and 180 eV. The curves have had the inelastic background subtracted.

experimental conditions. Electron energy distribution curves (EDC) were collected for photon energies between 20 and 180 eV. Constant-initial-state (CIS) studies of certain features were also made. For experiments on both photoemission stations, both types of spectra were collected over a period of several days. This allowed the possibility of error to creep in, owing to variations in precise beam conditions and small differences in channel electron multiplier potential, etc. For this reason, the photocurrents in all of the EDC spectra reported here have been adjusted so that they are consistent with the CIS spectra. The CIS spectra represent measurements at various photon energies made under the same conditions in a short space of time, and therefore they are ideal for correcting EDC spectra made at different photon energies at different times. The photon flux was always monitored using a tungsten mesh on both stations, and the spectra reported here have all been normalized to this flux.

3. Results and discussion

Photoemission spectra collected from the Pd₂TiAl ingot can be seen in figure 1. These are EDCs collected at photon energies between 30 and 180 eV photon energies in 10 eV steps. The 30, 40 and 50 eV spectra were collected on station 6.2 and the rest were collected on

station 6.1. The EDCs have been background subtracted using a Shirley-type algorithm [16].

The EDCs shown in figure 1 show valence band structure extending to a binding energy of around 7 eV. The spectra will be dominated by photoemission from the Pd 4d and the Ti 3d states as all the other states have a much lower cross-section [17]. It can be seen that the spectra exhibit a dominant feature centred at 3 eV binding energy. This feature is strong at 80 eV photon energy but falls to a minimum at around 130 eV photon energy. This behaviour is consistent with photoemission from a Pd 4d state which has a maximum cross-section at around 70 eV [17] and a Cooper minimum at a photon energy of around 130 eV. Thus the photoemission structure at 130 eV must be dominated by transitions from the Ti 3d states and so reflect the Ti 3d density of states (DOS). It can be seen that the Ti-associated DOS has a maximum at the Fermi level and falls away at higher binding energies. This is consistent with band-structure calculations for this material [3].

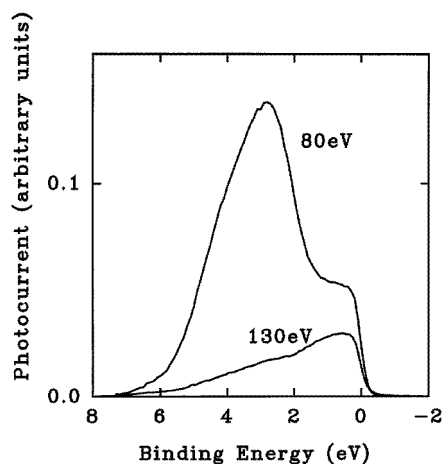


Figure 2. The background-subtracted electron energy distribution curves from Pd₂TiAl for photon energies of 80 eV and 130 eV following correction for the difference in Ti 3d photoemission cross-section between the two photon energies. 130 eV corresponds to the Cooper minimum for Pd 4d photoemission.

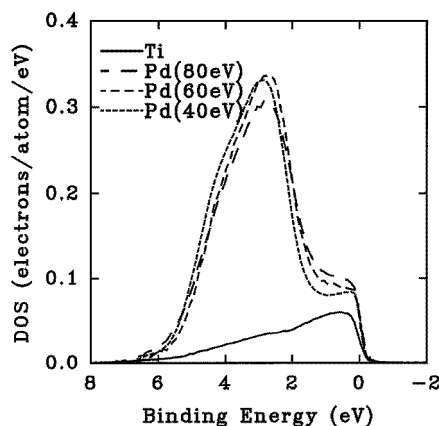


Figure 3. The experimental density of states of Ti 3d and Pd 4d in Pd₂TiAl determined from spectra collected at three different photon energies, assuming Ti 3d², Pd 4d¹⁰.

Using the Cooper minimum for Pd photoemission we can determine the DOS for the Pd 4d states using a technique previously employed by other workers [18]. In figure 2 the 130 and 80 eV photoemission spectra are shown following correction for the differing Ti 3d cross-sections at the two energies. At first sight, it would appear that a subtraction of one from the other would yield the Pd 4d contribution to the spectrum; however, the absolute photon flux for the two spectra is not known. The flux is monitored by a tungsten grid, but tungsten has strong photo-absorption structure in this energy region, so the beam monitor yield is a function of photon energy as well as flux. The optical photo-absorption of tungsten has been measured by several workers [19, 20], but it is not obvious that the drain current from the monitor will be exactly proportional to this. Measurements of the beamlines [21] indicate that correction for the absorption of tungsten will not yield the correct photon flux. There is also a possibility that the CMA transmission will also vary slightly with energy, even though it was operated with a constant pass energy. This inability to be sure about the absolute intensity of the spectra is not a problem, however, because the photon flux only

affects the intensity of a spectrum, not its shape. Thus we have only a single-parameter fit provided that we can constrain the density of states in some way [18]. The constraint that we have chosen is the number of d electrons expected to be associated with the Pd and Ti atoms. We have assumed that the Pd atoms will have ten d electrons and the Ti atoms two.

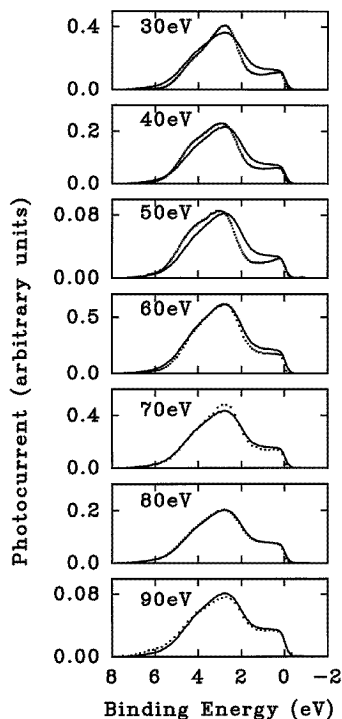


Figure 4. A comparison of the experimental electron energy distribution curves (\cdots) obtained from Pd_2TiAl with those calculated (—) from the DOS determined assuming Ti $3d^2$, Pd $4d^{10}$.

Figure 3 shows the density of states determined for Pd using the photoemission spectra collected at 40, 60 and 80 eV—far away from the Cooper minimum. These photon energies were selected because reliable cross-sections are known for them. In each case the spectra have been corrected for the change in photoemission cross-section of Ti from 130 eV and have been fitted so that the integral of the DOS fits the above constraints. The experimental densities of states are remarkably consistent. The shapes of both the Ti $3d$ states and the Pd $4d$ states are similar to those that have been calculated [3]. It can be seen that the Fermi level has a contribution from Pd $4d$ in addition to that from Ti $3d$.

To verify that the DOS that have been determined do conform to those for Pd and Ti, the DOS obtained from the 80 eV spectrum have been used to calculate the expected photoemission spectra at energies between 30 and 90 eV—the energy range where the calculated cross-sections are likely to be most accurate. Again, these spectra have been fitted using a single parameter to account for the photon flux variation. The spectra calculated from the Pd and Ti DOS are shown in figure 4. These calculated spectra show good agreement with the actual data and, in particular, do not differ greatly in shape.

The experimentally determined DOS reported here is very similar in shape to that calculated by Jezierski [3]. Figure 5(a) shows the total DOS calculated for ordered Pd_2TiAl . The solid curve in figure 5(b) shows the calculated DOS after broadening to account for

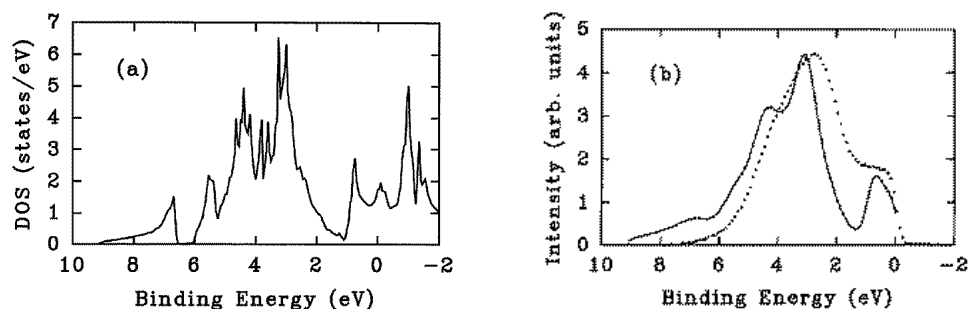


Figure 5. A comparison of the experimental and calculated DOS. (a) The total DOS calculated by Jeziarski [3] (adapted with permission). (b) The calculated DOS after broadening (solid curve) in comparison with the experimental DOS (closed circles).

lifetime effects and finite instrumental resolution. Lifetime broadening was accounted for by convolution with Lorentzians of half-width at half-maximum (HWHM) increasing, in proportion with the square of the binding energy, from 0 eV at E_F to 0.6 eV at the bottom of the band [22]. Instrumental broadening was accounted for by convolution with a Gaussian of HWHM equal to 0.2 eV. The closed circles in figure 5(b) represent the experimental DOS obtained from the photoemission spectra at 80 and 130 eV. In comparing photoemission results with band-structure calculations it must be borne in mind that photoemission probes an excited state, not the ground state. A photoemission transition creates a hole that interacts with the surrounding electrons. Depending on the level of screening and degree of localization, this can change the measured initial-state energy by a significant fraction of an electron volt. It is necessary to be aware of this effect when making direct comparison of the photoemission results and a band-structure calculation. However, the overall shape of the experimental DOS agrees well with the calculations. In particular, we can observe the features at 0.7 eV and 3.2 eV. The feature at approximately 7 eV binding energy in the calculated DOS is due to the s states of Al and is, therefore, not observed in our experimental DOS.

The binding energy of the Ti 3p electrons is at 32.6 eV. It would therefore be expected that the photoemission probability of the Ti 3d electrons would show a resonant enhancement at photon energies close to this value. Figure 6 shows a CIS measurement made for a binding energy of 0.6 eV. This spectrum shows a weak enhancement at a photon energy of 36 eV which we ascribe to a resonance event. Resonance events are also observed at larger binding energies, but with less intensity. The increased magnitude of the resonance for small binding energies confirms that the Ti 3d DOS is largest near the Fermi level.

Figure 7 shows CIS measurements made at binding energies of 0.8 and 5 eV, corresponding to the near-Fermi-edge region and the large peak in the density of states, for the energy range 45–85 eV. Both quite clearly show an enhancement commencing at around 54 eV. The 4p binding energies of Pd are 50.9 eV and 55.7 eV, so any enhancement arising from a 4p-to-4d resonance in the Pd will show up here. The fact that resonant enhancement is seen indicates that the Pd d band is not completely full, and the enhancement near the Fermi edge shows that the Pd 4d contributes here. This fits in well with the determination of the Pd DOS from the EDC measurements and with the proposed model for Pd₂TiAl suggesting that the Pd 4d band is not full.

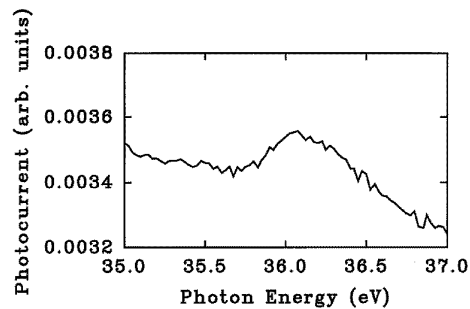


Figure 6. The CIS measurement of the photocurrent obtained for a binding energy of 0.6 eV from Pd₂TiAl, in the photon energy region of the Ti 3p-to-3d resonance.

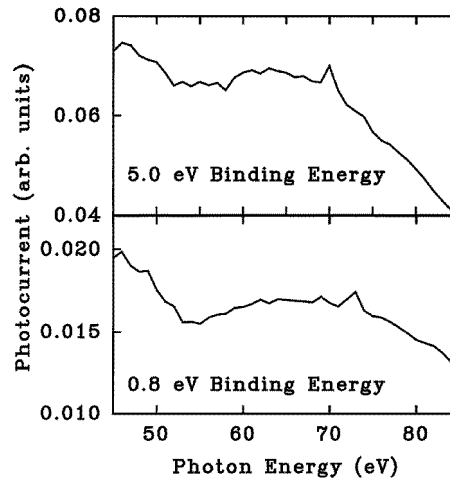


Figure 7. CIS measurements for Pd₂TiAl made at binding energies of 0.8 and 5 eV for the energy range 45–85 eV.

4. Conclusion

Photoemission measurements of the intermetallic alloy Pd₂TiAl have been made using synchrotron radiation. Use of the Pd 4d Cooper minimum has allowed determination of the DOS of the Ti 3d and Pd 4d states. Pd 4d shows a large DOS centred at a binding energy of 3 eV but with a shoulder extending to the Fermi level. The DOS of Ti 3d is a maximum at the Fermi level, but extends the full width of the EDC spectrum. Resonance photoemission measurements are consistent with these conclusions and indicate that the Pd 4d band is not completely full.

Acknowledgments

This work was supported by the EPSRC under SRS grant numbers 23/119 and 25/170. Thanks are due to Klaus Neumann and Kurt Ziebeck for valuable discussions and advice. Thanks are also due to Nadum Zayer for producing the ingot and Andrzej Jezierski for sending us pre-publication data. We would also like to thank Dave Teehan, Stuart Downes, Bruce Cowie and Ron Hearsey for their invaluable assistance at Daresbury.

References

- [1] Neumann K-U, Crangle J, Smith J G, Zayer N K and Ziebeck K R A 1994 *J. Magn. Magn. Mater.* **137** 264
- [2] Neumann K-U, Crangle J, Smith J G, Zayer N K and Ziebeck K R A 1995 *J. Magn. Magn. Mater.* **140–144** 185
- [3] Jezierski A 1995 *Phys. Status Solidi b* **190** 471
- [4] Matthias B T, Clogston A M, Williams H J J, Corenzwit E and Sherwood R C 1961 *Phys. Rev. Lett.* **7** 7
- [5] Craveling L, Luo H L and Knapp G S 1967 *Phys. Rev. Lett.* **18** 851
- [6] Matthias B T and Bozorth R M 1958 *Phys. Rev.* **109** 604
- [7] Neumann K U, Lipinski S and Ziebeck K R A 1994 *Solid State Commun.* **91** 443

- [8] Feuerbacher B, Fitton B and Willis R F 1978 *Photoemission and the Electronic Properties of Surfaces* (Chichester: Wiley)
- [9] Cooper J W 1962 *Phys. Rev.* **128** 681
- [10] Cole R J, Evans J A, Duò L, Laine A D, Fowles P S, Weightman P, Mondio G and Norman D 1992 *Phys. Rev. B* **46** 3747
- [11] Fano U 1961 *Phys. Rev.* **124** 1866
- [12] Barth J, Gerken F and Kunz C 1985 *Phys. Rev. B* **31** 2022
- [13] A preliminary report of this work was published in Liddiard A J, Crapper M D, Telling N D, Skull P A, Petty M, Zayer N K, Smith J G, Neumann K U and Ziebeck K R A 1995 *J. Magn. Magn. Mater.* **140–144** 187
- [14] Bailey P and Quinn F M 1993 *SERC Daresbury Laboratory Technical Memorandum DL/SCI/TM94E*
- [15] Turner T S and Teehan D 1985 *SERC Daresbury Laboratory Technical Memorandum DL/SCI/TM85E*
- [16] Shirley D A 1972 *Phys. Rev. B* **12** 4709
- [17] Yeh J J and Lindau I 1985 *At. Data Nucl. Data Tables* **32** 1
- [18] Wright H, Weightman P, Andrews P T, Folkerts W, Flipse C F J, Sawatzky G A, Norman D and Padmore H 1987 *Phys. Rev. B* **35** 519
- [19] Weaver J H and Olsen C G 1976 *Phys. Rev. B* **14** 3251
- [20] Haensel R, Radler K, Sonntag B and Kunz C 1969 *Solid State Commun.* **7** 1495
- [21] Downes S W, private communication
- [22] Winter H, Durham P J, Temmerman W M and Stocks G M 1986 *Phys. Rev. B* **33** 2370