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Ultraviolet photoelectron spectroscopy of the valence bands of some Au alloys

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Ultraviolet photoelectron spectra taken with 40.81-eV photons are presented for three series of Au alloys: AuGa, AuIn, and AuCd. The results are discussed with reference to similar work on a series of Ag alloys previously reported and are also compared with x-ray photoelectron spectroscopy data. The results are consistent with the previous work on Ag alloys in that the Au 5*d* doublet width and splitting are (i) independent of the secondary or alloying metal, and (ii) strongly dependent on the mean number of nearest Au neighbors. The behavior of the Au 5*d*-band width, as a function of Au concentration, as measured here using He II radiation, differs significantly from that measured previously using x-ray photoelectron spectroscopy. This difference cannot be attributed wholly to the difference in linewidth of the two-photon sources or to surface enrichment of the samples. The similar variations of the Ga, In, and Cd *d* bands as a function of Au concentration are discussed with reference to previous work on the alloys of AgIn and AgCd.

I. INTRODUCTION

In this paper we report the ultraviolet photoelectron emission spectra (UPS) of the AuGa, AuIn, and AuCd alloy systems, with at least one example from each of the single-phase regions.[1]

The investigation of a series of Ag alloys by Nicholson *et al.*[2] led to the suggestion that the valence *d* bands in many noble-metal alloy systems exhibit similar behavior; namely that the *d*-band peaks move to higher binding energy and the *d*-band width decreases linearly with increasing concentration of the secondary constituent. Furthermore this behavior appears to be independent of the crystal phase of each individual alloy, such trends being shown by a wide variety of Ag alloy systems.

In order to investigate the validity of these trends in other noble-metal alloys, we have studied the AuGa, AuIn, and the AuCd systems in detail and complemented these results by reference to x-ray photoelectron spectroscopy (XPS) results from a number of Au alloy systems (AuCd, AuGe, AuSn, AuAl, $AuGa_2$, $AuAl_2$, and $AuIn_2$).

It is clear from the results obtained that the Au *d*-band behavior is independent of the secondary alloying metal and does follow the general trends reported for the Ag alloys. A comparison of XPS and UPS results, however, reveals discrepancies in the apparent Au *d*-band width as determined by these two methods; in particular, the UPS results exhibit a narrower Au *d* band than do the XPS results. This is discussed in terms of surface effects and possible photoionization–cross-section differences.

The *d* bands of the secondary alloying metals Ga, In, and Cd are also studied and it is found that, in the case of Ga and In, they are little affected by the alloying process. The Cd *d* band, however, displays a significant narrowing of the bandwidth and a decrease in the doublet splitting on alloying. The present results are strikingly similar to those obtained previously for a series of silver alloys containing In and Cd.[3]

II. EXPERIMENTAL

The alloys were prepared from weighted amounts of 99.99% pure constituents melted together in a vitrified carbon crucible under an argon atmosphere using an induction furnace. The samples were remelted in a graphite crucible under an argon atmosphere to form 3-mm-diam rods. These were then mounted in the 40.81-eV ultraviolet photoelectron spectrometer described by Poole *et al.*,[4] and were cleaned using the scraping method of McLachlan *et al.*[5] Gallium is a soft solid of low strength, and to prepare a pure-Ga sample it was necessary to cast it as a rod and then to drill and glue it to a brass rod to provide the necessary support for the scraping procedure.

Three AuGa, four AuIn, and seven AuCd alloy samples were prepared in this laboratory. Two further samples, $Au_{33}Ga_{67}$ and $Au_{33}In_{67}$, were prepared at the Max Planck Institüt in Stuttgart, and their valence-band spectra were obtained using a monochromatized 40.81-eV photon source. The structures, lattice constants, and other characteristics of all the alloys and pure metals used are given in Table I.

III. RESULTS

The 40.81-eV ultraviolet photoelectron spectra of the pure metals and of the AuGa, AuIn, and AuCd alloys, smoothed and corrected for analyzer transmission effects using the model of McLachlan *et al.*,[7] are shown in Figs. 1–3, respectively. The Fermi level (E_F) for each sample was determined

TABLE I. Structural details of Au alloys studied as obtained from Ref. 6.

Sample	Type	Structure and lattice constants
Au_{100}	Pure metal	fcc $a = 4.069$ Å
$Au_{90}Ga_{10}$	Solid solution	fcc $a = 4.064$ Å
$Au_{70}Ga_{30}$	Single phase	
$Au_{50}Ga_{50}$	Intermetallic compound AuGa	Orthorhombic $a = 6.267$ Å $b = 3.421$ Å $c = 6.397$ Å
$Au_{33}Ga_{67}$	Intermetallic compound $AuGa_2$	Cubic $a = 6.075$ Å
Ga_{100}	Pure metal	Orthorhombic $a = 4.523$ Å $b = 7.661$ Å $c = 4.524$ Å
$Au_{92}In_8$	Solid solution	
$Au_{82}In_{18}$	Intermediate phase alloy Au_4In	Hexagonal $a = 2.930$ Å $c = 4.790$ Å $c/a = 1.635$
$Au_{70}In_{30}$	Intermediate phase	Cubic $D8_{13}$ $a = 9.82$ Å
$Au_{50}In_{50}$	Intermediate compound AuIn	Triclinic $a = 4.30$ Å $b = 10.59$ Å $c = 3.56$ Å
$Au_{33}In_{67}$	Intermetallic compound $AuIn_2$	Cubic $a = 6.517$ Å
In_{100}	Pure metal	Tetragonal $a = 4.698$ Å $c = 4.947$ Å
$Au_{94}Cd_6$	Solid solution	
$Au_{90}Cd_{10}$	Solid solution	
$Au_{85}Cd_{15}$	Solid solution	
$Au_{75}Cd_{25}$	Intermetallic compound Au_3Cd	Tetragonal $a = 4.1157$ Å $c = 4.1309$ Å $c/a = 1.0037$
$Au_{50}Cd_{50}$	Intermetallic compound AuCd	Cubic $a = 3.323$
$Au_{39}Cd_{61}$	Intermetallic compound Au_5Cd_8	Cubic $D8_{1,3}$ type
$Au_{25}Cd_{75}$	Intermetallic compound $AuCd_3$	Cubic $D8_{1,3}$ type
Cd_{100}	Pure metal	Hexagonal $a = 2.979$ Å $c = 5.617$ Å $c/a = 1.886$

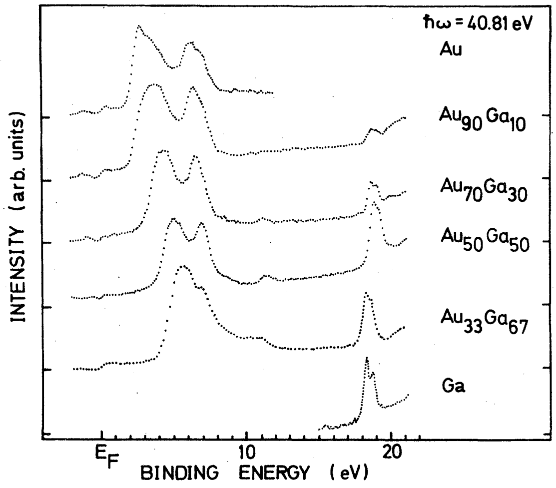

FIG. 1. 40.81-eV photoelectron spectra of Au, Ga, and selected alloys.

as the midpoint of the distinct rise in the spectrum at the onset of emission. All binding-energy measurements were then made relative to this level.

The binding energies, full widths at half maxima (FWHM), and peak separations or splittings (ΔE)

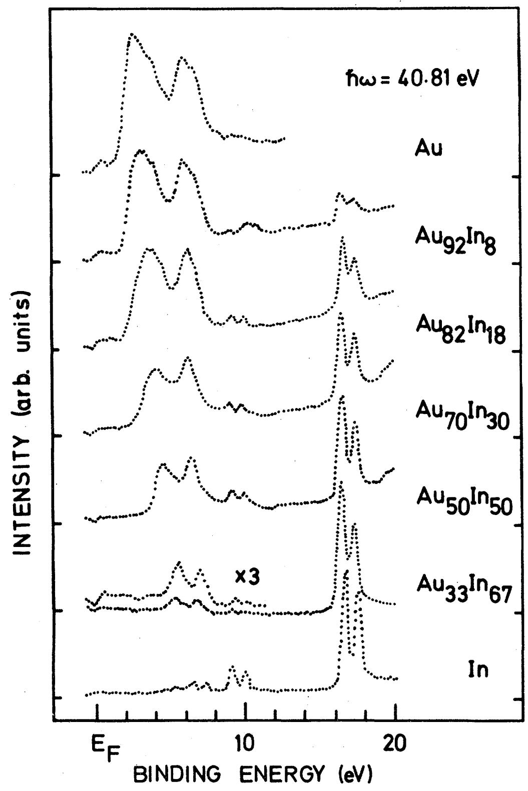

FIG. 2. 40.81-eV photoelectron spectra of Au, In, and selected alloys.

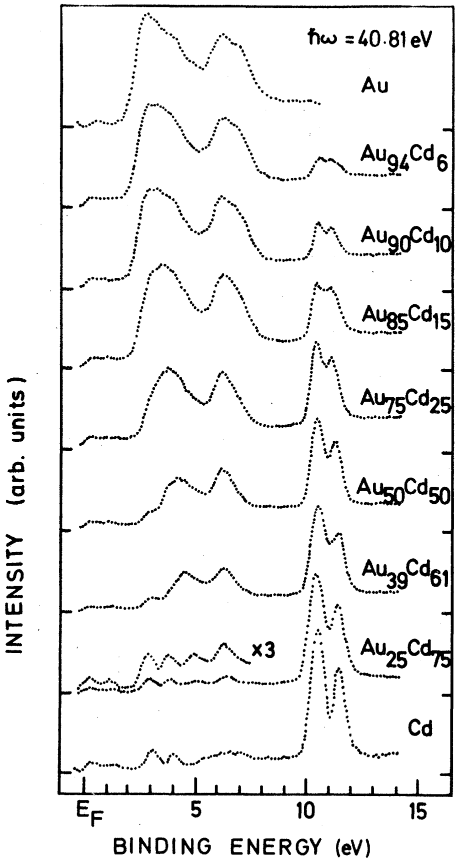

FIG. 3. 40.81-eV photoelectron spectra of Au, Cd, and selected alloys.

TABLE II. Binding energies, ΔE, and FWHM values for the Au 5d band in the alloys studied. Representative uncertainties are indicated in the case of pure Au.

	Binding energy (eV)			
Alloy	Au 5$d_{5/2}$	Au 5$d_{3/2}$	ΔE (eV)	FWHM (eV)
Au_{100}	3.10(5)	6.30(5)	3.20(2)	5.52(5)
$\mathrm{Au}_{90}\mathrm{Ga}_{10}$	3.66	6.34	2.68	4.91
$\mathrm{Au}_{70}\mathrm{Ga}_{30}$	4.32	6.58	2.26	3.82
$\mathrm{Au}_{50}\mathrm{Ga}_{50}$	4.86	6.77	1.91	3.27
$\mathrm{Au}_{33}\mathrm{Ga}_{67}$	5.54	6.87	1.33	3.00
$\mathrm{Au}_{92}\mathrm{In}_{8}$	3.19	6.21	3.02	4.96
$\mathrm{Au}_{82}\mathrm{In}_{18}$	3.81	6.34	2.53	4.40
$\mathrm{Au}_{70}\mathrm{In}_{30}$	4.35	6.50	2.15	3.70
$\mathrm{Au}_{50}\mathrm{In}_{50}$	4.60	6.55	1.96	3.07
$\mathrm{Au}_{33}\mathrm{In}_{67}$	5.13	6.81	1.68	2.51
$\mathrm{Au}_{94}\mathrm{Cd}_{6}$	3.17	6.26	3.09	5.12
$\mathrm{Au}_{90}\mathrm{Cd}_{10}$	3.32	6.32	3.00	5.04
$\mathrm{Au}_{85}\mathrm{Cd}_{15}$	3.61	6.34	2.73	2.73
$\mathrm{Au}_{75}\mathrm{Cd}_{25}$	3.78	6.26	2.48	4.18
$\mathrm{Au}_{50}\mathrm{Cd}_{50}$	4.48	6.52	2.04	3.28
$\mathrm{Au}_{39}\mathrm{Cd}_{61}$	4.56	6.21	1.65	2.95
$\mathrm{Au}_{25}\mathrm{Cd}_{75}$	5.07	6.40	1.33	2.13

TABLE III. Binding energies, ΔE, and FWHM values for the Ga, In, and Cd d bands in the alloys studied.

	Binding energy (eV)			
Alloy	Ga 3$d_{5/2}$	Ga 3$d_{3/2}$	ΔE (eV)	FWHM (eV)
$\mathrm{Au}_{90}\mathrm{Ga}_{10}$	18.71	19.04	0.33	0.83
$\mathrm{Au}_{70}\mathrm{Ga}_{30}$	18.78	19.14	0.36	0.85
$\mathrm{Au}_{50}\mathrm{Ga}_{50}$	18.79	19.17	0.38	0.87
$\mathrm{Au}_{33}\mathrm{Ga}_{67}$	18.61	18.92	0.31	0.89
Ga_{100}	18.27	18.75	0.44	0.90
	In 4$d_{5/2}$	In 4$d_{3/2}$	ΔE (eV)	FWHM
$\mathrm{Au}_{92}\mathrm{In}_{8}$	16.71	17.60	0.89	1.28
$\mathrm{Au}_{82}\mathrm{In}_{18}$	16.91	17.78	0.87	1.23
$\mathrm{Au}_{70}\mathrm{In}_{30}$	16.99	17.86	0.87	1.40
$\mathrm{Au}_{50}\mathrm{In}_{50}$	16.85	17.72	0.87	1.37
$\mathrm{Au}_{33}\mathrm{In}_{67}$	16.76	17.62	0.86	1.45
In_{100}	16.68	17.54	0.89	1.35
	Cd 4$d_{5/2}$	Cd 4$d_{3/2}$	ΔE (eV)	FWHM
$\mathrm{Au}_{94}\mathrm{Cd}_{6}$	10.65	11.20	0.55	1.25
$\mathrm{Au}_{90}\mathrm{Cd}_{10}$	10.57	11.13	0.56	1.26
$\mathrm{Au}_{85}\mathrm{Cd}_{15}$	10.42	11.02	0.60	1.34
$\mathrm{Au}_{75}\mathrm{Cd}_{25}$	10.46	11.14	0.68	1.39
$\mathrm{Au}_{50}\mathrm{Cd}_{50}$	10.49	11.32	0.84	1.52
$\mathrm{Au}_{30}\mathrm{Cd}_{61}$	10.43	11.34	0.91	1.64
$\mathrm{Au}_{25}\mathrm{Cd}_{75}$	10.46	11.45	0.99	1.68
Cd_{100}	10.48	11.41	0.95	1.69

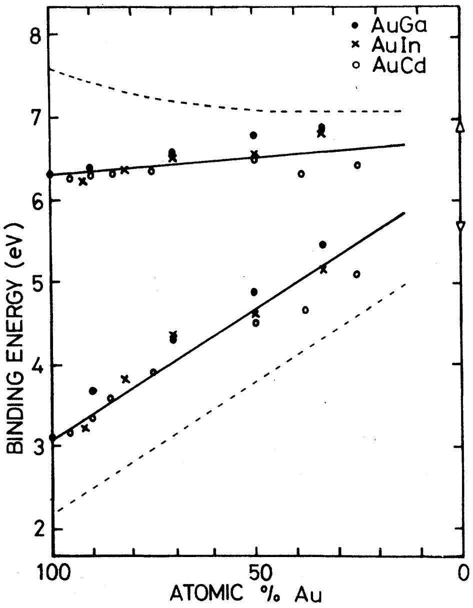

FIG. 4. Au concentration dependence of the binding energies of the Au 5d band for the alloy systems indicated. The solid lines show the concentration dependence of the peaks and the broken lines indicate the variation of the half maxima points. The arrows at 0% Au indicate the Au free-ion value of 1.5 eV obtained from the tables of Moore (Ref. 8).

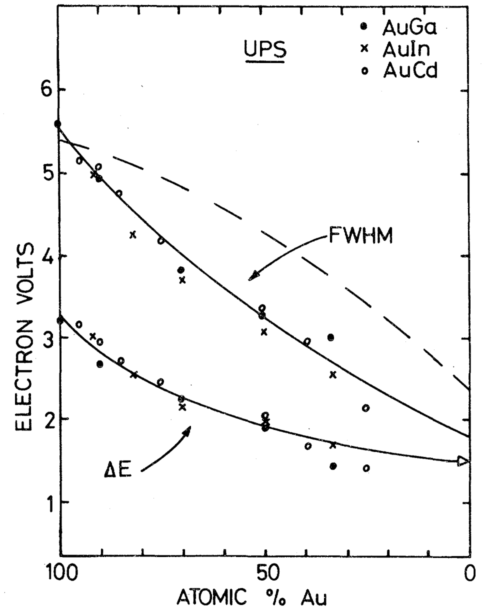

FIG. 5. Au concentration dependence of the FWHM and ΔE of the Au $5d$ doublet for the particular alloy systems indicated. The broken line indicates the variation of the FWHM of the XPS results. The arrow at 0% Au indicate the Au free-ion value of 1.5 eV obtained from the tables of Moore (Ref. 8).

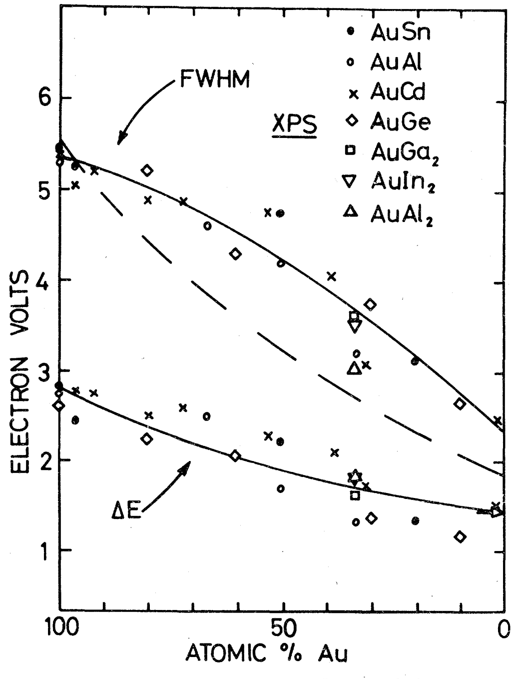

FIG. 6. Au concentration dependence of the FWHM and ΔE for the corresponding XPS results with the broken line indicating the UPS results. The arrow at 0% Au indicate the Au free-ion value of 1.5 eV obtained from the tables of Moore (Ref. 8).

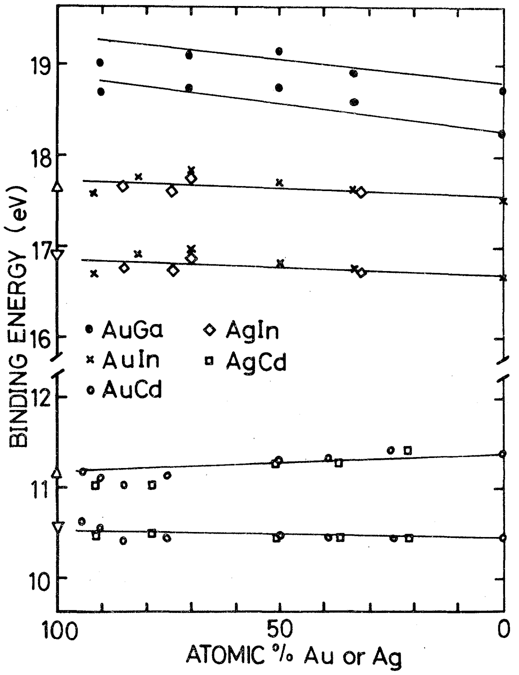

FIG. 7. Concentration dependence of binding energy of binding energy of the Ga $3d_{3/2,5/2}$, In $4d_{3/2,5/2}$, and Cd $4d_{3/2,5/2}$ peaks. The arrows at 100% Au indicate the free-ion value in each case as obtained from Ref. 8. The free-ion value for Ga is unavailable.

of the Au $5d$ doublet are given for AuGa, AuIn, and AuCd in Table II. The corresponding data for the Ga $3d$, In $4d$, and Cd $4d$ doublets are given in Table III. The positions of the peaks derived from the Au $5d_{3/2,5/2}$ levels are plotted against Au concentration in Fig. 4. Also shown in Fig. 4 are dashed lines indicating the positions in energy of the half height points of the Au $5d$ band. The FWHM and ΔE for the Au $5d$ band are plotted against Au concentration in Figs. 5 and 6. These two figures include XPS data for the following Au-alloy systems: AuCd,[9] AuSn,[10] AuGe,[11] AuAl,[12] and the single alloys AuGa$_2$, AuIn$_2$, and AuAl$_2$.[13]

The positions of the Ga $3d$, In $4d$, and Cd $4d$ doublets are plotted against noble-metal concentration in Fig. 7, with their FWHM and ΔE plotted against noble-metal concentration in Fig. 8.

IV. DISCUSSION

From the spectra it may be seen that the respective d bands in the alloy systems AuGa, AuIn, and AuCd are well separated in energy. Such a case has been treated theoretically by Velický *et al.*,[14] where a single-band model Hamiltonian was used to describe the electronic structure of a three-

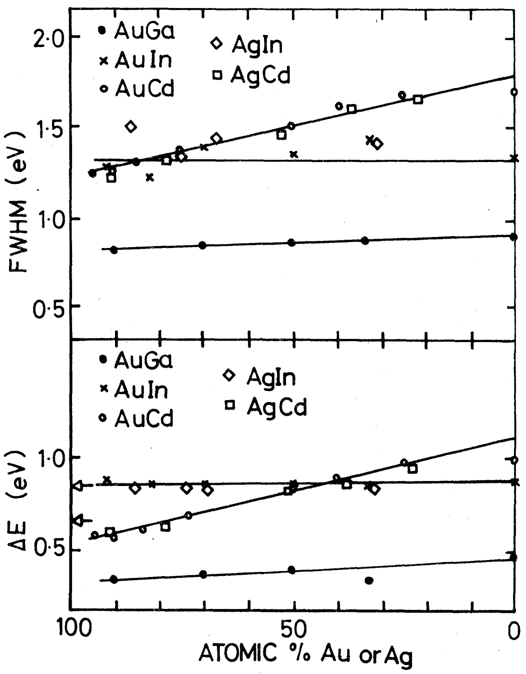

FIG. 8. Concentration dependence of the FWHM and ΔE of the Ga, In, and Cd d bands. The arrows at 100% Au indicate the free-ion value in each case as obtained from Ref. 8. The free-ion value for Ga is unavailable.

dimensional disordered binary alloy. In particular, these authors discuss the "split-band limit" in which the two d bands retain their individual identity on alloying, and predict that the width of the d band of each constituent will vary roughly as the square root of the concentration of that constituent.

Moruzzi *et al.*[15] have also treated theoretically the case of an intermetallic compound with two d-band constituents. They have considered $3d$-band narrowing in compounds with a CsCl structure; but it would appear that their conclusions may be applied more generally. They attribute d-band narrowing in the alloy to a lack of available d states on neighboring atoms into which electron tunneling can occur. In the case of compounds with two d-band constituents they find an additional d-band narrowing due to mutual d-band repulsion, the narrowing increasing with decreasing d-band separation in energy.

Shevchik[9] proposed a simple molecular-orbital model which demonstrates some of the d-band features found in the noble-metal alloys.[12] Shevchik suggests that the d-band width is due to d-orbital overlap, and hence that the d-band width and splitting are dependent on both the mean number of neighboring like noble-metal atoms and on the interatomic distances. In the alloy systems described here the interatomic distances vary by only a few percent and so the variation of mean number of like neighbors would appear to be the dominant influence.

A. Behavior of the Au 5*d* band

From Figs. 1–3 it may be seen that the Au $5d$ band behaves qualitatively the same for the three different secondary constituents. The band retains its distinctive double-peaked shape as the Au concentration decreases as required by the "split-band limit" model. The band narrows and retreats from the Fermi edge with decreasing Au concentration in all three sets of spectra. The peak intensity naturally decreases with Au concentration but even at low concentrations of Au (e.g., $Au_{25}Cd_{75}$) the d band retains its distinctive two-peaked shape. Using XPS, Shevchik[9] has shown that the Au $5d$ band is still recognizable at extremely low Au concentrations (Au_2Cd_{98}). The overlap of the 48.37- and 51.02-eV He II satellites of the Cd $4d$ band masks the Au $5d$ band at lower concentrations of Au in the AuCd system in the present work, thereby limiting the investigation of very low Au concentration alloys.

From Fig. 4 the movement of the Au $5d_{5/2}$ derived peak away from the Fermi level towards higher binding energy is quite rapid with decreasing Au concentration, whereas the Au $5d_{3/2}$ derived peak, although it does move to higher binding energy, exhibits much less change. Similarly, from the XPS results, it is also found that the peak closer to the Fermi edge and therefore farthest from the secondary metal constituent's d band moves most significantly, but not to the extent exhibited in the UPS data. This movement of the peaks away from the Fermi edge was observed in the Ag alloys reported by Nicholson *et al.*[2] and a possible explanation is offered by Moruzzi *et al.*[15] They explain the different rates of movement of the two peaks by considering the mutual repulsion between the two d bands of the alloy constituents as being a function of the d-band separation; that is, the Au $5d_{5/2}$ peak, being further away in energy from the other constituent d band, is less strongly repelled and hence moves more freely towards the atomic binding energy value. Nicholson *et al.*[3] found that in AgPd, where the Pd $4d$ band is closer to the Fermi edge than the Ag $4d$ band, the movement of the two peaks of the Ag $4d$ band is the reverse of that observed here for the Au alloys, again in agreement with the prediction of Moruzzi *et al.*

From Figs. 5 and 6 it may clearly be seen that the behavior of the Au $5d$-band width is significantly different in the UPS data to that obtained from the XPS results. The UPS and XPS results for ΔE do not appear to differ significantly. Velický *et al.*[14] suggest that the width of a d band of one constituent in a binary alloy will vary approximately as the square root of that constituent's concentration. From Fig. 5 it may be seen that the UPS results show more of a linear than a square-root dependence on concentration, within the accuracies of this experiment. On the other hand the XPS results (Fig. 6) do tend towards a possible square-root dependence. The fact that the UPS and XPS data are different in this respect is a more interesting result. This discrepancy cannot entirely be explained on the basis of the different resolution R of the XPS and UPS experiments as is illustrated by a comparison of the present AuCd results ($R \simeq 0.3$ eV) and those of Shevchik, who used monochromatic x rays ($R \simeq 0.6$ eV).

A check was made concerning the composition of the alloys using electron-microprobe analysis, the bulk compositions being verified to within ~2%. To bring the UPS results into agreement with the XPS results a surface variation in composition of approximately 30% would have to exist. Two recent experiments have yielded conflicting conclusions concerning the liklihood of significant surface enrichment in Au-Ag alloys. Bouwman *et al.*,[16] using Auger spectroscopy, have concluded that the surface composition of the alloys remains equal to the bulk compostion up to 650 °C. On the other hand, Nelson,[17] using ion-scattering techniques, has found strong surface enrichment of Ag over the bulk composition in certain Au-Ag alloys. The scraping technique used in the present work continually provided a new surface and data are collected within 0.5 sec of each scraping operation. Given this time scale we do not consider that surface enrichment will be a significant feature of the present results. It is similarly unlikely that surface enrichment could be significant in the XPS data due to the greater sampling depth of this technique.

The possibility still exists, however, that the difference in behavior of the Au 5d FWHM between UPS and XPS spectra may be due to differences between the electronic density of states at the surface and in the bulk.

An alternative explanation may well exist in terms of variations in the photoionization cross section across the 5d band for the two different incident radiations. Such an explanation has previously been suggested to account for the fact that the Ag and Cu pure-metal UPS conduction bands are significantly narrower than either the XPS or the theoretical values.[18]

B. Behavior of the Ga, In, and Cd *d* bands

The d bands of the three secondary constituent metals Ga, In, and Cd can be seen from the spectra of Figs. 1–3 to retain their characteristic shape, and, from Fig. 7, to remain relatively stationary in energy compared with the movement of the Au band as their concentration varies.

In Fig. 8 we show the behavior of the FWHM and splitting ΔE of the d bands of these metals for each of the samples studied. It may be seen that, in the case of In and Ga, both FWHM and ΔE remain substantially unaltered by the alloying process, whereas Cd displays a significant and almost linear decrease in FWHM and in ΔE with increasing concentration.

The enhanced splitting of the Cd 3d levels of the pure metal over the free-atom valve has been attributed to crystal-field effects by Ley *et al.*,[19] whereas Shevchik[9] suggested that the overlap between like atoms was the mechanism causing the enhancement. The linearity of the splitting as a function of concentration for Cd in Ag alloys favored the latter model. The Cd 3d splittings (ΔE) plotted in Fig. 8 cover a very wide range of phases of both AuCd and AgCd alloys with different crystal structures. Thus the linearity of the ΔE with concentration confirms the overlap model.[9]

Figure 7 shows the remarkable agreement between binding energies of the $4d_{3/2,\,5/2}$ peaks of Cd and In for both Au and Ag alloys with these metals. The observed binding energy with respect to the Fermi level may be written

$$E_{\text{obs}} = E_a + E_{\text{ch}} - E_R - \phi ,$$

where E_a is the atomic binding energy, E_{ch} is the chemical shift in the alloy, E_R is the relaxation energy, and ϕ is the work function. Since the values E_{ch}, E_R, and ϕ may reasonably be expected to vary from sample to sample the observed agreement is surprising.

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