EXPERIMENTAL AND THEORETICAL STUDIES OF THE ELECTRONIC STRUCTURES OF AuAl_2 AND PtGa_2

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Synchrotron-radiation-excited angle-resolved photoemission spectra for the (100) and (111) faces of AuAl_2 and the (111) face of PtGa_2 are presented, along with derived experimental dispersion relations. These bands are compared with those obtained from the first-principles theoretical band-structure calculations. The total densities of states at the Fermi energy for these two materials are compared with those obtained from the specific-heat measurements. The energy variations of Au and Pt 5d bands for AuAl_2 and PtGa_2 , respectively, show atomic-like behavior in the photon-energy range of 80–220 eV.

1. Introduction

AuAl_2 and PtGa_2 are intermetallic compounds of both technological and scientific importance. The former has potential applications as a selective solar absorber,¹ and the latter was proposed to be used as a thermodynamically stable conducting contact to GaAs.² They both crystallize in the cubic fluorite structure, and superconduct at low temperatures.³ They are also prototype materials for studying the Au and Pt 5d bands in intermetallic compounds, since group-III metals contribute only s-p states to the valence band (VB). The purple and gold colors of AuAl_2 and PtGa_2 , respectively, also strongly motivated researchers to study the electronic structures of these two materials. Many electronic and physical properties of these two compounds have been measured, and a majority of these works were reviewed by Hsu.³ This paper will focus on angle-resolved photoemission-spectroscopic (ARPES) study and theoretical band-structure calculation of AuAl_2 and PtGa_2 .

2. Experiment and Theory

Procedures for preparation of the (100) and (111) faces of AuAl_2 and the (111) face of PtGa_2 single crystals were the same as those reported previously.^{4,5} The ARPES experiments were performed at the Advanced Light Source. Photon energies in the range of 80–220 eV were selected with a spherical-grating monochromator, and a Physical Electronics 137-mm hemispherical analyzer was used in the fixed-analyzer-transmission mode to collect the photoemission spectra. With 150 lines/mm for grating setting and 3 eV for analyzer pass-energy setting, the energy resolution was less than 80 meV. The angular resolution was less than $\pm 1^\circ$, which corresponds to a momentum resolution of roughly $0.2 \text{ \AA}^{-1}$ at 125 eV kinetic energy. The vacuum chamber was also equipped with a double-anode (Al and Mg) X-ray source for X-ray photoemission spectroscopy (XPS) and X-ray photoelectron diffraction (XPD) measurements, and with a low-energy electron diffraction (LEED) system. The chamber

pressure during the experiments was 2×10^{-10} Torr. The samples were cleaned by repeated cycles of sputtering with Ar ions and annealing to 500°C until XPS spectra showed no traces of O or C contamination on the sample surfaces. The observed XPD and LEED patterns⁶ also confirmed the cleanliness and ordering of the sample surfaces.

To interpret the ARPES data, we have calculated the relativistic band structures of AuAl_2 and PtGa_2 with the CaF_2 structure and at the experimental lattice constants of 5.99 and 5.91 Å, respectively. We used the highly accurate all-electron full-potential linear augmented-plane-wave (FLAPW) method.⁷ The calculations are based on the first-principles density functional theory with the standard local density approximation to the exchange-correlation potential.⁸ The muffin-tin radii used for the constituent atoms of AuAl_2 and PtGa_2 are 1.27 Å. The shallow 5p and 4f core states of Au and Pt and the 3d states of Ga were also treated as band states by using the so-called local orbitals.⁷ The wave functions, the charge densities, and the potentials are expanded in terms of the spherical harmonics inside the muffin-tin spheres. The cutoff angular momentum (l_{max}) is 10 for the wave functions and six for the charge densities

and the potentials. The Brillouin zone (BZ) integration is carried out by using the improved tetrahedron method.⁹ The number of the augmented plane waves included is about 120 per atom, i.e. $R_{\text{mt}}K_{\text{max}} = 9$.⁷ The number of the k points in the irreducible BZ wedge (IBZW) used in the self-consistent calculations is 72. To calculate the total density of states (DOS) at the Fermi energy (E_F), 165 k points in the IBZW were used. We have checked the convergence of the calculated eigenvalues with respect to the number of augmented plane waves used and the number of k points used. In particular, we found that increasing $R_{\text{mt}}K_{\text{max}} = 9$ to 10 changed the relative positions of the eigenvalues at the Γ points by up to a couple of meV only.

3. Results and Discussion

Figure 1 shows a set of VB photoemission spectra from the (100) and (111) faces of AuAl_2 , and from the (111) face of PtGa_2 at normal emission. The normals to the sample surfaces were determined from the Au and Pt $4f_{7/2}$ XPD polar and azimuth scans.⁶ The photon energy ($h\nu$) was varied so as to probe the third to the fourth BZ's for the (100) face,

Fig. 1. Angle-resolved photoemission spectra taken at normal emissions from the (100) and (111) faces of AuAl_2 , and the (111) face of PtGa_2 .

and the fourth to fifth BZ's for the (111) face of these two materials. The E_F was assigned at half height on the onset of a plateau, which is caused by photoemission from the Au or Pt s-p band. In general, s-p bands disperse much more rapidly than the d bands, thus accounting for the broader features seen in the photoemission spectra. At $h\nu \geq 160$ eV, more final states are accessible for the Au and Pt s-p states, which causes the higher intensity observed in the VB spectra. In Fig. 1, a three-peak structure with much higher intensity at higher binding energy (E_B) is due to the Au or Pt 5d states. The E_B 's of these peaks change less than 0.3 eV by varying $h\nu$, and are listed in the first three columns of Table 1. We note that the E_B values at the three Γ points (at approximately $h\nu = 110$ or 220 eV) determined from the present ARPES data for PtGa₂ are 3.40, 4.35, and 5.45 eV, which are essentially the same as those obtained from the total DOS features in the angle-integrated photoemission spectra.⁴ This means that the Pt 5d bands in PtGa₂ are well localized. We should also point out that these E_B values are within 10% of the corresponding values (3.55, 4.45, and 5.90 eV) for elemental Au,¹⁰ which explains why PtGa₂ is gold-colored.

By using a direct-transition model and assuming free-electron conduction-band structures, the energy-versus-momentum dispersion relations for AuAl₂ along X- Γ -L and for PtGa₂ along L- Γ -L are plotted in Figs. 2 and 3, respectively, as open circles. The values of the inner potentials used for AuAl₂ and PtGa₂ were estimated to be 12.0 and 12.3 eV, respectively. These values were taken to be the differences between the muffin-tin zeros of energy in

the present FLAPW calculation (7.4 and 7.7 eV) and the vacuum levels as determined from the work function (4.63 eV)¹¹ of AuGa₂. The band structures calculated by the FLAPW method for AuAl₂ along Δ and Λ and for PtGa₂ along Λ are plotted as closed circles in Figs. 2 and 3, respectively. The

Fig. 2. Band structure of AuAl₂ along X- Γ -L. Open circles are bands derived from the ARPES data. Closed circles are theoretical band structure calculated by the FLAPW method.

Fig. 3. Band structure of PtGa₂ along L- Γ -L. Open circles are bands derived from the ARPES data. Closed circles are theoretical band structure calculated by the FLAPW method.

Table 1. The experimental (ARPES work, first line) and theoretical (FLAPW work, second line) binding energies (E_B) of the Au and Pt 5d states at Γ , the crystal field parameters (10Dq), and the spin-orbit parameters (ξ) for Au metal, AuAl₂ and PtGa₂. All values in eV.

Material	E_B (Γ_8^1)	E_B (Γ_7)	E_B (Γ_8^2)	10Dq	ξ
Au	3.55	4.45	5.90	1.22	0.71
	3.09	4.34	5.52	1.60	0.61
AuAl ₂	4.90	5.80	6.85	1.18	0.53
	5.47	6.23	7.25	1.02	0.51
PtGa ₂	3.40	4.40	5.47	0.9	0.56
	3.34	4.88	5.45	1.80	0.33

agreement between the experimental and theoretical bands is rather good for both compounds, which indicates that the spin-orbit effect is important in calculating the band structures of these materials. The E_B values at Γ points determined from present FLAPW calculation for Au, AuAl₂, and PtGa₂ are listed under the corresponding ARPES values in Table 1. The crystal-field and the spin-orbit parameters of AuAl₂ and PtGa₂ were determined in the same manner as was done previously,⁴ and are listed in the last two columns of Table 1. The experimental band for PtGa₂ around $E_B = 7$ eV is due to emissions from the one-dimensional DOS.¹² It is identified as such because it resonates strongly at $h\nu = 160$ and 170 eV, at which energies the BZ boundary is reached; and is rather weak between $h\nu = 110$ and 130 eV, at which energies the center of the BZ is covered. The experimental PtGa₂ band at $E_B = 4.7$ eV for $h\nu = 100$ –130 eV involves a surface state. This surface state was checked by exposing the sample surface with oxygen and observing its gradual disappearance.

The DOS at E_F [$n(E_F)$] values calculated by the FLAPW method for AuAl₂ and PtGa₂ are 0.92 and 1.15 states/eV-cell, respectively. These values are comparable to those (1.08¹³ and 1.09¹⁴ states/eV-cell, respectively) calculated by using the mixed-basis band-structure interpolation scheme method. The $n(E_F)$ values for AuAl₂ and PtGa₂ obtained from the specific-heat measurements (1.28¹⁵ and 1.67¹⁶ states/eV-cell, respectively) are these “band-structure” DOS enhanced by a factor $1 + \lambda$, where

λ is the electron–photon mass enhancement parameter. The λ values thus determined for AuAl₂ and PtGa₂ are 0.39 and 0.45, respectively. We note that the λ value for AuAl₂ is 34% larger than the value (0.29) calculated by using McMillan’s formula¹⁷ with critical temperature (T_c) of 0.095 K and Debye temperature (θ_D) of 297 K.¹⁸ In comparison, the λ value for PtGa₂ is within 8% of the value (0.49) calculated by using the same formula with $T_c = 2.15$ K and $\theta_D = 220$ K.¹⁶ The photon-energy dependence of the Au and Pt 5d-band intensities for AuAl₂ and PtGa₂ in the range $80 \leq h\nu \leq 220$ eV are shown in Fig. 4 as filled squares and crosses. Also shown in Fig. 4 as solid lines are the atomic cross sections of the Au and Pt 5d states calculated by Yeh and Lindau¹⁹ for elemental Au and Pt. The data points were obtained by correcting the photoemission spectra for a Shirley-type inelastic background,²⁰ measuring the areas under the photoemission energy distribution curves in the range $3.5 \leq E_B \leq 9.0$ eV and $2 \leq E_B \leq 6.5$ eV for AuAl₂ and PtGa₂, respectively, and correcting these areas with respect to the incident photon flux. They were then normalized to the atomic cross-section values at $h\nu = 80$ and 200 eV for AuAl₂ and PtGa₂, respectively. The bump in the experimental data for PtGa₂ in the range $h\nu = 100$ –140 eV is caused by non-d-weight bands dispersing outside of the energy window, 2–6.5 eV, for area integration. Namely, the sharp peak at $E_B = 5.5$ eV for PtGa₂ in Fig. 1 exists precisely in this range of 100–140 eV, which corresponds to the top of the lower Pt 5d band. This lower 5d band disperses to below 7 eV along

Fig. 4. Photon-energy dependence of the Au and Pt 5d-band intensities for AuAl₂ and PtGa₂, respectively. The solid lines are the atomic cross sections¹⁹ of the Au and Pt 5d states for elemental Au and Pt, respectively.

Γ -L and mixes more with the s-p bands than the other two 5d bands do (the present FLAPW calculation shows that the Pt d weight for PtGa₂ is 96%, 43%, and 48% at the Γ_8^1 , Γ_7 , and Γ_8^2 points, respectively). We note that in this photon-energy range, the Au and Pt 5d states of AuAl₂ and PtGa₂, respectively, show atomic-like behavior, which is in sharp contrast to the solid-state effect observed for the Au and Pt 5d states in Au and Pt metals.^{21,22}

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