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"GOLD 5d BANDS" IN AuAl_2 AND AuGa_2

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A NOTE ON THE POSITION OF THE "GOLD 5d BANDS"

*
IN AuAl_2 AND AuGa_2

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Switendick and Narath¹ recently proposed a solution for the "AuGa₂ dilemma" pointed out by Jaccarino, et al.² This solution was based on the results of band structure calculations.¹ The density of states for AuAl₂ derived from these band-structure calculations were presented at this Conference.³ A surprising result of this calculation was the position of the "gold d-band" states. These states were located at about -7 eV in AuAl₂ and at similar energies in AuGa₂ and AuIn₂.¹ The interesting optical properties of gold intermetallic compounds (e.g., AuAl₂ is violet) are often attributed to the proximity of the gold d-bands to the Fermi energy, E_F . If these states really lay at $E_F - 7$ eV, and were as flat (i.e., the $\rho(E)$ peak was as narrow) as the calculation indicated, then they could scarcely affect the compounds' optical properties.⁴ To help resolve this "d-band dilemma", we undertook measurements of the valence-band spectra of AuAl₂ and AuGa₂ by x-ray photoelectron spectroscopy (XPS). This method has been described elsewhere:⁵ accordingly we describe below only those experimental features of this work that were peculiar to the AuAl₂-AuGa₂ problem. The two compounds are first treated in separate sections. The results are then discussed in the final section.

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144

AuAl₂

This compound was prepared by heating stiochiometric amounts of metallic Au and Al to $\sim 1000^\circ\text{C}$ in an induction furnace which was flushed a few times with argon and then pumped down to 2×10^{-6} . One of the compounds (sample B.1) was further remelted at $\sim 1000^\circ\text{C}$ in an arc furnace also flushed with argon and then pumped down to 10^{-6} . The resulting alloys were spark-cut and polished with size 600 sand paper and, in two cases, with one micron diamond paste and kerosene on a canvas wheel; but they were not etched. They were rinsed with absolute ethanol before mounting. A total of three samples were used to collect the data that were accepted for final analysis. The samples were studied in a H_2 atmosphere ($p \cong 0.01$ Torr) at temperatures indicated in Table I. The signal-to-noise ratio for energies near E_F was unusually low, and it was not possible to make a detailed study of the density-of-states function $\rho_{\text{AuAl}_2}(E)$. The spectra showed one dominant peak at $E_F - 6$ eV, however. A least-squares analysis was made on each spectrum. The trial function consisted of a linear, sloping background plus a Gaussian with a constant tail on the low energy side. This combination usually fits XPS spectra quite well, and it did in this case. For some of the spectra the "d-band" peak appeared on visual inspection to be slightly asymmetric, and two-Gaussian fits were made. These fits gave a very weak higher-energy peak of variable position and shifted the main peak only a few tenths eV. We therefore did not regard the experimental evidence for a second peak as being conclusive, and the question was of no particular interest, so only the one-Gaussian fits are presented in Table I.

One of the AuAl_2 spectra is shown in Fig. 1. Our final values for the position and width of the "d-band" peak are

$$E = E_F - (6.0 \pm 0.3) \text{ eV},$$

$$\Delta E = (4.1 \pm 0.5) \text{ eV FWHM}.$$

The Al 2p peak was found to be at

$$E = E_F - 75.05 \pm 0.20 \text{ eV}.$$

AuGa_2

Dr. Narath kindly provided one of our AuGa_2 samples: the other two were prepared in our Laboratory as described above for AuAl_2 . The experimental and data reduction procedures were also similar to those used for AuAl_2 . Again a single Gaussian was fitted to the "d-band" peak; in this case the peak was quite symmetrical and no attempt was made to fit two Gaussians to it. The Ga 3d peak, which lay about 20 eV below E_F , was asymmetric, however. It appeared to consist of two peaks, each of width 2 eV FWHM, and spaced about 2 eV apart, with the higher-energy peak about 0.4 as intense as the lower-energy peak. We attributed the high-energy peak to free Ga, and auxiliary experiments on non-stoichiometric samples seemed to support our assignment, although we were not able to eliminate this peak. Further support is given by the Au $4f_{5/2}$, $4f_{7/2}$ doublet in AuGa_2 , which showed no evidence of a second phase. It is also possible that the asymmetric 3d peak shape reflects real broadening arising from its proximity to E_F .

A spectrum of AuGa_2 is shown in Fig. 2. Our final values for the "d-band" peak are

$$E = E_F - (5.8 \pm 0.2) \text{ eV},$$

$$\Delta E = (4.6 \pm 0.4) \text{ eV}.$$

Discussion

The peaks at $\sim E_F - 6 \text{ eV}$ in the photoemission spectra from AuAl_2 and AuGa_2 can be attributed to the "gold 5d bands" with considerable confidence. We interpret these spectra as giving strong support for Switendick's band structure calculations, in a qualitative way: the positions of these peaks are in good agreement with his predictions. On closer inspection, however, there are points of difference. The experimental peaks are not quite so deep ($E_F - 6 \text{ eV}$) as the theoretical value ($E_F - 7 \text{ eV}$), and the experimental linewidth ($\sim 4 \text{ eV}$) is about twice theoretical. In fact the combination of less depth and greater width for the experimental d bands somewhat weakens the conclusion that these bands are not important in optical phenomena.

Comparison with the $\text{Al}(L_{2,3})$ soft x-ray emission spectrum from AuAl_2 , reported by Williams, et al.,⁶ is interesting. These workers studied x-ray spectra from transitions in which holes in the 2p shell of Al were filled by electrons from s-like states at Al sites. States derived from Al 3s atomic states are of course s-like at Al sites, but so also are some states that are d-like on Au sites. Thus the strong peak that Williams et al. found at $E_F - 8 \text{ eV}$ could be attributed in part to the "gold 5d bands", and they took this as support of Switendick's calculation. Our results are basically in very good agreement with Switendick's band structure results and the x-ray spectra results of Williams, et al., but the small differences are also of interest. The soft x-ray work shows a peak at $E_F - 8.3 \text{ eV}$, while the XPS peak in the

AuAl_2 is at $E_F - 6.0$ eV. We attribute this difference to the fact that XPS is most sensitive to d electrons and thus determines the position of the "gold 5d bands" directly, while the soft x-ray emission work is sensitive to bands with s-like symmetry at the Al sites. Switendick³ has calculated, for AuAl_2 , peak positions of $E_F - 8.0$ eV and $E_F - 7.1$ eV, respectively, for the peak in the Al 3s-like states and the peak in the total density of states. This would account for some, but not all, of the difference between the positions of the experimental peaks obtained by the two methods. Another more direct point of disagreement is the position of the Al 2p state. Switendick calculated $E = E_F - (73.8 \pm 0.1)$ eV for this state, and he quoted an experimental value of $E_F - (73.5 \pm 0.5)$ eV. Our XPS spectra showed this peak at $E_F - (75.1 \pm 0.2)$ eV. While these points of disagreement in detail are worth further study, it now seems clear that the three investigations mentioned here--Switendick's theoretical work, the x-ray emission work of Williams, et al., and our XPS results--all concur on one major point: the gold 5d bands in the AuAl_2 -type alloys lie 6 - 8 eV below the Fermi energy.

Acknowledgments

Several people contributed significantly to the success of this work, Dr. Albert Narath suggested the problem. Dr. Jack Hollander and Mr. Charles Fadley gave valuable advice during the experiments. Miss Carol Martinson assisted in preparing the alloys. Dr. A. C. Switendick elucidated the relationships among his work, that of Williams, et al., and ours. Dr. R. E. Watson and Dr. L. H. Bennett encouraged us to prepare this note for the Proceedings during a discussion of the AuAl_2 problem. Mr. Charlie Butler and Mr. Lee Johnson provided technical assistance in the preparation of the experiments.

Table I

AuAl ₂ sample no.	T(°C)	Reference Peak	-E ^a	ΔE (FWHM)	-E(5d-band)	ΔE (FWHM)
B.1	25	---	---	---	5.99(14)	4.6(3)
B.2	25	Al 2p	75.0(2)		5.71(19)	4.6(4)
B.3	600	Al 2p	75.2(2)		6.42(14)	3.3(4)
Adopted Values ^b			75.1(2)		6.0(3)	4.1(5)
AuGa ₂ sample no.						
A.3	400	Ga 3d(1) ^e	20.1	1.8 ^d	5.62(21)	5.9(5)
		" (2)	18.2	1.8		
A.4	400	Ga 3d(1)	20.8	1.95	5.81(14)	4.6(3)
		" (2)	18.9	1.95		
A.5	375	Ga 3d(1)	20.5	2.0	5.90(8)	4.2(4)
		" (2)	18.7	1.5		
Adopted Values ^b			20.5(4)	1.9	5.8(2)	4.6(3)
			18.6(4)	1.8		

^aAll energies in eV, relative to the Fermi Energy. Errors in last place are indicated paranthetically.

(continued)

Table I (continued)

^bAdopted values and assigned errors reflect some systematic errors.

^cThe Ga 3d(2) peak was 0.4 - 0.6 times as intense as the Ga 3d(1) peak.

^dFor samples A.3 and A.4, peak widths were constrained to be equal.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

1. A. C. Switendick and Albert Narath, Phys. Rev. Letters 22, 1423 (1969).
2. V. Jaccarino, M. Weber, J. H. Wernick, and A. Menth, Phys. Rev. Letters 21, 1811 (1968).
3. A. C. Switendick, "Orbital Symmetry Contributions to Electronic Density of States of AuAl_2 ", these proceedings.
4. A wavelength of 3000 Å corresponds to an energy of 4.14 eV.
5. The application of XPS to valence-band studies in metals is discussed by C. S. Fadley and D. A. Shirley, these proceedings.
6. M. L. Williams, R. C. Dobbyn, J. R. Cuthill, and A. J. McAlister, "Soft X-ray Emission Spectrum of Al in AuAl_2 ", these proceedings.

FIGURE CAPTIONS

Fig. 1. Typical x-ray photoemission spectrum for AuAl_2 near the Fermi energy.

Filled circles represent data points. Top solid curve was fitted to the data. It was composed of background, indicated by sloping solid line, plus a response curve indicated by dashed curve. The main peak of this dashed curve arises through photoemission from the "gold 5d" bands by $\text{MgK}\alpha_{12}$ radiation. Core-level peaks in inset indicate chemical purity of sample.

Fig. 2. Typical x-ray photoemission spectrum from AuGa_2 near the Fermi energy.

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Fig. 1.

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Fig. 2.

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