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## Experimental determination of the partial density of states for the binary alloys Pt<sub>3</sub>V and Pt<sub>3</sub>Mn

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**Abstract.** The valence band electronic structure of the intermetallic compounds Pt<sub>3</sub>V and Pt<sub>3</sub>Mn has been investigated by means of synchrotron radiation ultraviolet photoemission. The spectra exhibit band structure extending to approximately 8 eV below the Fermi level for each alloy. Utilizing the Cooper minimum in the Pt 5d photoionization cross-section, the partial densities of states have been empirically determined. The results indicate that the d bands of the constituent metals completely overlap. The V 3d states contribute most strongly to the valence band immediately below the Fermi level. In contrast, the highest occupied density of states for the Mn 3d band lies approximately 2.6 eV below the Fermi level. For Pt<sub>3</sub>Mn, 3p to 3d resonant photoemission confirms the results obtained at the Pt 5d Cooper minimum. However, no clear evidence for a corresponding V 3p to 3d resonance was observed in Pt<sub>3</sub>V. This may indicate that the V d states in Pt<sub>3</sub>V are significantly less localized than the Mn d states in Pt<sub>3</sub>Mn. The empirical results for each alloy have been compared with theoretical calculations from the literature and provide good agreement in each case.

### 1. Introduction

Alloys of composition Pt<sub>3</sub>X, where X is a first-row transition element, have been widely studied experimentally [1–6] and theoretically [7–12]. They provide model systems for the investigation of magnetic ordering and are useful in the evaluation of energy band calculation schemes. The alloys have an *L*<sub>1</sub><sub>2</sub> (Cu<sub>3</sub>Au-type) structure with four interpenetrating simple cubic sub-lattices, three occupied by Pt atoms and one by atoms of element X. The band structures have been calculated by a variety of methods, including augmented plane wave (APW) [7], augmented spherical wave (ASW) [8], tight-binding (TB) [9], and linear muffin tin orbital (LMTO) [10, 11] schemes. However, there have been comparatively few attempts to elucidate the electronic structure by experimental methods. Recently, the valence band structure of the (110) surface of the Pt<sub>3</sub>Cr alloy has been investigated by means of ultraviolet photoemission employing angle integrating [13, 14] and angle resolving [15, 16] detectors. The aim of the present research has been to extend this investigation to polycrystalline ingots of the alloys Pt<sub>3</sub>V and Pt<sub>3</sub>Mn.

For orbitals with a radial node in the wavefunction, the cancellation of matrix element integrals for transitions to particular final states results in a minimum in the photoionization cross-section. This minimum, originally predicted by Cooper [17], has been widely used to determine the partial density of states for alloys comprising 4d or 5d metals such as Pd,

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Pt or Au [18,19]. For 3d metals, at photon energies corresponding to the 3p threshold, photoemission can occur either directly, or via promotion of a p electron to an unoccupied d state followed by autoionization. Interference of the direct and indirect processes results in a characteristic modulation in photocurrent [20]. Such 3p to 3d resonances can be used to identify contributions from corresponding 3d states within an alloy [19]. In the present study, reduction in the Pt 5d cross-section in the region of the Cooper minimum and modulations arising from 3p to 3d resonances have been exploited to provide information on the contribution of each constituent element to the density of states of Pt<sub>3</sub>V and Pt<sub>3</sub>Mn. The results are discussed in relation to previous experimental and theoretical studies.

## 2. Experimental details

The alloy samples, supplied by the Condensed Matter Group at Loughborough, were manufactured by argon arc melting the constituent metals. The samples were then annealed using procedures outlined in the literature for producing an ordered  $L1_2$  structure [2,4]. After manufacture, the samples were characterized by electron probe microanalysis and x-ray diffraction. Portions of the ingots to be used for photoemission measurements were cut to shape by spark erosion and the front faces polished to a final finish of 1  $\mu\text{m}$ . Samples were mounted on a stainless steel platen and the assembly was cleaned ultrasonically in degreasing solvents.

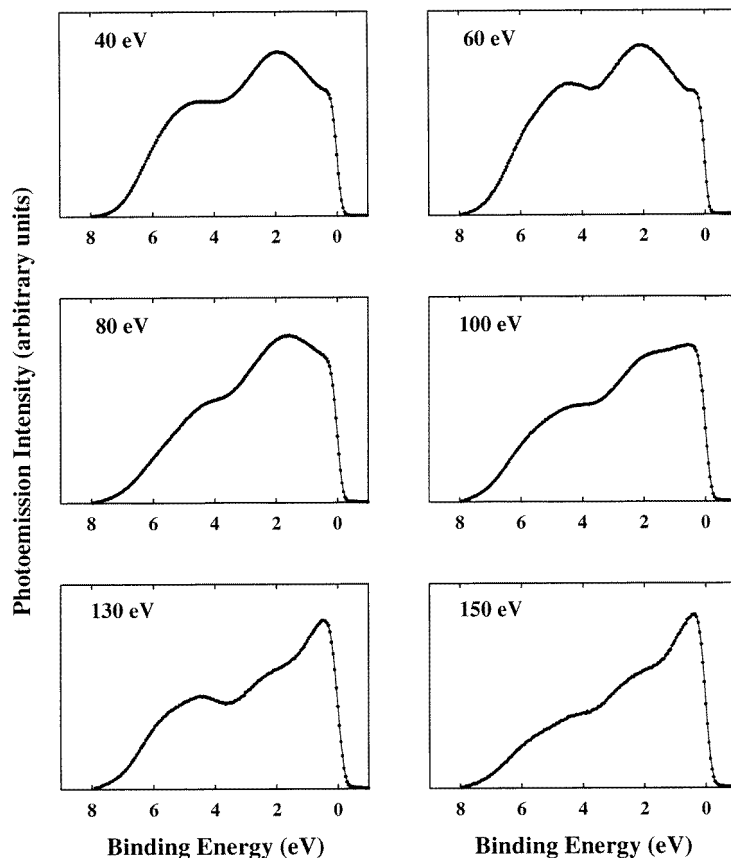
Ultraviolet photoemission was performed utilizing the second-generation 2 GeV synchrotron source at the Daresbury laboratory. Experimental measurements were performed under ultrahigh-vacuum conditions on stations 6.2 [21] and 6.1 [22], providing an accessible photon energy range of 15–140 and 40–200 eV respectively. Energy analysis of the emitted electrons was performed with an angle integrating double-pass cylindrical mirror analyser operated with a pass energy of 10 eV. The analyser was positioned at 90° to the incoming photon beam. Photon flux was monitored by measuring the drain current from a W mesh located between the monochromator and experimental chamber. All photoemission spectra were normalized to this flux.

Sample surfaces were cleaned *in situ* by scraping with a diamond file. Auger spectra from the scraped surfaces indicated a stoichiometry comparable to that of the bulk. No major problems with surface contamination were encountered, although a small residual C peak was observed in the Auger spectra even after vigorous scraping.

Electron energy distribution curves (EDCs) were obtained for each alloy in the photon energy range 20–180 eV. Binding energies were referenced to the Fermi level ( $E_F$ ), which was arbitrarily given a value of zero. A Shirley algorithm was used to remove the inelastic background from each EDC [23]. Spectra were initially obtained from different regions of each ingot and employing a range of take-off angles. However, no differences in spectral shape were observed and all reported spectra were obtained from the central area of the sample surface at a take-off angle of 45°. Constant-initial-state (CIS) measurements were obtained by synchronous variation of photon and detected electron kinetic energies. This allowed any modulations in photocurrent arising from p to d resonances to be investigated across the 3p thresholds of V and Mn.

## 3. Results and discussion

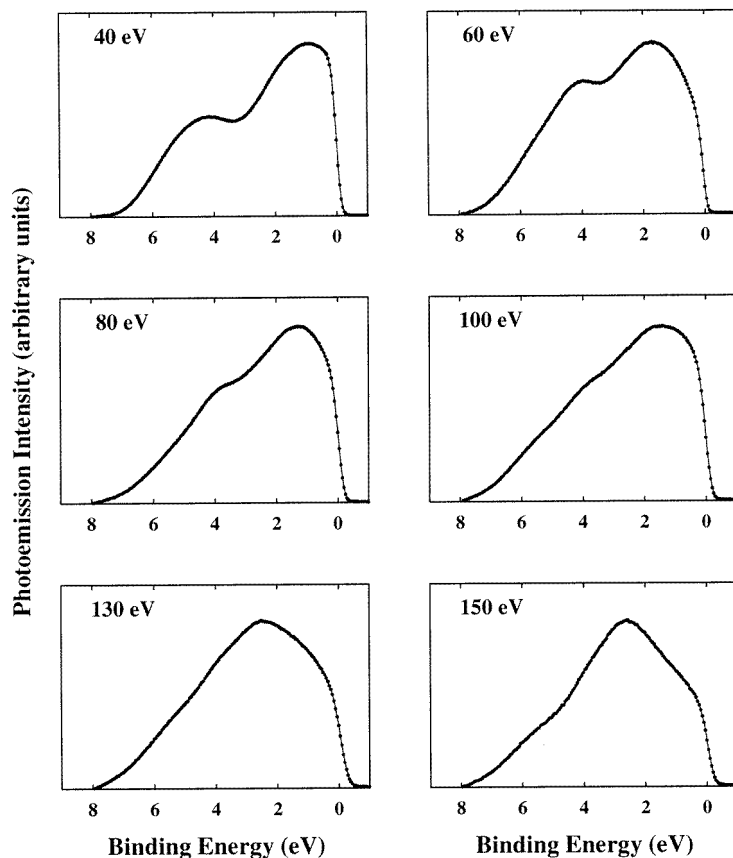
Valence band EDCs are shown at selected photon energies for Pt<sub>3</sub>V (figure 1) and Pt<sub>3</sub>Mn (figure 2). The photoemission spectra for the V alloy show band structure extending to



**Figure 1.** Electron energy distribution curves for the valence band region of the  $Pt_3V$  alloy. Photon energies in the range 40–150 eV were employed. Spectra have been normalized to account for variations in photon flux and the inelastic contribution has been removed.

8 eV below  $E_F$ . At lower excitation energies the spectrum exhibits two peaks at binding energies of approximately 4.5 and 1.9 eV and a shoulder immediately below the Fermi edge. The spectrum obtained at 40 eV is very similar to that obtained for tetragonal (TiAl<sub>3</sub>-type)  $Pt_3V$  with a fixed-energy source [24]. However, the shoulder is enhanced compared to the features at higher binding energies as the photon energy is increased and eventually resolves into a peak at a binding energy of 0.5 eV. The changes in spectral shape induced by increasing excitation energy are similar to those reported for  $Pt_3Cr$  [13]. The spectra for  $Pt_3Mn$  also indicate a valence bandwidth of 8 eV. At lower excitation energies the EDCs for the Mn alloy exhibit two peaks at approximately 4.2 and 1.0 eV binding energy. At excitation energies greater than 100 eV a new peak at a binding energy of 2.6 eV emerges and dominates the valence band spectra.

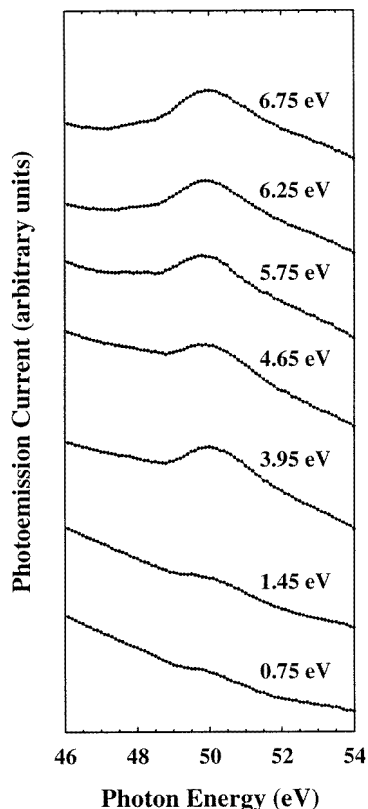
The variation in spectral shape with photon energy for both alloys can most plausibly be explained by consideration of the respective photoionization cross-sections. The spectra for both alloys will be dominated by transitions from the d bands [25]. At a photon energy of 40 eV the Pt 5d cross-section is far superior to that of the V or Mn 3d states. At 80 eV the cross-sections become almost comparable, so that spectra at this photon energy are most



**Figure 2.** Electron energy distribution curves for the valence band region of the  $\text{Pt}_3\text{Mn}$  alloy. Photon energies in the range 40–150 eV were employed. Spectra have been normalized to account for variations in photon flux and the inelastic contribution has been removed.

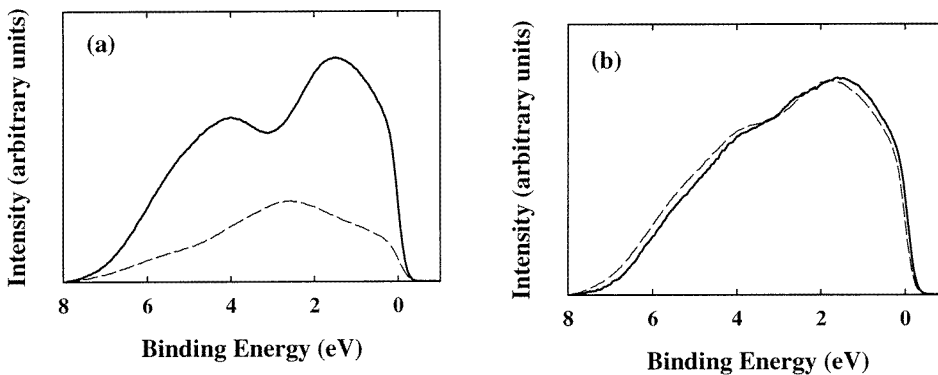
representative of the shape of the total density of states (DOS). However, at a photon energy of 150 eV, corresponding to the Cooper minimum for Pt 5d photoemission [26], transitions from the V or Mn 3d states will dominate. If the Pt 5d cross-section can be considered to be negligibly small by comparison, then the spectra at 150 eV will reflect the V or Mn 3d partial density of states (PDOS) for each alloy. Spectra obtained in the region 150–180 eV did not show any further change in spectral shape, indicating that the Pt Cooper minimum is fairly broad.

To further investigate the contributions from states with 3d character to the valence band spectra, CIS measurements were obtained across the region of the V and Mn 3p thresholds [27]. The results for  $\text{Pt}_3\text{Mn}$  are shown in figure 3. It can be seen that, at binding energies across the full width of the valence band, modulations in photocurrent are observed with maxima at approximately 50 eV photon energy. Assuming that the Pt 5d cross-section does not show any strong photon energy dependence across such a narrow range of excitation energies, the most likely explanation for the modulation is an enhancement of the Mn 3d contribution resulting from 3p to 3d resonant photoemission. Since the CIS



**Figure 3.** Constant-initial-state measurements in the region of the Mn 3p threshold for  $Pt_3Mn$ . Spectra have been normalized to account for photon flux, but retain the inelastic contribution. The spectra have been arbitrarily displaced along the ordinate for clarity and corresponding binding energies are indicated adjacent to each curve.

spectra retain an inelastic contribution, background subtracted EDCs were obtained at the resonance maximum (50 eV) and immediately below it (47 eV). This allowed any changes in spectral shape occurring on resonance to be more clearly demonstrated. The off- and on-resonance EDCs are shown as the solid curves in figures 4(a) and 4(b) respectively. The off-resonance spectrum exhibits two peaks separated by a clearly defined minimum at approximately 3 eV below the Fermi edge. In the case of the on-resonance spectrum, this minimum has almost completely disappeared. This indicates that the contributions from states lying approximately 3 eV below  $E_F$  are enhanced relative to the contribution from states closer to the top and bottom of the band. The broken curve in figure 4(a) shows the spectrum obtained at the Pt 5d Cooper minimum. In an attempt to crudely simulate the on-resonance spectrum, the spectrum obtained at the Cooper minimum has been arbitrarily scaled and added to the off-resonance spectrum. The procedure is similar to that used by other workers [28]. The resulting simulation will only provide good agreement if the 150 eV spectrum is representative of the Mn 3d PDOS and there are no significant differences in resonant intensity due to variations in hybridization across the band [28, 29]. The resulting fit of the data to the on-resonance spectrum is shown as the broken curve in figure 4(b).



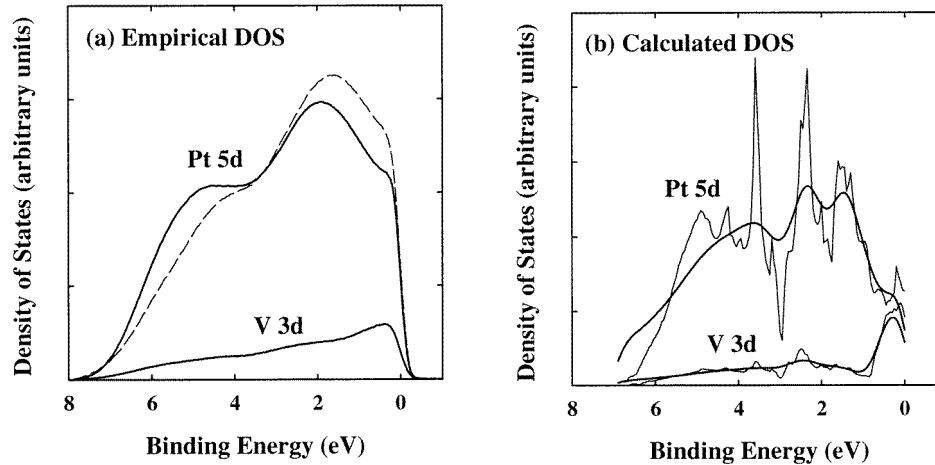
**Figure 4.** (a) The solid curve shows the background subtracted electron energy distribution curve obtained just below the Mn 3p to 3d resonance (47 eV). The broken curve shows the spectrum obtained at the Pt 5d Cooper minimum and is assumed to be representative of the Mn 3d PDOS. (b) The solid curve shows the background subtracted electron energy distribution curve obtained at the Mn 3p to 3d resonance maximum (50 eV). The broken curve is a simulation of the on-resonance spectrum obtained by arbitrarily adding the assumed Mn 3d PDOS to the off-resonance spectrum.

There is very good agreement between the two curves, suggesting that the assumed shape of the Mn 3d PDOS obtained from the Cooper minimum result is essentially correct.

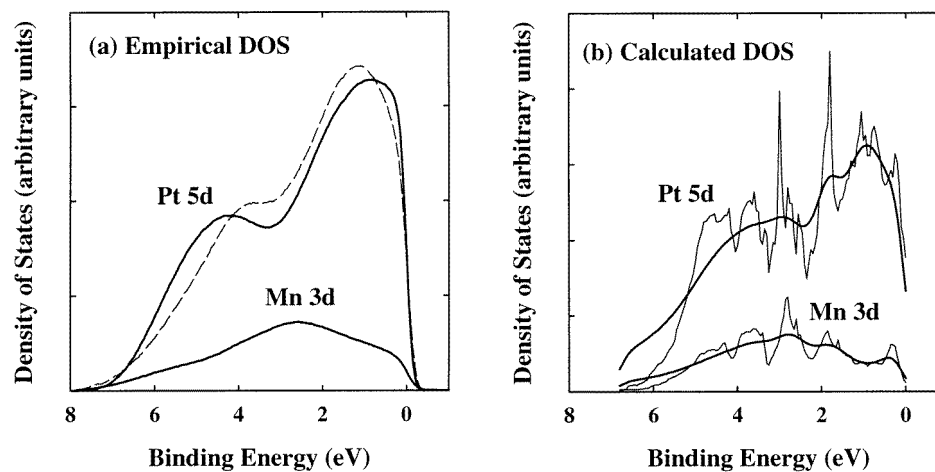
In contrast to Pt<sub>3</sub>Mn, CIS measurements for Pt<sub>3</sub>V across the region of the V 3p threshold did not reveal any clear modulations in photocurrent. Since the Pt 5d cross-section is greatly superior to that of V 3d across this photon energy range, it is possible that weak V 3p to 3d resonances might be masked by the dominant contribution from non-resonating Pt 5d states. However, this argument would be equally true for the Mn 3d states in Pt<sub>3</sub>Mn, where a clear, albeit weak, modulation is still observed. Although V 3d cross-sections are consistently lower than those of Mn 3d, and V will contribute fewer d electrons to the valence band, the absence of resonant modulation in Pt<sub>3</sub>V is still surprising. Initial-state hybridization is known to strongly influence the shape and intensity of a resonant lineshape, with strong resonances associated with states that are more localized in nature [28]. It is possible, therefore, that this result reflects differences in the degree of hybridization of the V and Mn 3d states for each alloy. Without further evidence, however, such a conclusion can only be speculative.

By utilizing spectra obtained at and well away from the Pt 5d Cooper minimum, it is possible to empirically determine the PDOS. The procedure adopted was essentially the same as that used by Wright *et al* for Cu<sub>3</sub>Pd [18]. The V and Mn 3d PDOSs were determined by assuming the contribution from Pt 5d states to be zero at 150 eV. The Pt PDOS was determined in each case employing spectra obtained at 40 and 80 eV and constraining the PDOS such that the sum across all binding energies was equal to the fractional contribution of d electrons supplied by each metal to the valence band. The average number of d electrons supplied per atom of V, Mn and Pt were taken to be 3.89, 6.02 and 8.74 respectively [30]. Differences in cross-section between the photon energies employed were accounted for using the calculated values of Yeh and Lindau [25].

The experimentally derived PDOSs for Pt<sub>3</sub>V and Pt<sub>3</sub>Mn are shown in figures 5(a) and 6(a) respectively. There are some differences in the detailed shape of the Pt 5d PDOS depending on the choice of excitation energy. These differences may be due to the fact that



**Figure 5.** (a) Experimentally determined partial density of states for  $Pt_3V$ . The V 3d band was determined assuming the Pt 5d cross-section to be zero at the Cooper minimum (150 eV). The Pt 5d band was determined using spectra obtained well away from the Cooper minimum at photon energies of 40 eV (solid curve) and 80 eV (broken curve). (b) Tight-binding calculations of the occupied partial density of states for  $Pt_3V$  before convolution (fine curves) and after convolution (bold curves). Details of the convolution procedure are described in the text. The results have been adapted from the original data of Tohyama *et al* [9].



**Figure 6.** The partial density of states for  $Pt_3Mn$  derived (a) experimentally and (b) from the tight-binding calculations of Tohyama *et al* [9]. Details are as described in the caption for figure 5.

no account has been taken of possible variations in cross-section across the band arising from solid state effects [26]. Although the empirical calculations cannot accurately reproduce the quantitative detail of the Pt 5d band, a qualitative interpretation is still possible. For each alloy, the 5d and 3d bands completely overlap and the Pt 5d PDOS has a large concentration of states in the region close to  $E_F$ . The V 3d band in  $Pt_3V$  exhibits the highest occupied density of states immediately below the Fermi edge, showing similarities with the Cr 3d



band in Pt<sub>3</sub>Cr [13]. This peak in the V PDOS overlaps with a large contribution from degenerate Pt 5d states close to the Fermi edge. For Pt<sub>3</sub>Mn, the peak in the Mn PDOS at approximately 3 eV below  $E_F$  overlaps with a dip in the Pt 5d band. It is possible that this may result in a difference in the degree of 3d–5d hybridization between the two alloys, with the Mn derived states retaining more 3d character than the corresponding V states. Although this is a speculative interpretation, such a difference would qualitatively explain the resonant behaviour.

Comparing the empirical PDOS with available energy band calculations, the ASW calculations of Kubler [8] and the TB calculations of Tohyama *et al* [9] for Pt<sub>3</sub>V indicate a bandwidth of 7–8 eV. The results also indicate that the V 3d band has the largest concentration of occupied states at  $E_F$  and completely overlaps with the Pt 5d band. For Pt<sub>3</sub>Mn, the APW calculations of Hasegawa [7] indicate a total bandwidth of about 5 eV, with a large concentration of Mn d states lying in the region up to 2 eV below  $E_F$  and a relatively small contribution at higher binding energies. However, the TB calculations for the Mn alloy indicate valence band structure extending to about 7 eV below  $E_F$ , with completely overlapping Pt and Mn d bands [9]. The highest occupied density of states for the Mn 3d band is situated approximately 2.8 eV below the Fermi level. The LMTO calculations of Jezierski [11] also indicate a bandwidth of approximately 8 eV for Pt<sub>3</sub>Mn, but no details of the PDOS are given. When comparing experimental photoemission results with theoretical calculations, differences may arise due to solid state effects on the cross-sections and self-energy effects. In addition, the limited escape depth for emitted photoelectrons ensures that only the near-surface regions of the alloys are investigated and the corresponding band structure may differ from that of the bulk. Nevertheless, from the above discussion it is clear that, with the possible exception of the APW calculations for Pt<sub>3</sub>Mn, there is qualitative agreement between experiment and theory in terms of the width and shape of the valence bands.

To provide a clearer comparison of experiment with theory, figures 5(b) and 6(b) show the results of tight-binding calculations for Pt<sub>3</sub>V and Pt<sub>3</sub>Mn respectively. The fine curves have been adapted from the original data of Tohyama *et al* and the bold curves show a convolution of the data to represent broadening effects. Lifetime effects have been modelled by convolution with Lorentzians of half-width varying in proportion with the square of the binding energy from zero at  $E_F$  to 1.0 eV at the bottom of the band. Identical functions have been used to represent intrinsic effects in Cu<sub>3</sub>Pd alloys [18]. To represent extrinsic broadening resulting from the finite resolution of the monochromator and energy analyser, the data were further convoluted with a Gaussian function of 0.2 eV half-width. This value was obtained by fitting a Fermi–Dirac distribution convoluted with Gaussians of varying half-width to the experimental spectra in the region of the Fermi edge. Although there are some differences in detail, the agreement between empirical and calculated DOS is quite good, particularly in terms of the V and Mn d bands. It would appear, therefore, that the valence electronic structure of these alloys is well represented by band theory.

#### 4. Conclusion

Cooper minimum and 3p to 3d resonance effects have been employed to provide information on the valence bands of the Cu<sub>3</sub>Au-type alloys Pt<sub>3</sub>V and Pt<sub>3</sub>Mn. The results indicate that the bands extend to 8 eV below  $E_F$  and that the Pt 5d band completely overlaps with the corresponding V or Mn 3d band in each case. The partial densities of states have been empirically determined employing spectra obtained at and well away from the Pt 5d Cooper minimum. The results indicate that the Mn d states contribute most strongly at a binding

energy of 2.6 eV. The V d states contribute most strongly immediately below  $E_F$ . Resonant photoemission in the region of the Mn 3p threshold has confirmed the Cooper minimum result for Pt<sub>3</sub>Mn. No corresponding resonance effect was observed in Pt<sub>3</sub>V, suggesting delocalization of the V d states. A comparison of the experimentally determined partial density of states for both alloys with tight-binding calculations reveals good agreement in terms of the width and shape of the d bands.

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