Studies of the electronic structure of the ferrimagnetic alloy Pt_3Cr using normal take-off angle-resolved photoemission

Studies of the electronic structure of the ferrimagnetic alloy Pt$_3$Cr using normal take-off angle-resolved photoemission

R B Patel†‡, A J Liddiard† and M D Crapper†§

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

Abstract. The ordered alloy, Pt$_2$Cr has the L1$_2$ structure and is ferrimagnetic with $T_c = 170\,°C$. Angle-resolved photoemission experiments using synchrotron radiation (18–45 eV) have been made in normal take-off geometry from the (110) surface in order to elucidate the band structure. The valence band energy–momentum relationship in the $\Gamma\Sigma M$ direction has been determined assuming a free-electron final state. The symmetries of these initial states have been determined using the polarization of the synchrotron radiation.

1. Introduction

Transition metal alloys have been the subject of many recent experimental and theoretical investigations [1–4]. They are regarded as one of the main proving grounds of modern solid-state theory and have a wide variety of potential applications in technology. One common theme has been the investigation of the electronic structures of such materials using angle-resolved ultraviolet photoemission spectroscopy, as the electronic properties of metals underlies many other properties and is a key feature in the understanding of such alloys. This technique provides a method for the direct investigation of band structures by application of momentum conservation rules to the inter-band transitions. One of the alloys that has been the subject of many interesting studies is Cu$_3$Au [3,4]. This is an ordered alloy that possesses well-understood surface properties and for which experimental determinations of the band structure have been extensively compared with theoretical calculations.

The ordered transition metal alloy Pt$_3$Cr [5] has the same (L1$_2$) structure as Cu$_3$Au. This is a simple cubic basis with chromium atoms at the vertices of the unit cell and platinum atoms in face centred positions. One of the more interesting properties of this alloy is that it is ferrimagnetic with $T_c = 170\,°C$. The magnetic moment is owing to the chromium atoms, which have only platinum neighbours allowing for little overlap of the chromium d band wavefunctions, so making them effectively independent magnets. The structural and magnetic properties of this alloy have been investigated in detail by x-ray diffraction and neutron scattering measurements [6,7]. Platinum and chromium form alloys with continuous compositions between 100% platinum and 100% chromium. The 75% platinum alloy has the largest magnetic moment and is completely ordered with a lattice parameter, $a = 3.87$ Å. As a logical extension of this work, Jezierski has made

‡ Present address: Surface Science Research Centre, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK.
§ To whom correspondence should be addressed.

calculations of the electronic density of states of Pt_3Cr using the cluster coherent potential approximation [8], but to date the only experimental work on the electronic structure that has been reported is a preliminary ultraviolet photoemission study of the valence band using an angle-integrating detector [9]. In the work reported here, we have extended this work to the use of angle-resolved photoemission measurements that have allowed us to determine the experimental dispersion of the d bands of the material.

2. Experimental procedure

The experiments were performed using beamline 6.2 at the SRS Daresbury [10]. This is a two-level turbo-molecular pumped system with a base pressure of 2×10^{-10} mbar. Ultraviolet monochromation is achieved using one of two toroidal gratings; 1800 lines mm^{-1} or 700 lines mm^{-1}. It was the latter that was used in the measurements reported here to give a photon energy range of 18–45 eV. The beam line has two Pt coated SiC mirrors and an Au coated post-focusing mirror, and delivers around 10^{11} photons per second. It has an energy resolution of 0.08 eV at low energy, reducing to 0.24 eV at high energy (including the effects of both the electron energy analyser and the ultraviolet monochromator). A VG ADES quasi-concentric hemispheres analyser that rotates around the crystal in the horizontal polarization plane was used to measure the electron distribution curves (EDCs). This instrument has an angular resolution of 5° and was operated at a pass energy of 10 eV.

The sample was a small (approximately 5 mm × 5 mm × 3 mm) irregularly shaped single crystal of Pt_3Cr previously prepared from high-purity materials. It was oriented using Laue x-ray diffraction and cut to within 1° of the (110) face using spark erosion. The resulting surface was carefully polished using descending grades of diamond paste to 0.1 μm grade and then stress relieved by heating to 400 °C for four hours in high vacuum. Pre-preparation of the surface included many hours of sputtering with 500 eV Ar$^+$ ions at 5 μA ion current followed by annealing (to temperatures between 400 °C and 800 °C) in one hour cycles. The in-situ preparation comprised several cycles of argon ion bombardment (2 keV and 5 μA) followed by annealing at 400 °C. This had previously been shown to produce an ordered surface that is stoichiometric within the accuracy of the analysis techniques [9].

Surface cleanliness and composition were checked using Auger electron spectroscopy (AES) using a PHI double pass CMA in differential mode. The main contaminant detected on the surface of the alloy was a small amount of carbon that decreased with successive cleaning cycles. The AES spectra from this surface are consistent with stoichiometry (following quantification using elemental standard materials with identical experimental conditions). The clean surface, as previously reported [9], forms a reconstruction (as does $Cu_3Au(110)$ [11]). Low-energy electron diffraction (LEED) using a Varian four-grid system was used to determine the azimuthal orientation of the surface prior to the photoemission experiments. The surface was found to remain clean enough for sensible experiments for around two and a half hours before further cleaning was necessary. After this, build up of photoelectron peaks due to contamination (which appeared to be from the residual vacuum in a reaction stimulated by the ultraviolet radiation) occurred in the UPS spectrum. Therefore the crystal was regularly cleaned, although the changes to the main features in the EDCs induced by the contamination appeared not to be significant.

Following cleaning and alignment of the azimuthal angles, EDCs were collected from the surface with a normal photoelectron take-off geometry and at an angle of photon incidence of 45°. Measurements were made with the crystal in two azimuthal orientations. The first of these was with the (horizontal) linear polarization of the synchrotron radiation lying in

the plane defined by the surface normal and the [1$\bar{1}$0] direction and the other (orthogonal orientation) with the polarization in the plane defined by the surface normal and the [001] direction.
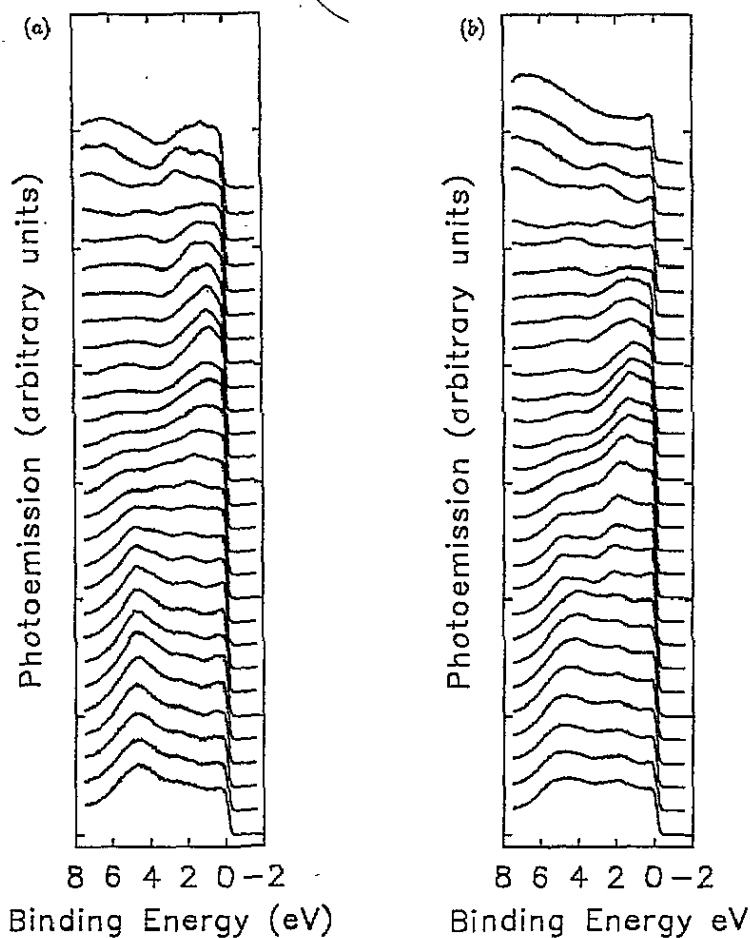

Figure 1. (*a*) The electron distribution curves for Pt_3Cr for the polarization vector in the plane defined by the surface normal and the [1$\bar{1}$0] azimuthal direction. The spectra increment in 1 eV steps from 18 eV (top) to 45 eV (bottom) photon energy; (*b*) the electron distribution curves for Pt_3Cr for the polarization vector in the plane defined by the surface normal and the [001] azimuthal direction. The spectra increment in 1 eV steps from 17 eV (top) to 45 eV (bottom) photon energy.

3. Results and discussion

The spectra collected from the crystal for both geometries and for a series of photon energies are shown in figures 1(*a*) and 1(*b*). The curves have been normalized to photon flux and the Fermi edges aligned to zero binding energy. Strong transitions can be seen in the spectra from 7 eV binding energy right up to the Fermi level, in qualitative agreement

with Jezierski's calculation of the band width [8]. There are clearly strong differences between the two sets of data collected with each principal azimuth in the horizontal plane. In particular there are strong states present near the Fermi level for the [1$\bar{1}$0] azimuthal orientation but not for the [001] azimuthal orientation for photon energies around 20 eV. For higher photon energies, there is a peak with binding energy of 2 eV present for the [001] oriented spectra but not for the [1$\bar{1}$0] orientation. There is also a feature at 5 eV binding energy that shows up strongly in the [1$\bar{1}$0] azimuth data. The reason for the differences between the spectra from different azimuthal directions arises from the symmetry selection rules for photoemission. These rules can be applied to determine the symmetry of the initial states giving rise to normal take-off photoemission [12]. For our experimental geometry, photoemission from the (110) surface of a simple cubic metal would, in the absence of spin–orbit coupling, sample Σ_1 and Σ_4 states when the radiation polarization vector lies in the mirror plane defined by the [110] and [1$\bar{1}$0] directions. With the polarization vector in the mirror plane defined by the [110] and [001] directions then the Σ_1 and Σ_3 are sampled. However, with platinum spin–orbit effects are to be expected resulting in a change of the symmetry rules to the double group representation [13]. This would result in a mixing of the Σ_3 and Σ_4 states making these selection rules less appropriate [14]. For an alloy where relativistic effects are likely to be more important for one element (Pt) than the other one (Cr) the situation is more complicated. Work on similar materials indicates that the simple selection rules would apply fairly well for Cr derived states but not for the Pt derived states [4]. We clearly have symmetry rules operating because the spectra are very different. For the Pt derived states, the mixing of states would still result in certain transitions having a higher probability than others but would not give the same absolute selection rules found when no splitting is apparent. The mixing will be strongest, with a total breakdown of selection, where the bands cross.

The feature at 5 eV binding energy ([1$\bar{1}$0] azimuthal orientations) is particularly interesting. It is much larger than any of the other transitions and it may be an enhancement of the transition owing to a p–d resonance. In Pt_3Cr, chromium has a 3p state at 41.1 eV binding energy that may lead to a resonance at around this photon energy. If this is the case, then it indicates that this state is largely chromium like and is highly localized. A high degree of localization however would not easily tie in with the azimuthal dependence of the feature. Therefore any assignment must be regarded as tenuous. The 3p levels of platinum are found at around 51.8 and 65.3 eV binding energy, so any resonances in platinum derived states will be out of the energy range used here. Previous photoemission studies of platinum have revealed a rich band structure extending from the Fermi edge to around 6 eV below [15, 16]. Studies of chromium indicate an electronic structure extending to a binding energy almost as deep as for platinum but with a much stronger and sharper Fermi edge [17, 18]. We would expect the whole of the valence band region of Pt_3Cr to reflect a contribution from both of these elements. In previous measurements [9], ultraviolet photoemission measurements made using a CMA in the 50 to 100 eV photon energy range it was tentatively suggested that this was the case. The Fermi edge was thought to be dominated by electrons associated with the Cr component of the alloy; this assignment being made using the variation of cross sections with photon energy.

We have analysed the binding energy of the photoemission peaks as a function of photon energy in order to determine the band structure of the material. The photoemission process involves a direct transition of an electron from an occupied to an unoccupied state. This transition must be k conserving within the reduced zone scheme. So, a determination of the initial state can only be made if the final state is known. Ideally, interpretation of the data would require calculation of initial and final state bands for comparison with

and interpretation of the photoemission data. In the absence of calculations of the final state band, we have assumed a free-electron-like final state for the photoelectron using a procedure that has been shown before to give reasonable results for similar alloys [1, 3]. The main problem in interpretation lies in the fact that photoemission probes an excited state of the electronic structure rather than the ground state [1]. The event creates a hole that will interact with surrounding electrons (depending on the level of screening) and so change the energetics of the measurement. This effect is more important where the hole is localized rather than delocalized and will differ in magnitude according to how the full d band is. A recent study of Cu₃Au [19] found that these self-energy effects were important in this material. These effects were accounted for by moving the (theoretically calculated) final state band by 2.5 eV in energy, resulting in a shift in the initial state band by around 0.3 eV. Thus it must be born in mind that our results are for the excited state of Pt₃Cr and that these may differ by a sizeable fraction of an electronvolt from the ground state.
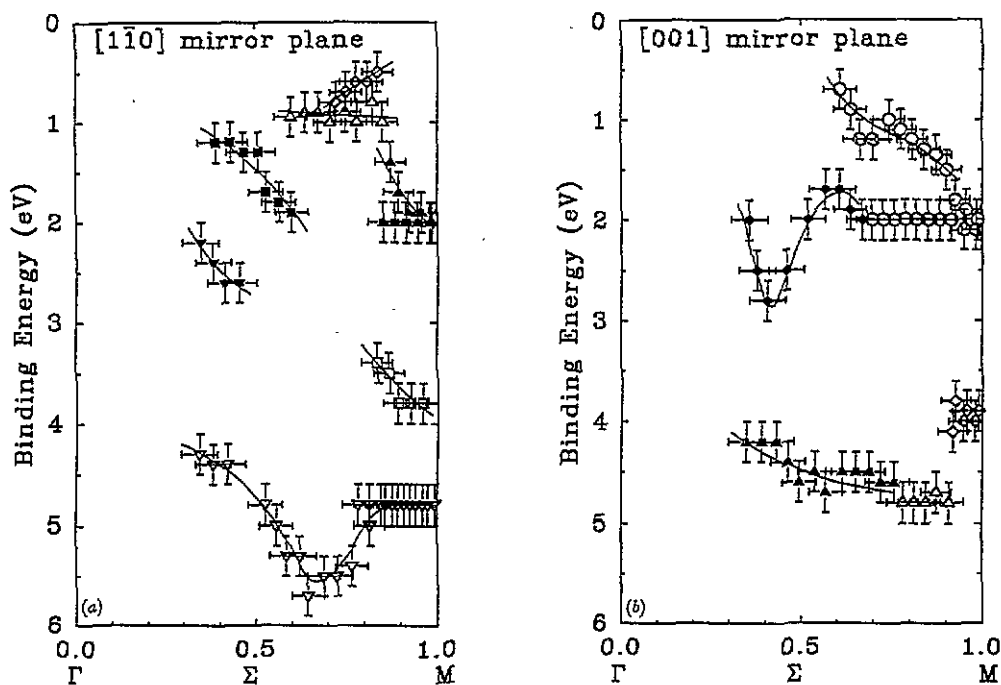

Figure 2. (*a*) The experimentally determined band structure of Pt₃Cr between the Γ and M points determined with the polarization vector in the [1̄10] mirror plane; (*b*) the experimentally determined band structure of Pt₃Cr between the Γ and M points determined with the polarization vector in the [001] mirror plane. The different symbols indicate points from different photoemission peaks.

The perpendicular component of the k vector of the photoelectron is not conserved on crossing the surface of the alloy owing to the difference in potential energy zero inside and outside the crystal that leads to a deceleration of the electron. The final state momentum of the electron (in Å^{-1}) inside the crystal will be given by

$$k_f = 0.512(h\nu - E_i + V_0)^{1/2}$$

Where $h\nu$ is the photon energy, E_i is the initial state binding energy and V_0 is the inner potential (all in eV). The estimation of V_0 is the most problematic feature of the analysis. We selected $V_0 = 12\pm1$ eV, which is consistent with previous photoemission measurements on other similar metals. We have used this value to calculate the binding energy and momentum associated with each peak in the spectra between 18 and 45 eV photon energy, for both azimuthal orientations.

In the photoemission process, the electron momentum can only be changed by multiples of $\hbar g$ where g is a reciprocal lattice vector. In the geometry we selected and for a simple cubic lattice, the appropriate reciprocal lattice vector is $2\pi(1/a, 1/a, 0)$ where a is the lattice parameter (3.87 Å). Multiples of this were subtracted from the calculated k values to map all the data points into the first Brillouin zone. The experimentally determined bands are shown in figure 2(a) and (b). The normal take-off direction from the (110) surface corresponds to the $\Gamma\Sigma M$ symmetry line. Figure 2(a) shows the transitions excited with the electric vector in the $[1\bar{1}0]$ direction and figure 2(b) shows those excited in the [001] direction. The different symbols indicate the points obtained from different photoemission peaks. The bands disperse weakly in k; this is a property characteristic of d bands. Most of the transitions appear to be excited by the polarization vector in both azimuthal directions. The notable differences between the two azimuths are the bands between 4 and 6 eV between 0.3 and 0.8 of the way along ΓM and the band between 1 and 2 eV in the middle of the zone.

Clearly a fuller interpretation would require theoretical calculations of the band structure that are not available at present. The bands that are of most interest are those near the Fermi level which we believe to be associated with chromium. This is the element that carries the magnetic moment and these electrons will be responsible for the magnetic properties.

4. Conclusion

We have performed the first direct investigations of the electronic structure of the ferromagnetic alloy Pt_3Cr. Normal take-off photoemission spectra from the (110) surface show valence structure extending to around 6 eV below the Fermi energy. We have determined the experimental dispersion of the Σ states along the $\Gamma\Sigma M$ symmetry line.

References

[1]   Lui S-C, Davenport J W, Plummer E W, Zehner D M and Fernando G W 1990 *Phys. Rev.* B **42** 1582
[2]   Rao R S, Bansil A, Asonen H and Pessa M 1984 *Phys. Rev.* B **29** 1713
[3]   Eberhardt W, Wu S C, Garrett R, Sondereicher D and Jona F 1985 *Phys. Rev.* B **31** 8285
[4]   Wang Z Q, Wu S C, Quinn J, Lok C K C, Li Y S and Jona F 1988 *Phys. Rev.* B **38** 7442
[5]   Williams D E G and Lewis B G 1979 *Z. Metallk.* **70** 441

[6]   Williams D E G and Jezierski A 1986 *J. Magn. Magn. Mater.* **59** 41

[7]   Jezierski A 1988 *Physica* B **149** 244

[8]   Jezierski A 1983 *J. Phys. F: Met. Phys.* **13** L111

[9]   Liddiard A J, Patel R B and Crapper M D 1994 *Surf. Sci.* at press

[10]   Turner T S and Teehan D 1985 *SERC Daresbury Laboratory Technical Memorandum* DL/SCI/TM85E

[11]   Krummacher S, Sen N, Gudat W, Johnson R, Grey F and Ghijsen J 1989 *Z. Phys.* B **75** 235

[12]   Hermanson J 1976 *Solid State Commun.* **22** 9

[13]   Elliott R J 1954 *Phys. Rev.* B **96** 280

[14]   Yagi K, Higashiyama K, Yanashima S, Ohnuki H, Fukutani H and Kato H 1990 *Surf. Sci.* **231** 397

[15]   Wei Di, Smith K E and Kevan S D 1992 *Phys. Rev.* B **45** 3652

[16]   Wern H, Courths R, Leschik G and Hüfner S 1985 *Z. Phys.* B **60** 293

[17]   Shinn N D 1992 *Surf. Sci.* **278** 157

[18]   Johansson L I, Petersson L-G, Berggren K-F and Allen J W 1980 *Phys. Rev.* B **22** 3294

[19]   Lau M, Löbus S, Courths R, Halilov S, Gollisch H and Feder R 1993 *Ann. Phys., Lpz.* **2** 450