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Electronic structure of aluminum and aluminum–noble-metal alloys studied by soft-x-ray and x-ray photoelectron spectroscopies

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X-ray photoelectron spectra (XPS) and Al K and Al $L_{2,3}$ soft-x-ray spectra (SXS) of valence bands for aluminum–noble-metal alloys are rationalized on the basis that SXS spectra are dominated by dipole selection rules while XPS spectra chiefly reflect the noble-metal d bands. We find, in agreement with theory, that the main peaks in the Al $3s$ partial densities of states are at higher binding energy than those for the noble metal d states. Peaks in the Al $3p$ partial densities of states approximately coincide with the higher-energy peaks in the partial densities of noble-metal d states. The remarkable large chemical shifts of core levels in these alloys are noted and the Au $N_{6,7}$ SXS emission from aluminum–noble-metal alloys also discussed. The Auger spectra from Al-Ag and Al-Cu alloys provide strong additional evidence that single-atom effects dominate in the Auger processes for these alloys.

I. INTRODUCTION

In this paper we aim to elucidate further the density of states and electronic structure of aluminum–noble-metal alloys using soft-x-ray and x-ray-photoelectron spectroscopies (SXS and XPS). SXS and XPS are complementary techniques for the study of electronic density of states. In SXS the emitted intensity is determined mainly by the dipole part of the matrix element, thus giving rise to the density of states of selected symmetry local to the emitting atom,[1] whereas in XPS the spectrum is determined by photoelectric cross sections.[2–5] In the few cases where the techniques have been combined they have produced excellent results (e.g., Refs. 6–11). The valence bands of aluminum–noble-metal alloys are especially suitable for combined study because Al $L_{2,3}$ and the Al K emission give the local partial densities of s states and p states, respectively, while the XPS spectra are dominated by the noble-metal d states.

The Al $L_{2,3}$ and K x-ray emission spectra for alloys of aluminum with transition, noble, and rare-earth metals have been extensively studied (see Refs. 12–18) and in many cases show strong features at energies that reflect deep-lying levels in the valence band. An early attempt to explain this feature in the Al $L_{2,3}$ emission from Al–Ag alloys[18] was considerably improved by a later comparison of these results with the XPS spectra from the same alloys.[8] In this paper we extend such comparisons to other aluminum–noble-metal alloys.

Papers relating to the XPS spectra of copper, silver, and gold are numerous.[4,5,19–23] The spectra are dominated by the noble-metal d bands which are split by more than the spin-orbit splitting found in the free atom.[24,25] The gold d band splitting is decreased on dilution with aluminum,[26] tin,[27] magnesium,[10] or cadmium.[28] Shevchik[28] and Ley *et al.*[29] have discussed the origin of this splitting. In this paper we show how the Au $N_{6,7}$ emission band shape relates to this problem.

Finally we attempt to derive information from the shifts of the core levels with respect to E_F as measured by XPS and from shifts of emission lines and bands as measured by SXS. Chemical shifts have been used as an indicator of charge transfer in chemical compounds (e.g., Refs. 2, 30, 31), but are complicated by interatomic relaxation or molecular relaxation effects.[32–36] Further the importance of the energy differences between the Fermi level and the inner potential (i.e., the chemical potential of the electrons[37–39]) cannot be overlooked.

II. EXPERIMENTAL

We consider the purity and constitution of samples for SXS and XPS to be important, and attention was paid to this in these studies. The procedures for preparation of bulk specimens used for SXS studies has been described elsewhere.[12,15] All SXS samples were scraped and outgassed in high vacuum immediately before recording spectra.

XPS is far more sensitive to surface contamination than SXS, and it was found that bulk aluminum-noble-metal alloys gave unacceptably high XPS signals from contamination even after scraping in ultrahigh vacuum,[40] and the alloys were thus prepared by evaporation *in situ*. As described in Ref. 26, the constituent metals were evaporated successively and in the correct proportions onto a stainless-steel substrate which could be cooled by liquid nitrogen when necessary. The sample was then heated until the required intermetallic phase had formed at the surface. Arguments used to confirm the identity of the phases present have been given elsewhere,[26] but we note here that all phases of Al–Ag alloys exist over wide composition ranges[41] and it was not possible to define precisely the Al–Ag alloys used for XPS studies, although it was possible to produce samples of solid solutions of Ag in Al and of the ζ phase (nominally labeled $AlAg_2$) as required. We believe that the cleanliness achieved by this technique justifies its use. Comparison of the O 1*s* peak intensities in these and other experiments[42,43] allows us to estimate that the freshly evaporated aluminum and noble-metal surfaces were covered with less than 0.15×10^{15} oxygen atoms cm^{-2} and that, even after heating to prepare the alloys, the contamination was always less than 2×10^{15} atoms cm^{-2}. As the oxygen was certainly present as Al_2O_3, which has a low-photoelectric cross section in the valence-band region, we do not believe there was sufficient to lead to distortion of the results presented here.

The x-ray spectrometers used for recording the Al $L_{2,3}$ and Au $N_{6,7}$,[44] the Al K emission spectra,[45] and the XPS spectrometer[46] have all been described elsewhere. The zero of binding energy in all cases was taken to be 50% of maximum intensity of the apparent Fermi edge. Core-level binding energies quoted are measured from the core-level peak maxima. Systematic errors may arise because of inaccuracy of the digital voltmeter used to measure retarding voltages and the difficulty of choosing a peak position when the peak is very broad and asymmetric. The latter is the major source of error for deep-lying core levels of noble metals and cannot be assessed by standard error treatments. The errors quoted for core-level binding energies are those we consider to be reasonable estimates of the above factors.

III. RESULTS

A. Core-level binding energies

The observed binding energies for core level peaks from Cu, Ag, and Au are presented in Tables I–III along with the values from x-ray tabulations given by Bearden and Burr[47] and some other literature values.[48–51] Our values are in good agreement with XPS data from other laboratories, and the small differences that occur are thought to be due to instrumental inaccuracies or small shifts arising from partial coverage of the surfaces by chemisorbed species[52] or oxides. It is seen that the XPS binding energies obtained are higher than those from x-ray emission results quoted by Bearden and Burr. This is tentatively attributed to difficulties in interpreting x-ray emission from the pure noble metals where the *d* bands lie only a few volts below E_F.

TABLE I. Cu XPS peak binding energies (measured in eV).

Peak	This work	Bearden and Burr (Ref. 47)	Schön (Ref. 50)	Johansson *et al*. (Ref. 48)
VB[a]	2.7 ± 0.2	1.6 ± 0.4		
M_3	75.1 ± 0.2	73.6 ± 0.4	75.2	
M_2	77.3 ± 0.3		77.1	
M_1	122.5 ± 0.4	119.8 ± 0.6	122.4	122.9
L_3	932.5 ± 0.2	931.1 ± 0.4	932.2	932.8
L_2	952.3 ± 0.2	951.0 ± 0.4	952.1	
L_1	1096.7 ± 0.3	1096.1 ± 0.4	1096.4	

Cu $L_{2,3}VV$ Auger peak kinetic energies

This work	Schön (Ref. 50)	Kowalczyk *et al*. (Ref. 60)	Johansson *et al*. (Ref. 48)	Chung and Jenkins (Ref. 57)
921.5 ± 0.2	921.7	920.6		
919.9 ± 0.4				
918.8 ± 0.2	919.0	918.0	918.3	920
916.4 ± 0.3	916.7	915.8		
914.3 ± 0.3	914.7	913.6		

[a] VB stands for valence band.

TABLE II. Ag XPS peak binding energies (measured in eV).

Peak	This work	Bearden and Burr (Ref. 47)	Umbach, Fuggle, and Menzel (Ref. 51)	Johansson *et al.* (Ref. 48)	Ebel (Ref. 49)	Schön (Ref. 50)
VB 1)^{b}	4.5 ± 0.2	3.3 ± 0.3	4.5 ± 0.2			
2)^{b}	6.2 ± 0.2		6.2 ± 0.2			
N_3		55.9 ± 0.3	58.3 ± 1.5 vb^{a}			
N_2		62.6 ± 0.3	63.7 ± 2.5 vb^{a}			
N_1		95.2 ± 0.3	96.7 ± 0.3			
M_5	367.9 ± 0.2	366.7 ± 0.3	367.9 ± 0.2	368.2 ± 0.2	368.0 ± 0.2	368.2 ± 0.2
M_4	373.9 ± 0.2	372.8 ± 0.3	373.9 ± 0.2			
M_3	573.0 ± 0.3	571.4 ± 0.3	572.7 ± 0.3	573.0 ± 0.3	573.2 ± 0.2	573.0 ± 0.3
M_2	603.7 ± 0.4	602.4 ± 0.3	603.6 ± 0.4			
M_1	718.9 ± 0.6	717.5 ± 0.3	718.7 ± 0.5			

[a] vb, very broad.

[b] VB 1, 2; two main peak energies in the valence band.

B. Core-level shifts

Tables IV–VI give the observed core-level binding energies derived from XPS and SXS measurements for Al and Al-Cu, Al-Ag, and Al-Au alloys. There are significant shifts in many of the peaks and these are tabulated for easier comparison in Table VII, where we observe that the majority of peaks of both components shift to higher binding energy upon alloying. A particularly striking visual example is illustrated in Fig. 1. A small amount of aluminum was evaporated onto the surface of a liquid-nitrogen-cooled gold film which caused shoulders to form on the high binding energy side of the peaks from clean gold. The area of the shoulder is approximately 35% of the whole. It has been found that in the kinetic energy region 1300–1500 eV approximately 30% of the XPS signal from mercury-on-gold and mercury-on-platinum samples arises in the top monolayer.[53,54] The low temperature of the gold substrate excludes consideration of extensive diffusion and we believe the shoulder to be due to a thin alloy layer on top of the gold surfaces.

Watson *et al.*[55] found the Au N_7 level to be 1.35 eV to higher binding energy in Al_2Au. This shift is 0.6 eV less than we find, but the studies of Watson *et al.* were made before the extreme surface sensitivity of XPS was fully realized and the cleaning procedures they described are not now considered adequate. We tentatively attribute the lower shift reported by Watson *et al.* to oxidation of the aluminum, and hence gold enrichment of the alloy left at the surface.

C. Auger peaks

The Cu $L_3M_{4,5}M_{4,5}$ (L_3VV) and Ag $M_{4,5}N_{4,5}N_{4,5}$ ($M_{4,5}VV$) Auger peak energies reported here in Tables II and III are also in reasonable agreement with recent literature data,[48,50–52,56–60] and we again attribute most differences to the greater contamination levels in some earlier reports. The resolution of our spectra is superior to all but the most recent reported data, and we have been able to resolve more features in the Cu L_3VV spectra.

TABLE III. Au XPS peak binding energies (measured in eV).

Peak	This work	Bearden and Burr (Ref. 17)	Ebel (Ref. 49)	Schön (Ref. 50)
VB 1)^{a}	3.3 ± 0.2	2.5 ± 0.5		
2)^{a}	6.1 ± 0.2			
O_3	57.2 ± 0.6	53.7 ± 0.7		
N_7	83.7 ± 0.2	82.8 ± 0.5	84.0 ± 0.2	84.0
N_6	87.5 ± 0.2	86.4 ± 0.4		
N_5	335.0 ± 0.3	333.9 ± 0.4		335.1
N_4	353.0 ± 0.3	352.0 ± 0.4		
N_3	546.2 ± 0.4	545.4 ± 0.5		
N_2	642.5 ± 0.6	643.7 ± 0.5		
N_1	761.9 ± 0.8	758.8 ± 0.4		

[a] VB 1, 2; two main peak energies in the valence band.

TABLE IV. XPS and SXS binding energies and selected Auger-peak kinetic energies for levels in Cu and Al_2Cu (measured in eV).

Peak	Cu	Al_2Cu	Al
VB[a]	2.7	4.3	
Cu M_3	75.1	75.9	
Cu M_2	77.3	78.4	
Cu M_1	122.5	123.5	
Cu L_3	932.5	933.6	
Cu L_2	952.3	953.5	
Cu L_1	1096.7	1097.7	
Cu	921.5	921.1	
L_3VV	919.9	919.5	
Auger	918.8	918.3	
Peaks	916.4	916.0	
	914.3	914.1	
Al $L_{2,3}$		72.8	72.8
Al L_1		117.9	117.9
Al K (SXS)		1559.6	1559.5[b]

[a] VB valence band.

[b] Taken from Ref. 9 and used as our reference point for all Al K spectra.

Figure 2 shows the Cu L_3VV Auger spectra from Cu and Al_2Cu. It can be seen that the shape of the Auger spectrum does not change significantly on alloying, and similar results were found for the Ag $M_{4,5}VV$ transitions. We note in Fig. 2 and Tables IV, V, and VII that the kinetic energies of the Auger peaks decrease on alloying, but not as much as the XPS peaks.

D. Valence-band studies

The XPS, Al $L_{2,3}$, and Al K x-ray emission spectra from aluminum, and the aluminum-noble-metal alloys studied have been summarized and superimposed in Figs. 3–8. Some spectral and theoretical data have been included in these diagrams to aid discussion of the phenomena involved. In general, the photoemission from the noble-metal d bands dominates the XPS valence bands. These d bands are narrower in the alloys than in the pure metals, and shifted to higher binding energy with respect to the Fermi level; however the position of the high-binding-energy limit of the d bands is much less sensitive to alloy composition. Splitting of the d bands is still observable in the XPS spectra of the alloys Al_2Au, AlAu, $AlAu_2$, and $AlAg_2$. The background photoemission on the high-binding-energy side of the XPS valence bands is more intense than that beyond the Fermi level, but no attempt has been made to correct for this.

TABLE V. Binding energies from XPS and SXS measurements in Al-Ag alloys (in eV).

Peak	Ag	$AlAg_2$	Al + Ag solid solution	Al
VB 1)[a]	4.5	5.7	6.2	
2)[a]	6.2	6.5		
Ag N_5	367.9	368.4	368.9	
Ag N_4	373.9	374.4	374.9	
Ag N_3	573.0	573.7	566.0	
Ag N_2	603.7	604.5	···	
Ag N_1	718.9	719.4	···	
Ag	358.4	358.0	357.6	
$N_{4,5}VV$	354.0	353.5	353.3	
Auger	352.4	351.9	351.6	
Al $L_{2,3}$		73.0	72.8	72.8
Al L_1		118.2	117.9	117.9

[a] VB 1, 2; two main peak energies in the valence band.

TABLE VI. Binding energies from SXS and XPS measurements in Al-Au alloys (in eV).

Peak	Au	$AlAu_2$	AlAu	Al_2Au	Al
VB 1)[a]	3.3	4.5	5.7	6.1	
2)[a]	6.1	7.0	7.4	7.4	
Au N_7	83.7	84.7	85.3	85.7	
Au N_6	87.5	88.4	89.0	89.4	
Au N_5	335.0	336.0	···	337.0	
Au N_4	353.0	353.9	···	355.1	
Au N_3	546.2	547.2	···	548.3	
Au N_2	642.5	643.2	···	644.6	
Au N_1	761.9	762.4	···	763.4	
Al $L_{2,3}$	···	···[b]	73.6[b]	72.9	72.8
Al $L_{2,3}$ (SXS)		73.40	73.40	73.06	72.76
Al L_1	···	118.8	118.3	118.0	117.9
Al K (SXS)	···	···	1560.3	1559.8	1559.5

[a] VB 1,2; two main peak energies in the valence band.

[b] This peak and the $K\alpha_{3,4}$ satellites of the Au N_7 peak overlapped.

The Al_2Au valence band has been studied previously by XPS[55,61,62] and differences concerning binding-energy values and structural features between the present result and these earlier ones can be attributed to oxidation effects in the earlier measurements.

The Al $L_{2,3}$ and Al K emission spectra from aluminum-noble-metal alloys have been studied by other workers,[13,14] in particular the Al–Au alloys have been the subject of a critical review.[63] Although there is some discrepancy in the relative peak intensities, the general agreement is good. The Al $L_{2,3}$ spectra are characterized by a distinct peak 6–8 eV below E_F. The Al-Cu system is complicated in high-copper-concentration alloys by the Cu $M_{2,3}$ emission overlapping the Al $L_{2,3}$ band in the region of the Fermi level. The Al K spectra from the alloys have two peaks, one near E_F and the other at higher binding energies

TABLE VII. Summary of level binding-energy increases with respect to the pure metals (measured in eV with respect to E_F).

Alloy	Al $L_{2,3}$ SXS	Al $L_{2,3}$ XPS	Al L_1 XPS	Al K SXS	Average of noble metal core levels XPS	Noble metal valence (d) bands XPS	Noble metal Auger peak kinetic energy increase
$Al_{0.88}Au_{0.12}$	···	···	···	0.0	···	···	···
Al_2Au	0.30	0.1	0.1	0.33	1.9	~2.0	···
AlAu	0.64	0.8[a]	0.4	0.78	1.5	~1.8	···
$AlAu_2$	0.64	···	0.8	···	0.9	~0.8	···
Ag dissolved in Al	···	0.0	0.0	···	1.0	~0.9	−0.8
$AlAg_2$	···	0.2	0.3	···	0.6	~0.8	−0.5
Al_2Cu	···	0.0	0.0	0.08	0.9	~1.6	−0.4

[a] These peaks overlapped with the $K\alpha_{3,4}$ satellites of the Au N_7 peak.

[b] These values are taken from shifts of estimated peaks as the position of the d-band centroid was strongly dependent on the background subtracted.

although not as pronounced nor as deep lying as the high-binding-energy peaks in the Al $L_{2,3}$ spectra.

A notable experimental observation is that the Al $L_{2,3}$ emission intensity decreases more rapidly with increasing noble-metal concentration than can be easily explained in terms of self-absorption effects, or of the number of emitting atoms. This decrease is especially marked at binding energies lower than the onset of the noble-metal d bands.

IV. DISCUSSION

A. Chemical shifts, chemical potentials, and work functions

Chemical shifts should, ideally, be measured with respect to the vacuum level. However, only the Fermi level is experimentally observable. We use what we believe to be the older definition of the "vacuum level," namely, the energy of an electron at rest at infinity. Some surface scientists define the vacuum level in terms of the energy of an electron far enough outside the surface of a sample for the image potential to be considered zero. In general, this energy is not the same as that at the vacuum level used here because of the surface dipole layer of metals.[37,39] The effect of this dipole layer is small for metals of low electron density[37,38], but is calculated to be a few eV for metals with high electron density[38,39] and is different for different surfaces of the same single crystal.[64,65] The measured work function of a metal is the difference between the potential of an electron at the Fermi level and that "just outside" the metal surface. Thus the work function is different for different single faces, and is the difference of the surface dipole of the face and the chemical potential of the electrons at the Fermi level. (The chemical potential of the electrons must be subtracted because it is defined for electrons added to the system, while the work function is defined for electrons leaving the sample.) Addition of the sample work function to the binding energy measured with respect to the Fermi level does not necessarily yield the binding energy with respect to the vacuum level. In the

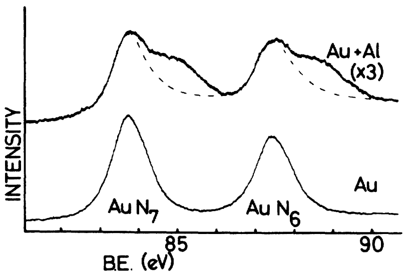

FIG. 1. XPS spectra, in the region of the Au $N_{6,7}$ peaks, of pure evaporated gold and liquid-nitrogen-cooled gold on to which a thin layer of aluminum has been evaporated. B.E., binding energy.

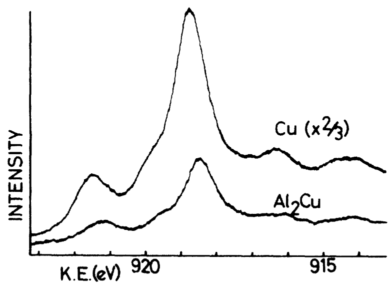

FIG. 2. Section of the Cu L_3VV Auger spectrum from Al_2Cu and pure Cu. K.E., kinetic energy.

following discussion the role of the chemical potential of the electrons must be remembered.

B. Interpretation of the observed shifts

As shown in Table VII, the binding energies of both the aluminum and noble-metal core levels generally increase on alloying. Normally shifts of core levels to higher binding energies are assumed to indicate decreased electron density at an atomic site.[2,30] The experimental evidence here shows that the situation is more complicated because it is not possible for both components to become positively charged. The alloy systems evidently show charge distributions more complex than in simple ionic compounds, but before we can interpret XPS data we must consider several effects:

(i) Differences in the chemical potential of the electrons in different materials;

(ii) Shifts of charge to the regions between the atoms. Watson and Perlman[66] have pointed out that there is no unique way to draw atom boundaries and that if an atom's valence shell was to expand in some way, the observed core-level shift would be the same as if charge were transferred from the atom. It has been suggested that the aluminum-gold alloys have some covalent character,[67] but the observed shifts are too large for covalency to be the dominant effect;

(iii) Relaxation (or polarization) effects. The core holes created in the XPS process, cause relaxation of all the electrons in the system[32–36] resulting in lowering of the core-hole state energy with respect to that predicted by Koopmans's theorem. Part of this relaxation is interatomic and can thus be different in different materials.

Shifts in x-ray lines are dependent on the symmetry of the valence states involved in the bonding.[68–70] For these aluminum–noble-metal alloys the shifts are very small, although consistently positive, and conclusions about bonding from these data are excluded because, for example, differences in relaxation could account for a considerable part of the shifts.

While interpretation of binding-energy chemical shifts in alloys is not feasible at present, we must emphasize the positive aspects of these measurements: the XPS shifts recorded include the largest yet observed on alloying, and where such large shifts do occur they have potential use in analysis of phase transitions at surfaces.

C. XPS and SXS valence bands of aluminum and aluminun-noble-metal alloys

Al XPS and SXS spectra have previously been compared with the density of states,[9] but we briefly repeat the comparison here in order to facilitate later discussion of the alloys. The dominant factor in determining SXS emission band shapes are dipole-selection rules, but effects of singularities show up close to the Fermi edge[71,72] and self-absorption causes slight distortion of the band[9] so that the spectra cannot be interpreted solely in terms of partial densities of states. With Fig. 3 we can, however, draw some conclusions from comparison of SXS, XPS, and the calculated density of states.[73,74] In agreement with earlier comparisons we believe that the higher intensity of Al *K* emission close to the Fermi level is due to a greater density of Al 3*p* states close to E_F. The greater intensity deeper in the Al $L_{2,3}$ emission band suggests that the Al 3*s* states are, on average, more bound than the Al 3*p* states. The XPS spectrum[75] is similar to the calculated density of states although the tail of the spectrum is more pronounced. The tails seen in the SXS spectra are due to many-body effects (in particular Auger transitions within the band[76]). In XPS spectra Auger broadening also plays a part, but in addition interband transitions (coupled to the main excitation in a form of shake-up) are more important than in SXS.[32]

The XPS spectra of metal valence bands do not always give a true picture of the total density of states. For example, in the aluminum–noble-

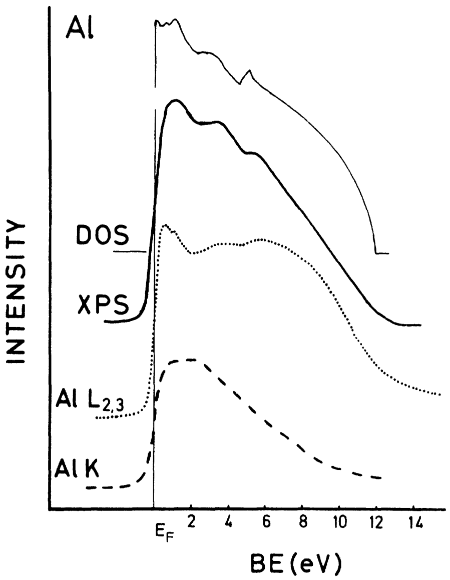

FIG. 3. Al valence-band density of states (from Ref. 73), XPS valence band (from Ref. 75), and Al $L_{2,3}$ and *K* valence-band emission spectra. The vertical scales are not simply related. For the Al $L_{2,3}$ spectra, here and throughout this paper, I/E^3 is plotted to allow for the energy dependence of the x-ray emission probability (Ref. 44).

metal alloys the partial cross sections of noble metal *d* states are larger than those of the Al 3*s* and Al 3*p* states. It has been suggested that the discrepancies between the calculated densities of states and XPS spectra of noble metals is due to systematic decreases in the photoelectric cross sections for the deeper-lying states.[4,5] The low intensity of the high-binding-energy Au 5*d* peaks in XPS spectra of Al_2Au, AlAu, and $AlAu_2$, and the Ag 4*d* peak in $AlAg_2$ is thus possibly a cross-section effect, not a density-of-states effect.

Switendick and Narath[77] have calculated the band structure of Al_2Au and Switendick also calculated partial densities of states for the same alloy.[78] We have plotted, in Fig. 4, a set of Switendick's data that he has smoothed by taking a 0.5-eV sampling width[78]; histograms plotted with smaller sampling widths would show features that could not have been resolved under our experimental conditions. As shown in Fig. 4, the agreement between the partial densities of Al 3*s* and 3*d* states and the Al $L_{2,3}$ spectra is very good.[78,79] Switendick's calculations also reproduce the gross features of the Al *K* spectra with the Al 3*p* density of states. The main peak in Switendick's calculated total density of states is largely due to Au 5*d* states which are not split in the calculated curve shown. However, the calculated density of *d* states does show a small splitting when plotted with 0.2 sampling width, and it is possible that the splitting is underestimated only because relativistic effects were not included. We also find that the calculated *d* bands are at higher binding energy than indicated by the XPS experiment. It is important to note that in the calculated results the position of the Au *d* bands lies above the position of the peak in the Al 3*s* states, just as the peaks in the XPS spectra are above the main peak in the Al $L_{2,3}$ SXS spectra. In all the alloys studied here it was found that the peak in the Al $L_{2,3}$ spectra lay not only below the centroid but also just below all the peaks in the densities of noble-metal *d* states as shown by the XPS spectra (see Figs. 4–8 and Table VIII).

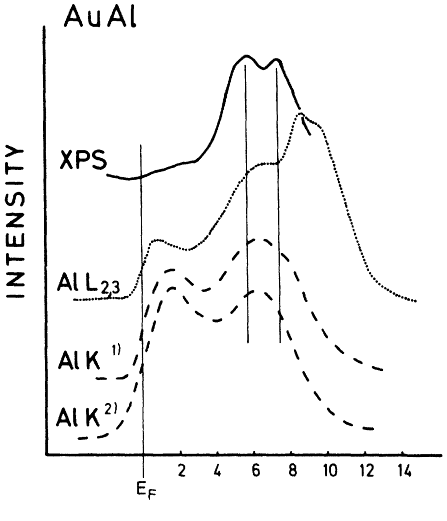

FIG. 5. Valence-band XPS, and Al $L_{2,3}$ and *K* emission spectra for AuAl. The Al *K* spectrum 1 is from this work, while 2 is from Baun and Fisher (Ref. 13). The vertical scales are not simply related.

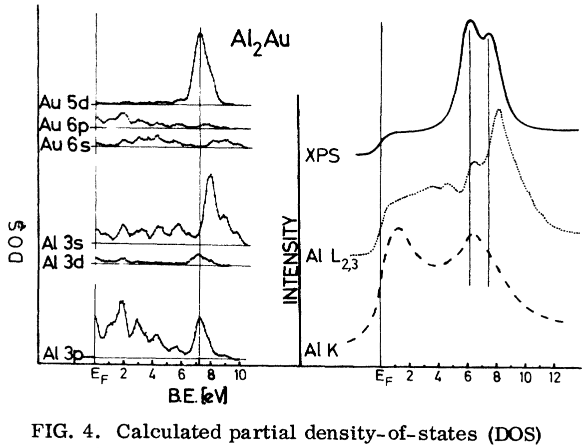

FIG. 4. Calculated partial density-of-states (DOS) curves (from Switendick, Ref. 78, see also text), valence-band XPS, and Al $L_{2,3}$ and *K*-emission spectra for Al_2Au. The vertical scales are not simply related.

At this point it is helpful to list the mechanisms by which the noble-metal *d* states might cause peaks in Al SXS spectra.

(i) Pure cross transitions: these would result from overlap of noble-metal *d* bands with the $L_{2,3}$ and *K* holes on the Al sites. Such transitions would always be weak and would be more weak in

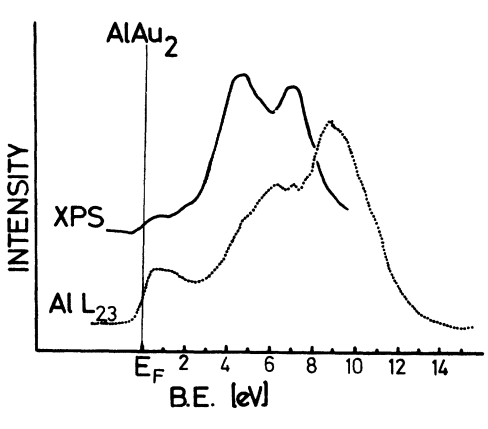

FIG. 6. Valence band XPS and Al $L_{2,3}$ SXS emission spectra from $AlAu_2$. The vertical scales of the different curves are not simply related.

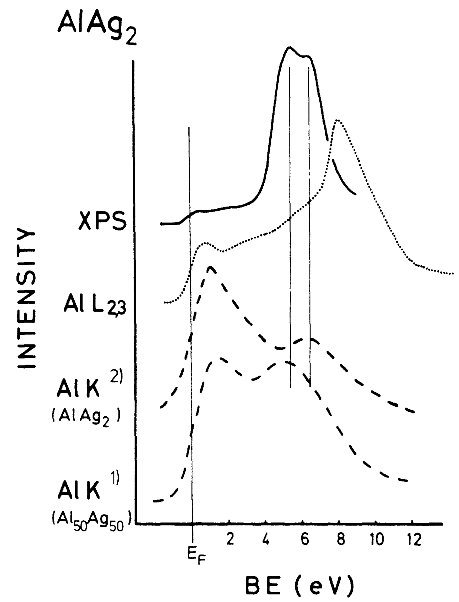

FIG. 7. Valence-band XPS, and Al $L_{2,3}$ and K emission spectra for $AlAg_2$. The Al K spectrum 1 is from Baum and Fisher (Ref. 13) while the Al K spectrum 2 is from Nemnonov *et al.* (Ref. 14). The vertical scales are not simply related.

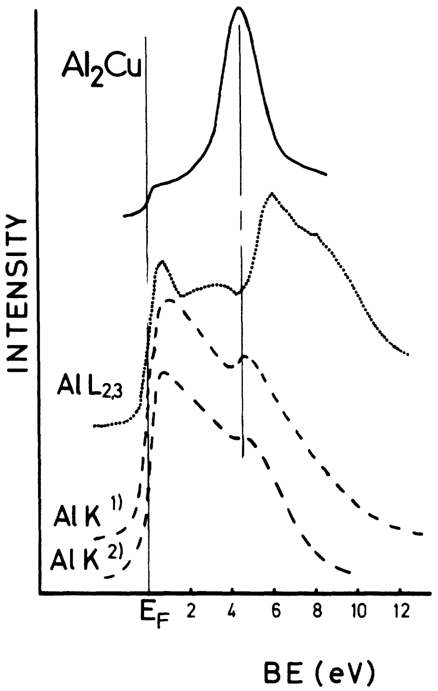

FIG. 8. Valence-band XPS, and Al $L_{2,3}$ and K emission spectra for Al_2Cu. The Al K spectrum 1 is from this work while 2 is from Nemnonov *et al.* (Ref. 14). The vertical scales are not simply related.

K spectra than L spectra because the K hole is more localized and has less overlap with orbitals on neighboring atoms. Cross transitions would result in peaks in SXS spectra at the same energy as those seen in XPS spectra. That such cross transitions are feasible is suggested by calculations of the probability of interatomic Auger transitions by Matthew *et al.*[80]

(ii) Redistribution of Al $3s$ and $3p$ state energies caused by noble-metal d states: there have been a number of coherent-potential-approximation calculations of the effect of d bands on the other bands in disordered alloys which suggested that the s- and p-band intensity is depressed in the energy region of the d bands.[81,82] Although most of the alloys studied here are not disordered, coherent-potential-approximation calculations are probably still relevant, as they are dominated by the hopping integrals between next-nearest neighbors which are not very order dependent. Also, SXS spectra from alloys are more concentration dependent than structure dependent.

(iii) Orbital mixing: if, after alloying, the noble metal d-like states had a little admixed character of the aluminum orbitals, then these new states would all contribute to the observed Al emission spectra. It is not necessary for the new peaks in the SXS spectra to have exactly the shape found in the XPS spectra because the amount of Al orbital character in these new Au $5d$-like states could vary as a function of their energy.

It has been noted previously[83] that it is not only in aluminum-noble-metal alloys that the main high-binding-energy peak in the Al $L_{2,3}$ spectra lies below the energy of the d bands of the other component. In AlPd the Al $L_{2,3}$ spectrum peaked below the bottom of the Pd d states[6] and for AlFe it has been calculated that not only do the Al $3s$ states not mix with the Fe $3d$ states, but the density of Al $3s$ states drops sharply at the energy where the Fe $3d$ states become important.[84,85] The strong peaks found in the Al $L_{2,3}$ spectra of aluminum-transition-metal alloys are all below the regions where we have reason to expect high density of transition d states.[6,10,11,86] In fact the spectral evidence seems to imply that the noble- and transition-metal d states repel the Al $3s$ states to other energies, and we infer that mechanism (ii) above is dominant in producing the low-energy peaks in Al $L_{2,3}$ spectra of alloys. Similar behavior has been found for most magnesium-noble-metal alloys.[10]

In the Al $L_{2,3}$ spectra of Al_2Au, AlAu, $AlAu_2$, and $AlAg_2$ weak peaks are observed above the main high-binding-energy peak and in the same energy region as the noble-metal d bands. This structure could be attributed either to cross transitions (particularly AlAu) or to mixing of the d states with

TABLE VIII. Compilation of energies of main features found in the valence bands of aluminum–noble-metal alloys by XPS and SXS, and by calculation (all energies in eV). (*m*, medium intensity; *w*, weak intensity; *b*, broad peak or feature; vb, very broad.)

	Al_2Au	AlAu	$AlAu_2$	Al + Ag	$AlAg_2$	Al_2Cu
XPS peaks	7.4 6.1	7.4 5.7	7.0 4.5	6.2	6.5 5.7	4.3
Al $L_{2,3}$ high B.E. peak	8.16 8.3[a] 8.0[b] 8.0[c]	8.80	8.60	7.5	8.1 8.0[d]	Distorted by Cu $M_{2,3}$ peaks
other Al $L_{2,3}$ peaks	6.5 *m*	5.5 to 7.5 } vb	5.5 to 7.5 } vb 7.1 *w* 6.4 *w*			Distorted by Cu $M_{2,3}$ peaks
Al *K* high B.E. peak	6.3 6.5[d] 7.3[b]	6.6 *b*			6.4[d]	4.7 4.5[d] 5.2[e]

[a] Williams *et al*. (Ref. 79).

[b] Switendick's calculation (Ref. 78).

[c] Curry and Harrison (Ref. 92).

[d] Taken from figures in Nemnonov *et al*. (Ref. 14).

[e] Fisher and Baun (Ref. 13).

aluminum 3*s* and 3*d* states.

In the Al *K* spectra the high-binding-energy peak comes higher in the band that in the *L* spectra; in most cases, although not all, it coincides with the upper noble-metal *d* states to within experimental error. However, the peak in the Al *K* spectra does not reproduce the splitting observed in the Au 5*d* bands and therefore may not be due to a mixing of the Al 3*p* and noble-metal *d* states, but rather to a redistribution of pure-Al 3*p* states under the influence of the *d* bands. Certainly we should note that the separation of the *d* and *p* peaks calculated by Kudrnovsky is much less than that calculated for *d* and *s* peaks.[81] Similar results were found by Switendick for the Al_2Au system.[78]

D. Auger spectra from Al-Cu and Al-Ag alloys

We chose to study the Ag $M_{4,5}VV$ and the Cu L_3VV Auger peak groups because these peaks are the strongest and sharpest from these elements. Comparison with observed XPS and SXS valence bands show that the shape of the Auger spectra does not result from folding of the valence-band density of the valence-band density of states with itself.[58–60,87,88] Calculations have indicated that the Auger spectra are due to multiplet coupling between the two holes in the 3*d* and 4*d* shells of copper and silver, respectively, and that the holes are seen as localized on one atom.[58–60] The Cu L_3VV (Fig. 2) and Ag $M_{4,5}VV$ spectra from the pure metals and their alloys with aluminum are very similar in shape, being only slightly shifted with respect to each other, in marked contrast to the corresponding XPS spectra.[11] This indicates the atomic character of the Auger transitions, by an approach quite different to that previously used.[58–60,87,88]

E. Interpretation of Au $N_{6,7}$ emission spectra

Earlier studies of the $N_{6,7}$ spectra of Pt and Au (Refs. 17, 89, 90) have been interpreted by assuming the $O_4 \rightarrow N_6$ and $O_5 \rightarrow N_7$ transitions to be stronger than the $O_4 \rightarrow N_7$ and $O_5 \rightarrow N_6$ as for gaseous Au.[91] In Table IX we list the observed binding energies for the Au $N_{6,7}$ levels and the two main peaks in the valence bands of Au and Al-Au alloys. Also listed are the Au SXS peaks observed and assigned in

TABLE IX. Au $N_{6,7}$ x-ray energies observed and calculated assuming pure O_4 and O_5 character for the peaks in the valence bands of aluminum-gold alloys.

Transition		Au	$AlAu_2$	AlAu	Al_2Au
$O_5 \rightarrow N_7$	Calculated	80.4	80.2	79.8	79.6
	Found	80.25	80.20	80.30	78.9
$O_4 \rightarrow N_6$	Calculated	81.4	81.4	81.6	82.0
	Found	81.00	80.75	80.80	81.00
$O_5 \rightarrow N_6$	Calculated	84.2	83.9	83.3	83.3
	Found	83.30	83.30	83.75	83.50
$O_4 \rightarrow N_7$	Calculated	77.7	77.7	77.9	78.3
	Found	77.00	77.15	77.70	77.00

Ref. 17 and transition energies calculated assuming assignment of pure O_4 and O_5 character to the maxima in the Au and Al-Au XPS valence bands. The agreement is good for pure Au; for alloys, especially Al_2Au, the agreement is not so good. The structure in the SXS spectra is probably due to the retention of some atomiclike character in the *d* bands. The discrepancies between the peak position calculated from XPS data and the position of the structure in the SXS spectra is due, at least in part, to convolution of the peaks in the latter spectra and hence the difficulty in locating the maxima.

V. CONCLUSIONS

(i) The aluminum–noble-metal alloys exhibit peaks at long wavelengths (high binding energies) in their Al $L_{2,3}$ and Al K emission spectra. These peaks reflect maxima in the densities of Al 3*s* and Al 3*p* states, respectively. The positions of the peaks in the Al $L_{2,3}$ emission spectra do not correspond to the positions of the peaks in the partial densities of noble-metal *d* states. We conclude that little of the peak in the density of 3*s* states should be attributed to mixing of the aluminum 3*s* and noble-metal *d* states; but the peak is more probably due to a sharp decrease in the aluminum–*s*-state density at energies corresponding to the onset of the noble-metal *d* bands. The high-binding-energy peak in the Al K spectra appears to coincide (to within experimental error) with the low-binding-energy maximum in the *d* bands.

(ii) Comparison of Cu (L_3VV) or Ag ($M_{4,5}VV$) Auger peaks from Cu, or Ag in the pure metals and alloys with aluminum provides evidence that Auger spectra of Cu or Ag do not reflect the density of states around the Cu or Ag atoms, but are dominated by single-atom effects.

(iii) The chemical shifts of XPS peaks and SXS emission edges in the aluminum–noble-metal alloys are large, but cannot at present be used to estimate distribution of charge between the aluminum and noble-metal sites.

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