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Electronic structure of ordered and disordered Cu_3Au: The behavior of the Au 5d bands

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The electronic behavior of the Au 5d bands in the ordered and disordered Cu_3Au has been investigated with x-ray-absorption near-edge structure (XANES) and Al $K\alpha$ x-ray (1486.6 eV) photoemission (XPS) measurements. The XANES and XPS results clearly show that Au loses 5d character (count) upon the formation of Cu_3Au in both ordered and disordered phases and that the Au 5d count depletes more in the ordered phase than in the disordered phase. In addition, the Au 5d hole population is found to be nonstatistical ($[h_{5/2}]:[h_{3/2}] < 1:1$) in Cu_3Au alloys as compared to a near-statistical 5d population ($[h_{5/2}]:[h_{3/2}] \sim 2:1$) in $AuAl_2$ and $AuGa_2$ (Au–non-transition-metal compounds). These observations are interpreted on the basis of the charge-compensation model. The nonstatistical Au 5d hole distribution derived from XANES together with the photoemission results indicates uneven Au $5d_{5/2}$ and $5d_{3/2}$ contribution (relativistic effect) in the Au 5d–Cu 3d interaction in Cu_3Au.

I. INTRODUCTION

The electronic structure of Au alloys and intermetallic compounds has been an interesting subject of investigation. The perhaps most intriguing observations[1–5] have been the positive ^{197}Au Mössbauer isomer shift (increasing electronic charge density at the nucleus relative to Au) and the positive Au 4f binding-energy shift (relative to Au) upon alloy and compound formation. The former measurements indicate that Au gains charge, while the latter indicate that Au loses charge, despite the fact that Au is the most electronegative among metallic elements. These observations have led to the proposal of a charge-compensation model.[1] In this model, Au, gains conduction (s,p) charge upon alloy formation, but this gain of charge is largely compensated by a depletion of Au 5d charge so that as much charge neutrality as possible can be maintained at the Au site and that the actual charge transfer onto Au is small ($\sim$0.1 electron). This model generally explains the electronic behavior of Au alloys and works particularly well for Au–non-transition-metal (metalloid) intermetallic compounds.[2,3] It shows that it is not only the net charge flow, but also the nature (s,p,d) of the charge that is important to the electronic behavior upon alloying. The validity of this model has been recently confirmed by Au $L_{2,3}$-edge x-ray-absorption near-edge structure (XANES) measurements[6] in which the unoccupied Au 5d count was probed with the $2p \rightarrow 5d$ dipole transition.[7–10]

Another interesting problem concerning the charge transfer (rehybridization) upon alloy formation is the behavior of the Au d bands. It has been generally realized that in Au–non-transition-metal systems the Au d band narrows and shifts away from the Fermi level[3,4] as the Au concentration decreases, although it is less obvious when Au alloys with transition metals such as Cu and Ag that have a full d band. It should be noted, however, that when hybridization is switched on, the Au 5d band is allowed to interact with the conduction (sp) band as well as the valence band of the other constituent involved in alloying. The large spin-orbit coupling in Au also enhances the mixing of electronic states. The result is that the band of Au 5d origin gets filled but at the same time some unoccupied density of states having Au 5d character are likely to be pushed to above the Fermi level. It is therefore reasonable to distinguish between a filled d band of primarily Au 5d origin and Au 5d counts, the latter is often less than full occupancy (10) in most of the Au intermetallic compounds of which the d band is conventionally considered filled. A similar situation has been encountered in Pd alloys.[11]

Cu_3Au is particularly interesting in connection with the studies of the behavior of the Au 5d bands in alloys of d-band metals. Eberhardt *et al.*[12] have reported a photoemission study of $Cu_3Au(001)$ and concluded that the Au 5d bands and the Cu 3d bands are well separated and the Au 5d bands are confined in the region of -4 to -8 eV relative to the Fermi level, while DiCenzo *et al.*[13] and Wertheim,[4] based on photon-energy-dependent photoelectron cross-section and mean-free-path considerations, have argued that the Au 5d bands are more likely to spread over the entire region of the alloy d bands. A recent linear augmented–Slater-type–orbital (LASTO) calculation[15a] and experiment[15b] seem to support the predominant contribution of Au and Cu in the -4 to -7 eV and -2 to -4 eV region, respectively. More recently, Grahm,[16] Hansen *et al.*,[17] and Wang *et al.*[18] have reported studies of surface alloying of Au adsorbed on Cu single crystals and related phenomena, and their results indicated the presence of a surface structure similar to that of the bulk Cu_3Au. Watson *et al.* have reported LASTO studies of Au–5*d*-transition-metal alloying.[19]

In view of the aforementioned developments and in connection with our recent interests in the electronic structure and surface reactivity of alloys, we have carried out x-ray-absorption and photoemission measurements of Cu_3Au in both the ordered and disordered phase. Our emphasis is placed on the near-edge structure, particularly the area under the Au L_2,L_3 white lines. Photoemission with monochromatized Al $K\alpha$ x rays and with vuv synchrotron radiation were also used for the study. Using a recently reported procedure,[8–11] we can estimate at least semiquantitatively the lower bound of the unoccupied *d* counts at the Au site of the alloys from the area under the $L_{2,3}$-edge white lines. The occupied *d* character is examined with photoemission experiments. The ordered and disordered phases of Cu_3Au present a very interesting case in which we can study the correlation of structure and electronic properties with the nearest Au-Au separation which is larger (3.75 Å) in the ordered phase than in the disordered phase, where previous extended x-ray-absorption fine structure (EXAFS) results[20] show that the probability of finding an Au-Au neighbor at ~2.65 Å is ~25%.

II. EXPERIMENT AND DATA ANALYSIS

The Cu_3Au samples were prepared by rapid quenching from the melt to room temperature. They were then rolled to thin foils of uniform thickness ($\sim 0.1 \times 10^{-3}$ in.) that are desirable for x-ray-absorption measurements in the transmission mode. The samples thus prepared are denoted disordered Cu_3Au, although some ordering may result from rolling. Our EXAFS data show that it has the characteristics of a disordered sample.[20] The order specimens were prepared by annealing the thin foils of the disordered alloy at ~280 °C for 8 days. The ordered and disordered samples have discernible color, and chemical and mechanical properties. X-ray-absorption measurements were carried out at room temperature in a transmission mode at the Cornell High Energy Synchrotron Source (CHESS) using a Si(220) double-crystal monochromator. The EXAFS (Fig. 1) of the quenched (disordered) and the thoroughly annealed (ordered) Cu_3Au samples exhibit previously reported oscillations characteristics[20] of those of the disordered (single oscillation dominates) and ordered samples[20] (multiple oscillations are evident and have larger amplitude), thus confirming the structural characteristics of these specimens.

Figure 2 shows the Au $L_{2,3}$ XANES of Cu_3Au in comparison with Au. The area under the white line in the $L_{2,3}$-edge analysis is normalized to the edge jump and compared with the edge of pure Au.[6] Corresponding edges for $AuAl_2$ and $AuGa_2$ are also shown in Fig. 3 for comparison. The profile of the white line in these alloys is determined by comparing the L_2 and L_3 XANES spectra. The high-energy tail of the white line extends to the position where the first oscillation beyond the white line on both spectra matches. This procedure would yield a

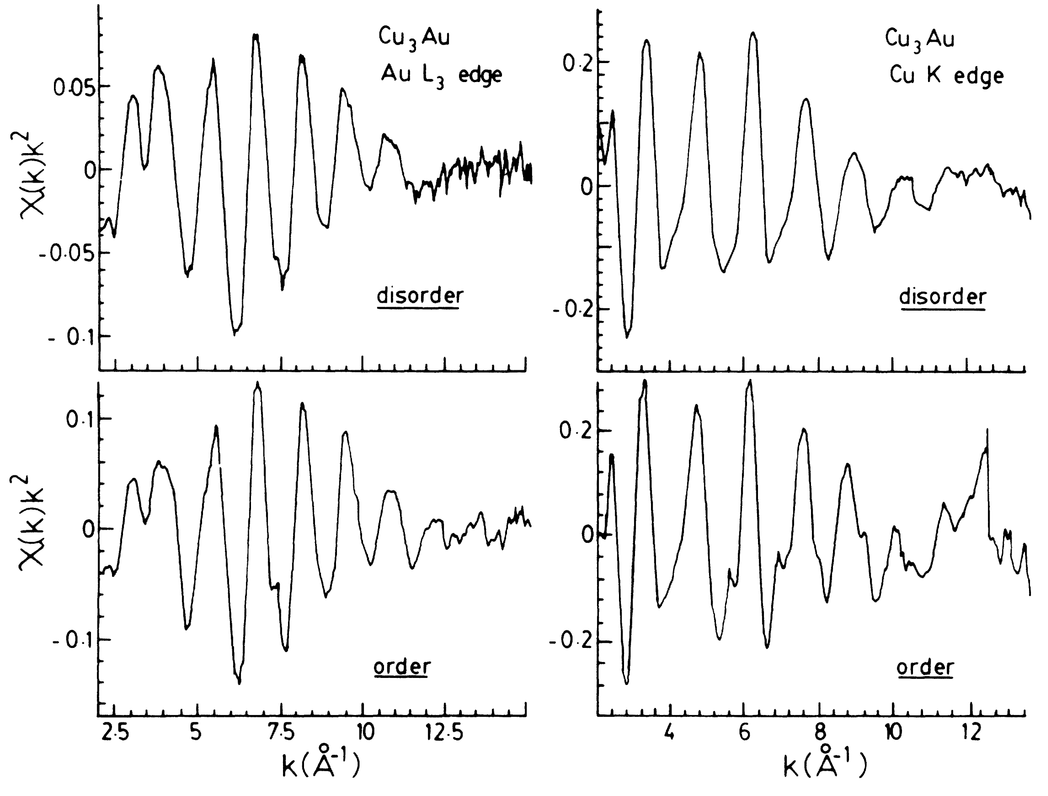

FIG. 1. EXAFS [$\chi(k)k^2$] of Cu_3Au (ordered and disordered) at the Au *L* edge and Cu *K* edge. The amplitudes are normalized to the edge jump and are directly comparable.

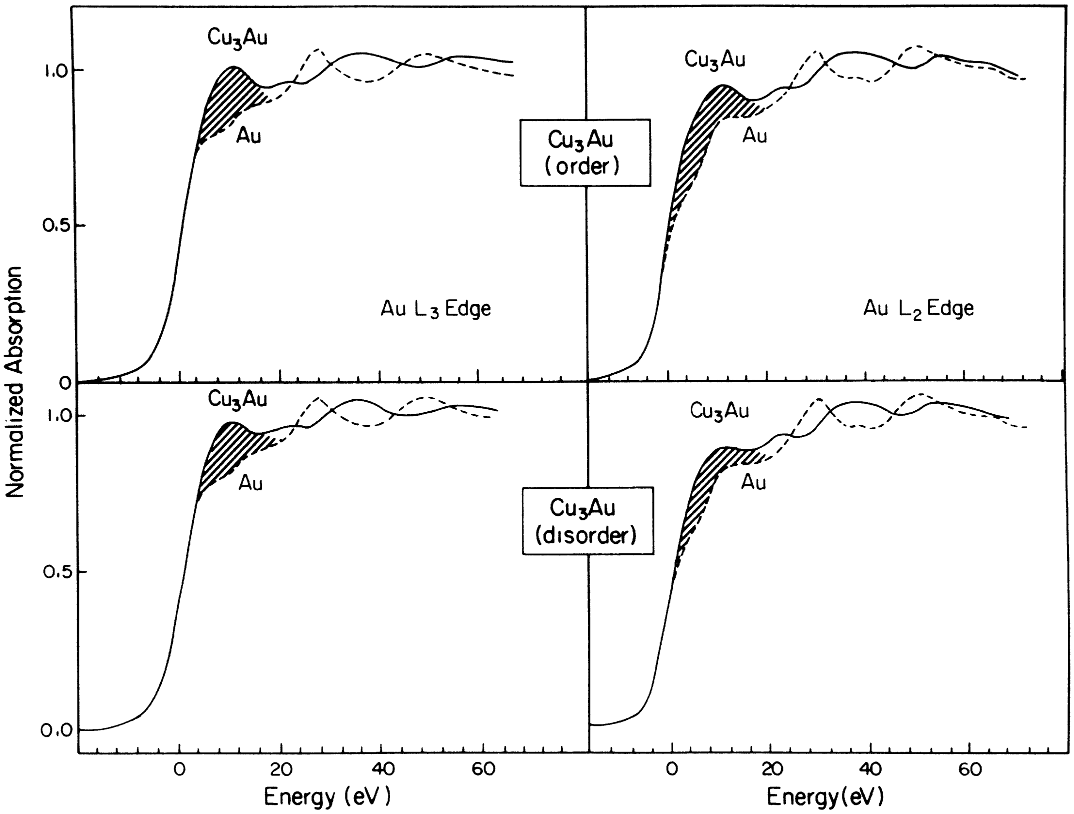

FIG. 2. Au L_3,L_2-edge XANES of Cu_3Au (ordered and disordered) and Au normalized to the edge jump. The shaded area represents the difference in white-line intensity relative to pure Au. The energy scale is relative to the point of inflection of the edge jump at $E = 0$.

position of the tail at ~15 eV from the onset of the edge jump. The uncertainty in the white-line area depends on the uncertainty in the energy positions of the smooth edge jump and of the high-energy tail in the white-line profile and is ~5% for an uncertainty of ±2 eV in these measurements. Using pure Au as the atomic background reduces some of the uncertainties. Thus all the derived parameters reported here are relative to pure Au that has a full *d* band and exhibits no white line.

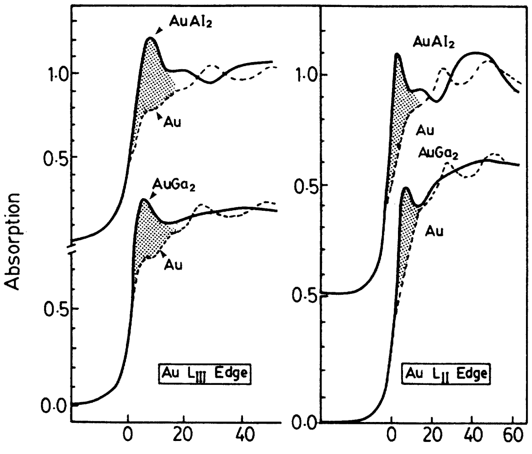

FIG. 3. Au L_3,L_2-edge XANES of $AuAl_2$ and $AuGa_2$ normalized to the edge jump. The shaded area represents the difference in white-line intensity relative to pure Au. The scale has the same meaning as in Fig. 2.

The Al $K\alpha$ x-ray-photoemission (XPS) experiments were carried out with a Surface Science XPS spectrometer (10^{-9} Torr base pressure), at Surface Science Western, the University of Western Ontario. This spectrometer is equipped with a monochromatic Al $K\alpha$ X-ray source, a 180° hemispherical analyzer, with electron lenses so that a sampling size of 100-μm spot can be achieved. All our measurements were made at normal emission with a 300-μm spot size and high resolution (~0.5 eV). vuv photoemission measurements of the valence band of the alloys have also been carried out under UHV conditions (10^{-9} Torr base pressure) using the stainless-steel Seya beam line at the Synchrotron Radiation Center, the University of Wisconsin–Madison. The results, however, are complicated by surface effects and will not be discussed here.

Characteristic XPS spectra are shown in Fig. 4. The specimens were cleaned with standard Ar^+ sputtering techniques and the surface cleanliness was checked with XPS. The XPS results clearly show that the ambient Cu_3Au surface contains copper oxide and carbon, which are easily removable by Ar^+ sputtering. The Cu_3Au samples employed in this study were both oxygen and carbon free after cleaning within XPS sensitivity.

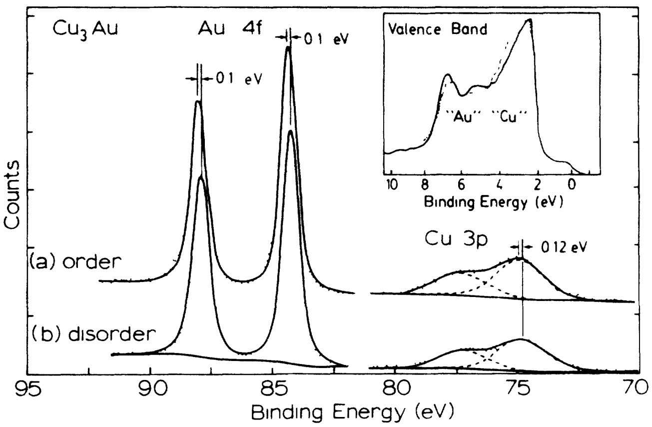

FIG. 4. Monochromatized Al $K\alpha$ XPS core-level (Au $4f$, Cu $3p$) spectra of ordered and disordered Cu_3Au. The valence-band spectra (dotted line, order; solid line, disorder) are also shown (inset).

III. RESULTS AND DISCUSSION

A. Au $5d$ hole population from Au L_3,L_2-edge white lines

The Au $L_{3,2}$ spectra of Cu_3Au shown in Fig. 2 clearly exhibit a white line at the onset, with appreciable intensity relative to that of pure Au, which has no white line. This observation immediately indicates that Au loses $5d$ character upon alloy formation. That is that, the unoccupied $5d$ counts (number of $5d$ holes) at the Au site in these alloys are greater than that in pure Au (where the d band is full). Following Mattheiss and Dietz[8] and Mansour *et al.*,[10] and assuming there is no countervailing symmetry arguments, we can relate the area under the L_3,L_2 white line A_3 and A_2 to the $5d$ hole population, $h_{5/2}$ and $h_{3/2}$ for the $d_{5/2}$ and $d_{3/2}$ states, respectively, with the expressions[6]

$$A_3=C_0N_0E_3(R_{d_{5/2}}^{2p_{3/2}})^2\left[\frac{6h_{5/2}+h_{3/2}}{15}\right], \tag{1}$$

$$A_2=C_0N_0E_2(R_{d_{3/2}}^{2p_{1/2}})^2\left[\frac{h_{3/2}}{3}\right], \tag{2}$$

where $C_0=4\pi^2e^2/3\hbar c$, N_0 is the number of atoms per unit volume, $R_{d,d_j}^{nl_j}$ is the radial dipole transition matrix element, and E_2 and E_3 are the L_2- and L_3-edge binding energies, respectively. Experimentally, however, A_3 and A_2 are difficult to extract. We employ here the $L_{3,2}$ XANES of pure Au to represent the smooth edge jump and obtain the difference in the integrated absorption between the compound and pure Au (shaded area). We can write

$$A_{2\,(3)}=\int_0^E[\mu_{L_{2\,(3)}}(\text{alloy})-\mu_{L_{2\,(3)}}(\text{Au})]dE\ . \tag{3}$$

Allowing the $E(R_{d_j}^{nl_j})^2$ terms in Eqs. (1) and (2) to have the ratio as in previous analysis, in which a factor of 2.22 instead of 2 is used to account for the difference in absorption between L_3 and L_2 edge,[6,8] we obtain to the first approximation

$$h_{5/2}=(2.25A_3-0.5A_2)/CE_2\ , \tag{4a}$$

$$h_{3/2}=3A_2/CE_2\ , \tag{4b}$$

where $C=C_0N_0(R_{5d}^{2p_{1/2}})^2=75\,213\ \text{eV}\,\text{cm}^{-1}$. The results of the analysis using Eqs. (4a) and (4b) are summarized in Table I together with previous results of $AuAl_2$ and $AuGa_2$ (Fig. 3) and the d electron depletion count Δn_d (relative to pure Au) derived from Mössbauer and XPS in Cu_3Au (see Sec. III B below).[1-3]

We observe from Table I that the area under the white line in the Cu_3Au alloys are smaller than those of $AuAl_2$ and $AuGa_2$ and so are their $5d$ hole population. These values are in qualitative accord with, but consistently smaller than, the Δn_d derived from XPS and Mössbauer results as discussed previously.[6] The most interesting observation is the relative population of $h_{5/2}$ and $h_{3/2}$. In Cu_3Au alloys, the $h_{5/2}$ population is slightly smaller than that of the $h_{3/2}$ in contrast to the expected statistical distribution ~2:1 that is observed in the case of $AuAl_2$ and $AuGa_2$. This observation has very interesting implications concerning the electronic properties of the Au $5d$ band upon alloying and intermetallic compound formation with noble metals (Cu, Ag, Pt, etc.) with a full or nearly full d band and nontransition metals (Al, Ga, etc.) without a d band. It indicates uneven involvement of Au

TABLE I. Relevant parameters derived from Au $L_{2,3}$ XANES analysis.

	White-line area (10^4 cm^{-1} eV)[a]			Unoccupied $5d$ count[b]		
Sample	A_3	A_2	$h_{5/2}$	$h_{3/2}$	h_t	Δn_d
Cu_3Au (disordered)	0.19	0.14	0.048	0.056	0.10	−0.23[c]
Cu_3Au (ordered)	0.23	0.19	0.056	0.076	0.13	−0.25[c]
$AuAl_2$	0.56	0.22	0.15	0.088	0.24	−0.41
$AuGa_2$	0.42	0.16	0.13	0.064	0.19	−0.35

[a] Edge jump values from W. H. McMaster, N. Kerr Del Grande, J. Mallett, and J. H. Hubbell, *Compilation of X-ray Cross Sections* (NTI Service, Springfield, VA, 1969).

[b] $C_0=0.096\,05$, $R_{5d}^{2p}=3.103\times10^{-11}$ cm, $N_0=5.922\times10^{22}$ atoms/cm^3 $E_2=13.733$ keV were used in the calculation, relative to pure Au.

[c] This work, using parameters given in Table II and Eq. (5). $F(c)-F(d)=-3.0$ eV and $F(c)-F(\text{latt})=7.7\pm1$ eV were used.

TABLE II. XPS parameters for Cu_3Au.

Sample	Au $4f_{7/2}$ (eV) energy[a]	width	Cu $3p_{3/2}$ (eV) energy[a]	width	Area (Au 4*f*) Area (Cu 3*p*)	Work function Φ (eV)[b]
Cu_3Au (disordered)	84.24	0.79	74.76	2.20	3.3	5
Cu_3Au (ordered)	84.34	0.73	74.88	2.22	2.5	5

[a] Relative to $4f_{7/2}$ (pure Au) at 83.94 eV.
[b] From uv photoemission, $\Phi(Au)=5.1$ eV.

$d_{5/2}$ and $d_{3/2}$ states in alloying. It appears that the $[h_{5/2}]$:$[h_{3/2}]$ ratio may be one of the unique features that can be used to distinguish between Au-noble metal and Au–non-transitional-metal intermetallic compounds or the presence of Au–non-Au *d*-*d* interaction in the former. Another feature is the behavior of the Au *d* band that narrows and shifts away from the Fermi level in $AuAl_2$ and related compounds but maintains its full width in Au-Ag alloys. More details concerning this trend will be discussed elsewhere. Here we focus on the Cu_3Au system.

B. Charge transfer in Cu_3Au from XPS and Mössbauer results

The procedure for the derivation of Δn_d from core-level binding energy and Mössbauer isomer shift (IS) has been described previously[1-3] and it is only outlined here. The Au 4*f* core-level shift ΔE_B (Cu_3Au-Au) is related to the Coulombic interaction [Slater integral *F* (core, valence)] of the core electron with the valence electrons of conduction and *d*-band nature within the Wigner-Seitz volume of the Au site. If we neglect any difference in final-state screening, the Au-site Au $4f_{7/2}$ binding-energy shift between Cu_3Au and Au is written

$$\Delta E_{\mathrm{Au}} = -(\Phi_{\mathrm{Cu_3Au}} - \Phi_{\mathrm{Au}}) - \Delta n_c\, F(4f,c) - \Delta n_d\, F(4f,5d) + \delta F(\mathrm{latt}) + \left[\frac{dE}{dV}\Delta V\right]_{\mathrm{Au}} , \quad (5)$$

where Φ's are the work functions, Δn_c and Δn_d are the change in conduction and 5*d* counts, $\Delta n_c = 0.086$ IS electron in metallic systems (IS denotes Isomer shift), δ is the sum of *d* and conduction electron count changes associated with the Au site ($\delta = \Delta n_c + \Delta n_d$), and the *F*'s are the changes in electron binding energy associated with the removal of a single valence electron from the site. The addition or removal of a single valence electron causes the system to relax and this relaxation is accounted for in the estimation of the *F* values. For these estimates, valence electrons were also normalized to the atomic Wigner-Seitz volume of Au.[1-3] The *F*(latt) term is a spherical Madelung-like potential energy associated with charge flow into or out of the site of the Wigner-Seitz volume.[1-3] The term $(dE/dV)\Delta V$ is the calculated binding-energy change associated with the difference of volume change between the volume of the Au site in the compound and the pure element. $(dE/dV)\Delta V$ is small for these alloys which follow Vegard's law

$$[V_{\mathrm{AuCu_3}}/(V_{\mathrm{Au}} + 3V_{\mathrm{Cu}})] \simeq 1.006$$

and is neglected in the calculation. The XPS Au 4*f*, Cu 3*p*, and valence-band spectra for ordered and disordered Cu_3Au are shown in Fig. 3 and relevant parameters are listed in Table II. Using ΔE_B (4*f*) value of 0.40 and 0.30 eV recorded here (Table II) and Mössbauer IS of 3.53 and 3.33 mm s^{-1} (Ref. 21) for the ordered and disordered Cu_3Au (relative to Au), respectively, we calculate Δn_d of 0.23 and 0.21 electron (negative sign means loss of *e* charge), respectively, for the ordered and disordered sample (Table I). It is interesting to note that the intensity ratio $I(\mathrm{Au}(4f))/I(\mathrm{Cu}(3p))$ is significantly larger in the disordered sample. This observation suggests that the ordered sample has a Cu-rich surface in contrast to the $Cu_3Au(001)$ surface of a single crystal which is Au-rich. The implication of the Cu 3*p* results and the valence band is discussed in a later section.

It is immediately apparent from Table I that Au loses *d* character upon Cu_3Au formation and that Au loses even more *d* counts when it is in the ordered phase than in the disordered phase. This may be qualitatively understood in terms of a considerable larger Au-Au separation in the ordered Cu_3Au (locally a more "dilute" alloy). We recall that in the ordered Cu_3Au, Au has no Au neighbors in the first shell, while in the disordered Cu_3Au, the probability of Au having a first-shell Au neighbor at ~2.65 Å is 25%.[20] It should be noted that the hole occupancy h_t, derived here represents the lower limit of the unoccupied *d* count change upon compound formation. The discrepancy between h_t and Δn_d may arise from matrix element effect as well as unoccupied density of *d* states at higher energies not accounted for, and possibly overestimates of Δn_d.

It is interesting to question whether or not the *d* count depletion in the order Cu_3Au relative to its disordered counterpart observed in the Au $L_{2,3}$-edge white line may be revealed in the photoemission measurements as occupied density of states of Au 5*d* character in the valence-band spectrum of the disorder Cu_3Au.

We can compare the XPS valence-band spectra (Fig. 4) of the ordered and the disordered Cu_3Au since the XPS results are relatively insensitive to final-state band dispersion and orientation effects, and we did not detect any noticeable differences by looking at a different spot on the surface. From Fig. 4, we can see that the intensity of the quasi-"Au" region (4.0–7.5 eV) relative to the "Cu" region is less intense and the quasi-Au "$5d_{3/2}$" peak is narrower in the ordered sample. The latter observation can be related to a locally more dilute Au in Cu (longer Au-Au distance). The ratio of the ratios of the area of "Au" (between 4.0–7.5 eV) to "Cu" (between 2–4.5 eV) for the (ordered):(disordered) is ~0.9. This observation may be within the uncertainty of matrix element, surface, and orientation effects of polycrystalline sample. If we assume negligible matrix element effects; however, this result indicates a small drop in Au $5d$ character on the basis of the band-repulsion model[12,22] or weak Au-Cu d-d interaction. This is in qualitative agreement with the increase of unoccupied Au $5d$ population from a disordered to ordered system (Table I). If the Au and Cu d bands interact significantly and the Au d band spans the entire alloy d band, this ratio is not relevant. It is apparent that valence-band photoemission data alone are not adequate in settling the Au d band-width issue. It is interesting to note that our XPS valence-band spectrum for the ordered Cu_3Au is similar to that of $Cu_3Au(001)$ single crystal[14] except in the region of 4–5 eV. This may be due to different segregation and orientation effects between polycrystalline samples and single crystal.

IV. CONCLUSION

We have reported the Au $L_{2,3}$-edge XANES and the XPS photoemission of the ordered and disordered Cu_3Au. The white-line intensity of the alloys were used to derive the unoccupied Au $5d$ counts at the Au site of the alloys. Both XANES and the XPS core level and Mössbauer analysis clearly reveal that the Au $5d$ count is depleted at the Au site upon Cu_3Au formation in qualitative agreement with the charge-compensation model, and that the $5d$ count depletes more in the ordered Cu_3Au than in the disordered alloy. The most interesting finding is the nonstatistical Au $5d$ hole population ($[h_{5/2}]:[h_{3/2}] < 1:1$) observed in Cu_3Au alloys when compared with the near-statistical $5d$ hole population ($[h_{5/2}]:[h_{3/2}] \simeq 2:1$) in $AuAl_2$ and $AuGa_2$ in which Au–non-Au d-d interaction is absent. This observation hints the importance of relativistic effect (uneven $d_{5/2}, d_{3/2}$ state involvement) in alloy formation of Au with elements of near-filled d bands. Using normal-emission XPS measurements, valence band of polycrystalline Cu_3Au exhibits only small emission intensity variations between the ordered and disordered sample, relatively insensitive to d hole redistribution exhibited in XANES and XPS core-level results.

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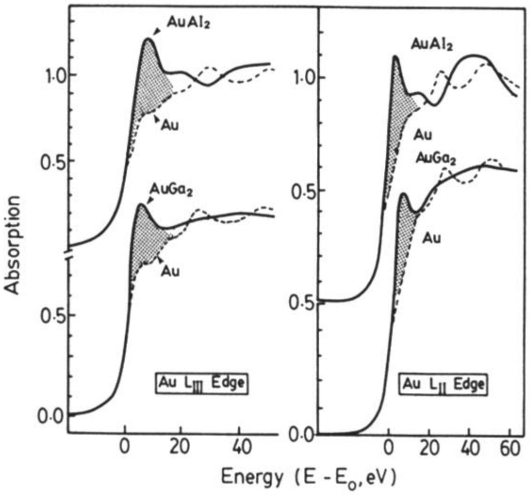

FIG. 3. Au L_3,L_2-edge XANES of $AuAl_2$ and $AuGa_2$ normalized to the edge jump. The shaded area represents the difference in white-line intensity relative to pure Au. The scale has the same meaning as in Fig. 2.