Photoemission study of the electronic structure of $PtGa_2$

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Synchrotron-radiation-excited angle-integrated photoemission spectra of $PtGa_2$ are presented. The spacings of the three Pt $5d$ bands were determined and were interpreted to yield the crystal-field and the spin-orbit parameters of 0.90 ± 0.05 and 0.56 ± 0.05 eV, respectively. The energy variation of the three Pt $5d$ photoemission-peak intensities has been derived at photon energies of 45, 80, and 120 eV from measurements on $PtGa_2$. The binding energies at Γ_8^1, Γ_7, and Γ_8^2 for $PtGa_2$ are within 10% of the corresponding values for Au metal, suggesting the electronic structures of these two materials are very similar.
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I. INTRODUCTION

During the last decade, the electronic structure and the physical properties of a less-common intermetallic compound $PtGa_2$ have been studied by performing band-structure calculation,[1] x-ray and uv photoemission spectroscopic (XPS and UPS) experiments,[1] and electrical-resistivity,[2] magnetic-susceptibility,[2,3] thermoelectric-power,[2] and specific-heat[4] measurements. The gold color of $PtGa_2$ was explained in terms of its Au-like density of states (DOS), while the similarity between $PtGa_2$ and Au as to their conduction mechanisms and the topologies of their Fermi surfaces was clearly shown by comparing thermoelectric-power data of these two materials. The superconductivity of this compound was first discovered by Hsu[4,5] and later confirmed by Wong.[6] Our work showed that $PtGa_2$ is a type-II superconductor with a critical temperature at zero magnetic field of 2.15 K, and an upper critical field of 443 G. The metallic normal state and the superconductivity state of $PtGa_2$ were also revealed in the electrical-resistivity measurements.[2,6] Recently, experimental and theoretical studies on this interesting compound and three isostructural compounds $AuAl_2$, $AuGa_2$, and $AuIn_2$ were reviewed by Hsu.[7]

Binary intermetallic compounds that contain a transition metal and a group-III metal are interesting both from technological and academic points of view. For instance, elemental Pt is unstable with respect to GaAs in a closed system at room temperature, and will react chemically to form compounds such as PtGa or $PtAs_2$.[8] On the other hand, conducting contacts of $PtGa_2$ are thermodynamically stable on a GaAs substrate up to 450 °C.[9,10] Thus, knowledge of the electronic and physical properties of $PtGa_2$ and related intermetallic compounds may be important in design of circuits for future field-effect devices. Such compounds are also excellent systems for studying d bands, since group-III metals contribute only s-p states to the valence band (VB). One example is the study of the electron correlation effects in Ni $3d$ bands of Ni-Al,[11] Ni-Ga,[12,13] and Ni-In (Ref. 13) intermetallic compounds. Another example is the study of the positions of Au $5d$ bands for Au(group-III)$_2$ intermetallic compounds, which was a controversial topic in the 1970s.[7]

In 1987, a semiempirical band structure for $PtGa_2$ (Ref. 1) was obtained in the mixed-basis band-structure interpolation scheme (MBBSIS) and found to give agreement between the calculated total DOS and XPS data. The energies of the Pt $5d$ bands were further checked by UPS. However, there are three drawbacks in that paper. Firstly, since a nonmonochromatic x-ray source was used in the XPS measurement, the energy resolution, though not explicitly mentioned in Ref. 1, could be as low as 1 eV.[14] Secondly, since Auger electron spectroscopic (AES) capability was not available in the UPS chamber, contamination of the sample surface by O or C could not be checked. Thirdly, since a noble-gas-discharge lamp was utilized as the excitation source in the UPS measurement, the VB spectra did not reveal any features other than the two peaks already observed in the XPS spectrum, even though the resolution of the UPS spectra (approximately 0.3 eV) was much better than that of the XPS spectra. It is also noted that the total DOS calculated by the MBBSIS method showed three Pt $5d$ bands (Γ_8^1, Γ_7, and Γ_8^2), but the middle Γ_7 band was not resolved by either the XPS or UPS study.[1] The present study of the VB's of $PtGa_2$ was motivated to improve the energy resolution by using synchrotron-radiation-excited photoemission spectroscopy, with the hope to resolve the Γ_7 band and thus to obtain the spin-orbit and crystal-field parameters of the (111) face of $PtGa_2$. Another purpose of this work is to bridge the UPS-XPS energy gap by using a tunable synchrotron-radiation photon source, and to study the amplitude-modulation effect of the Pt $5d$ bands in $PtGa_2$.

This paper is organized as follows. In Sec. II the experiments are described and in Sec. III the results and discussion are presented. The conclusions of this work are contained in Sec. IV.

II. EXPERIMENTS

A single-crystal sample[15] of $PtGa_2$ was oriented using Laue x-ray diffractometry, and then was cut by a wire saw to reveal a (111) surface. The $PtGa_2$ sample was mounted on a

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polishing fixture, reoriented to within 1° of the (111) plane by Laue photography, and polished to mirror smoothness using 0.5-, 0.3-, and 0.05-μm alumina grit. The choice of the (111) face was made for several reasons. This face has been studied in great detail for the 5d metals Au and Pt, and is the least difficult to prepare and characterize because it is closed packed and does not tend to reconstruct; in addition, it does not give rise to significant secondary Mahan emission,[16] which simplifies the analysis. Experiments were carried out on the beam line B-06A at the Synchrotron Radiation Research Center, Hsinchu, Taiwan. Photon energies in the range of 40–170 eV were selected with a low spherical grating monochromator, and a Vacuum Science Workshop 125-mm hemispherical analyzer was used in the fixed-analyzer-transmission mode to collect photoelectron spectra. With 900 lines/mm for grating setting and 3 eV for analyzer pass-energy setting, the energy resolution of the photons plus the electrons was 0.15 eV as estimated from the sharpness of the Fermi edge of the VB photoemission spectra. The pressure during the measurements was 2×10^{-10} Torr. The vacuum chamber was also equipped with a Physical Electronics 15-255 double-pass cylindrical mirror analyzer for AES measurement.

The sample was cleaned by repeated cycles of sputtering with Ar ions and annealing to 500 °C until Auger spectra showed that the combined O and C contamination on the sample surface was less than 4 at. %. The sample surface after cyclic cleaning contains about 21% less Ga atoms than those in the bulk as determined from the peak-to-peak intensity ratio of Ga LMM (1070 eV) to Pt MNN (1967 eV) Auger transitions and normalized Auger sensitivity factors.[17] It is worthwhile noting that these Auger electrons come from roughly 15–20 Å from the top of the $PtGa_2$ surface, while in the range of photon energies from 40 to 170 eV as used in this work, the kinetic energy of electrons from the Pt 5d band ranges from roughly 30 to 160 eV. For these latter energies the escape depth is near its minimum of 5 Å. Since the Pt-Ga bond length is about 2.56 Å (the lattice constant of $PtGa_2$ is 5.911 Å), only the first two atomic layers are probed by the photon energies used. The preferential sputtering of the Ga atoms from the $PtGa_2$ surface agrees with the observation made on surfaces of the Ni-Ga intermetallic compounds[12,13] and CoGa (Ref. 18) as for Ga deficiency after alternating cycles of Ar-ion bombardment and subsequent annealing. We should point out that the Ga deficiency is less than 14% for four stoichiometries of the Ni-Ga compounds.[12,13] We also note that the $PtGa_2$ bulk sample may contain some defects that result from the metastability of this compound at room temperature. This speculation is supported by the low residual-resistivity ratio (3.34) for this compound.[2] Due to the inherent defects and a larger Pt/Ga mass ratio than that of Ni/Ga, it is not surprising that the Ga deficiency on the $PtGa_2$ surface is larger than that on the surfaces of the Ni-Ga compounds under the same surface preparation procedures. Study on the $AuGa_2$ (001) surface[19] by AES and low-energy electron diffraction showed that it is primarily Ga terminated and Ga deficiency improves with annealing cycles. For the ideal case that the surface is not altered by ion bombardment and subsequent annealing, the stoichiometry of the bulk will be preserved on the (111) surface of ordered $PtGa_2$.

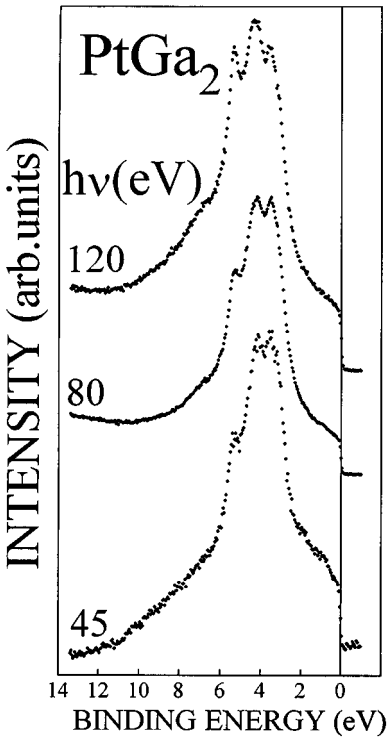

FIG. 1. Valence-band photoemission spectra of $PtGa_2$ for photon energies at 45, 80, and 120 eV. Note that the intensities for the three spectra are not to the scale.

III. RESULTS AND DISCUSSION

Figure 1 shows a set of angle-integrated VB photoemission spectra of $PtGa_2$ for photon energies ($h\nu$) at 45, 80, and 120 eV. The Fermi energy (E_F)was assigned at half height on the onset of a plateau in Fig. 1. This plateau extends from E_F to 2 eV binding energy (E_B) with a fairly low DOS and is caused by photoemission from the Pt s-p band (band 7). The s-p plateau was also observed in Pt,[20] Au,[20] and $AuGa_2$.[21] In general, s-p bands disperse much more rapidly than the almost flat d bands, thus accounting for the relative width of the features seen in the photoemission spectra. The ratios of the s-p to d-band intensities, after subtracting a linear background, for $h\nu=45$, 80, and 120 eV are 0.13, 0.07, and 0.08, respectively. These ratios are roughly the same as observed in Pt and Au at $h\nu=12$ and 15 eV.[20] At higher E_B there is a three-peak structure with a very high Pt 5d DOS, and there is essentially no change of the respective E_B's with $h\nu$. The small bump around $E_B=7$ eV is due to the O 2p-band emission mixed with emissions from the Pt s-p band (band 1). The photoemission spectra agree with every detail of the DOS curve calculated by MBBSIS,[1] and the middle Γ_7 band is resolved at $E_B=4.2$ eV. Since dispersion of the Pt 5d band is rather small along Λ in the Brillouin zone (BZ),[1] we can assign these three peaks as due to band emissions from Γ points. The E_B values at Γ_8^1, Γ_7, and Γ_8^2 for $PtGa_2$ are listed in the second, third, and fourth column, respectively, in Table I. Also presented in Table I are the experimental and theoretical E_B values at the three Γ points for Au, $AuGa_2$, and Pt.

The spacings of the Pt 5d bands at Γ for $PtGa_2$ can be used to determine the crystal-field (10 Dq) and the spin-orbit

TABLE I. The lattice constants, the experimental and theoretical binding energies (E_B) of the Au or Pt $5d$ levels at Γ, the crystal-field parameters ($10\,Dq$), and the spin-orbit parameters (ξ) for Au, $AuGa_2$, Pt, and $PtGa_2$. All values in eV.

	Lattice constant (Å)	$E_B(\Gamma_8^1)$		$E_B(\Gamma_7)$	$E_B(\Gamma_8^2)$	$10\,Dq$	ξ
Au	4.08	Expt.[a]	−3.55	−4.45	−5.90	1.22	0.71
		Theor.[b]	−3.38	−4.33	−5.75	1.28	0.70
		Theor.[c]	−3.29	−4.34	−5.65	1.39	0.66
$AuGa_2$	6.076	Expt.[d]	−4.92	−5.68	−7.31	1.07	0.78
		Theor.[e]	−6.88	−7.60	−7.60	0.72	
Pt	3.923	Expt.[a]	−1.40	−2.80	−4.07	1.78	0.66
		Theor.[f]	−1.40	−2.97	−4.05	1.94	0.58
$PtGa_2$	5.911	Expt.[g]	−3.55	−4.20	−5.35	0.90	0.56

[a]Reference 20.
[b]Reference 25.
[c]Reference 26.
[d]Reference 21.
[e]Reference 28.
[f]Reference 27.
[g]This work.

(ξ) parameters in the manner of Wehner *et al.*[22] Briefly, the Pt $5d$ energy levels at Γ lie at

$$E_B(\Gamma_8^1) = -4\,Dq - \tfrac{1}{2}\xi - \sqrt{\tfrac{3}{2}}\xi\,\cot\theta, \tag{1}$$

$$E_B(\Gamma_7) = -4\,Dq + \xi, \tag{2}$$

$$E_B(\Gamma_8^2) = 6\,Dq + \sqrt{\tfrac{3}{2}}\xi\,\cot\theta, \tag{3}$$

where θ is defined by

$$\tan 2\theta = -\frac{\sqrt{6}\xi}{10\,Dq + \frac{1}{2}\xi}. \tag{4}$$

The $10\,Dq$ and ξ values for $PtGa_2$ thus determined are listed in the last two columns of Table I, along with those for Au, $AuGa_2$, and Pt. It is worthwhile noting that these parameters are only meaningful at the Γ points in the BZ, where the crystal momentum is zero. However, the almost flat Pt $5d$ band across the BZ with an energy spread of less than 0.5 eV justifies the use of the DOS peaks for $PtGa_2$ to determine the $10\,Dq$ and ξ values. We note that the experimental ξ value for Pt (0.63 eV) (Ref. 23) was used in the MBBSIS band-structure calculation of $PtGa_2$.[1] This value is within 10% of the ξ value for $PtGa_2$ determined from this work. However the $10\,Dq$ value, obtained by fitting of the MBBSIS band structure of $PtGa_2$ to the XPS VB spectrum, is negative and carries a very high uncertainty.[1] These observations suggest that while the splitting of the Pt $5d$ band in $PtGa_2$ was well preserved in MBBSIS, the crystal-field effect was underestimated by the calculation. Underestimation of the $10\,Dq$ values was also a problem in the MBBSIS band-structure calculations of $AuAl_2$, $AuGa_2$, and $AuIn_2$.[24]

In Table I, the agreement is rather good (within 7%) for Au and Pt of the three E_B values at Γ points determined from either the angle-resolved photoemission spectroscopic (ARPES) study[20] or the relativistic band-structure calculations.[25–27] For $AuGa_2$, however, the agreement between the ARPES data of Nelson *et al.*[21] and the nonrelativistic band-structure calculation of Switendick and Narath[28] is very poor (maximum difference is close to 30%). This indicates that the spin-orbit effect is important in determining the electronic properties of this material, and should be comparably important in determining those of related materials such as $AuAl_2$ and $PtGa_2$. We should also point out that the E_B values at Γ_8^1, Γ_7, and Γ_8^2 for $PtGa_2$ from the MBBSIS calculation[1] are −2.79, −3.71, and −4.86 eV, respectively; while the corresponding values obtained from this work are −3.55, −4.20, and −5.35 eV. Thus, our experimental values for $PtGa_2$ are close to the experimental values for Au (−3.55, −4.45, and −5.90 eV, respectively, in Table I), and deviate as much as 21% from the theoretical MBBSIS values for $PtGa_2$. It seems that the combined crystal-field and spin-orbit effect makes the Pt $5d$ bands of $PtGa_2$ situated at positions within 10% of those of the Au $5d$ bands of Au metal. Therefore, this study gives one more quantitative support for the similarity between the electronic structures of $PtGa_2$ and Au. One may wonder at this point if the electronic structures of $PtGa_2$ and Au are so similar, why does $PtGa_2$ superconduct while Au does not? To answer this question, more understanding on the electron-correlation effects in $PtGa_2$ may help. We note that $AuGa_2$ is also a superconductor with a critical temperature at zero magnetic field of 1.12 K.[7]

In this study, the d-band splitting for $PtGa_2$, as defined by the energy difference between the upper and the lower Γ_8 bands, is 1.8 eV, which is smaller than that obtained from the XPS or UPS measurement and the MBBSIS band-structure calculation (2.1 eV).[1] The d-band width for $PtGa_2$, as determined from the full width at half maximum of the photoemission spectra of Fig. 1, is 2.8 eV, which is again smaller than the previous value of 3.9 eV obtained from the XPS study.[1] These observations show that the d-band splitting and the d-band width are strongly affected by the instrument-broadening effect. It should also be pointed out that the d-band splitting and the d-band width for $PtGa_2$ do not change with the three photon energies used in this study. The relative ratios of the intensities of the three d-band peaks for $PtGa_2$ starting from lower to higher E_B at $h\nu = 45$, 80, and 120 eV are 1:1:0.67, 1:1:0.68, and 0.90:1:0.90, respectively. These ratios were calculated after subtracting a linear background. The highest- E_B peak grows in relative intensity with increasing photon energy, with a minor increase from $h\nu = 45$ to 80 eV and a 32% increase from $h\nu = 80$ to 120

TABLE II. Binding energies of the Ga $3d$ and the Pt or Au $4f$ levels and the corresponding spin-orbit splittings for Au, $AuGa_2$, Pt, and $PtGa_2$. All values in eV. Estimated uncertainty is ± 0.1 eV unless otherwise stated.

	Ga $3d_{5/2}$	Ga $3d_{3/2}$	Spin-orbit splitting	$4f_{7/2}$	$4f_{5/2}$	Spin-orbit splitting
Au[a]				83.9	87.6	3.7 ± 0.4
$AuGa_2$	18.6[b]	19.2[b]	0.6 ± 0.2[b]	85.05[c]		
Pt[a]				71.2	74.5	3.3 ± 0.4
$PtGa_2$[d]	18.5	18.9	0.4 ± 0.2	70.3	74.4	4.1 ± 0.2

[a]Reference 34, estimated uncertainty is ± 0.2 eV.
[b]Reference 21.
[c]Reference 35. This value was corrected to conform to the binding energy of the Rh $4f_{7/2}$ level reported in Ref. 34.
[d]This work.

eV. The central peak maintains the same intensity while the lowest-E_B peak shows about 10% decrease in intensity within the photon-energy range. The photon-energy dependence of the d-band photoemission intensities has been studied on a number of metals.[29–31] However, to our knowledge the photon-energy dependence of the respective DOS peaks has not been reported in the literature. The Pt $5d$-band intensity was defined as the area under the photoemission energy distribution extending from $E_B=2$ to $E_B=6.5$ eV, corrected for a linear background. The area was normalized with respect to the incident photon flux. We note that in Fig. 1 the photoemission intensity is not to the scale for the three spectra. The resulting values for the Pt $5d$ relative intensities at $h\nu=45$, 80, and 120 eV are roughly 7:5:1, which are similar to those reported for elemental Pt.[29,31] It is well known that the Pt $5d$ atomic cross section shows a 100-fold decrease as the Cooper minimum[32] ($h\nu\sim200$ eV for the Pt $5d$ band) is approached from low photon energy.[33] The experimental, photon-energy-dependent photoemission intensity obtained from Pt metal[29,31] seems more appropriate for this analysis than the calculated atomic photoionization cross section in Ref. 33. This is because the former data show a more gradual decrease in relative d-band intensity from $h\nu=45$ to 80 eV than from $h\nu=80$ to 120 eV, while the latter data show about the same amount of decrease in atomic cross section in the two energy ranges studied.

Table II lists the binding energies of the Ga $3d$ and the Pt or Au $4f$ levels and the corresponding spin-orbit splittings for Au, $AuGa_2$, Pt, and $PtGa_2$. The values for the elements are taken from the XPS studies compiled by Fuggle and Martensson.[34] By using XPS, Watson, Hudis, and Perlman[35] reported 84.45 eV for the binding energy of the Au $4f_{7/2}$ level in $AuGa_2$, relative to a value of 306.6 eV assigned to the simultaneously monitored Rh $4f_{7/2}$ level. In Table II this value was corrected to be 85.05 eV in order to conform to the binding energy of the Rh $4f_{7/2}$ level reported in Ref. 34. The Pt $4f$ spin-orbit splitting for $PtGa_2$ is larger than that for Pt. We note that only very small core-level energy shifts are seen in Table II, which can be interpreted within the framework of band theory to mean that when Au or Pt is alloyed with Ga, the flow of Ga s charge onto Au or Pt sites is accompanied by a compensating depletion of $5d$ charge.[35]

The free-electron value for the bulk-plasmon energy for $PtGa_2$ is 13.7 eV, assuming each Pt and Ga atom contributes one and three electrons, respectively, to the free-electron-like VB's. This value is reasonably close to the values of 15.5 and 13.2 eV observed in previous[36] and present studies, respectively. The experimental bulk-plasmon energies are essentially the same as that of pure Ga (14.2 eV), while Pt as a pure metal shows almost no plasmon structure. The surface-plasmon energy for $PtGa_2$ is observed at 9.6 eV in this study.

IV. CONCLUSIONS

The spacings of the three Pt $5d$ bands for $PtGa_2$ were determined and were interpreted to yield the crystal-field and the spin-orbit parameters of 0.90 ± 0.05 and 0.56 ± 0.05 eV, respectively. The binding energies at Γ_8^1, Γ_7, and Γ_8^2 for $PtGa_2$ are within 10% of the corresponding values for Au, suggesting that these two materials have very similar electronic structure. The bulk- and surface-plasmon energies of $PtGa_2$ are 13.2 and 9.6 eV, respectively.

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