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Partial spectral weights of disordered Cu-Au alloys

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We present valence band photoemission spectra of polycrystalline Cu_xAu_{1-x} ($x = 0.10$, 0.25, 0.50, 0.75, 0.90) disordered binary alloys taken with variable incident-photon energies using synchrotron radiation. Taking advantage of the Cooper minimum phenomenon of the Au 5d band and taking proper account of the photoionization matrix element, we obtain experimental partial spectral weights for the alloys determined from the measured ratio of Au 5d and Cu 3d photoionization cross sections. We find that the Au partial density of states in dilute Au alloys is very strongly hybridized with the Cu host band and its bandwidth is not much reduced, contrary to the conclusion of some earlier work which claimed that the Au states have a greatly narrowed bandwidth due to the band repulsion between different d bands. Our finding is consistent with recent theoretical results. The lattice relaxation effect on the electronic structures of Cu-Au alloys is also investigated using ultraviolet photoemission spectroscopy. Compared with the bandwidths of ordered alloys which do not suffer lattice relaxation, those of disordered alloys are reduced by a small amount, which can be interpreted as the result of both the total volume change and the lattice relaxation effects, whose magnitudes are comparable.

I. INTRODUCTION

The substitutionally disordered binary alloy system Cu-Au has received much attention, because it can give information on the mechanism of band formation in binary alloys. Especially, Cu_3Au is the classical example of the order-disorder transition in binary alloys and has been the subject of many investigations.[1-20] Photoemission spectroscopy (PES) has been extensively utilized to study its electronic structure in both ordered and disordered phases, but there has been some controversy regarding the distribution of the Au partial density of states (DOS) and the nature of hybridization between Au 5d and Cu 3d states. Many angle-resolved and synchrotron PES studies[10,14,16,21] and the optical study[22] indicate a strong contribution of the Au 5d states in the binding energy (E_B) region of 5–7 eV in Cu_3Au and Cu-rich Cu-Au alloys. These results prompted some to conclude that the Au partial DOS in Cu_3Au or in Cu-rich alloys, become narrow and are confined within the binding energy region of 5–7 eV, and that the Au-related electronic band is almost nondispersive.[4,7,16] They argued that the Au 5d band and the Cu 3d band separate and form a split band, due to the band repulsion mechanism,[4] originally proposed as an explanation of the hybridization effect for nonoverlapped d bands.[23] This means that when the hybridization between d bands is neglected, the Au 5d states remain at $E_B = 5$–7 eV and the Au 5d related structure is very weak in the region of the host d band, as in the case of Ag-Pd alloys.[24] However, one can make strong arguments against this interpretation. The Au atomic site is known to be greatly compressed in the Cu host. The nearest neighbor distance in pure Au metal is 2.88 Å, but in $Cu_{99}Au_{01}$, it becomes 2.60 Å for the Au atomic site.[25] From this fact, one can expect strong hybridization between Au 5d and Cu 3d states in Cu rich Cu-Au alloy, as in the case of Cu rich Cu-Pt alloys, where strong hybridization yields a common band, due to the mixing of two overlapping d partial DOS.[26,27] Indeed, Wertheim and co-workers[5,6,9] proposed that there is a strong mixing of Au 5d and Cu 3d states in Cu_3Au, and that substantial Au partial DOS exists outside the binding energy region of $E_B = 5$–7 eV.

To resolve this controversy, it is important to deduce the partial DOS correctly from the photoemission spectra. In our previous publications,[28,29] we have developed a procedure to deduce correct partial DOS of constituent elements of alloys, using the Cooper minimum phenomena. We have also shown that the change of the photoionization matrix element with binding energy in the valence band can cause a substantial discrepancy between the density of states and the photoemission spectra for d band metals and alloys. In this paper, we will take this matrix element effect into account, to deduce correct partial DOS in Cu-Au alloys of various compositions from synchrotron-radiation photoemission spectra, in order to resolve the controversy on the electronic structures of this

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alloy system.

Another point of interest addressed in this work is the local lattice relaxation effect on the electronic structures of disordered binary alloy systems. Extended x-ray absorption fine structure experiments show that most disordered binary alloys have distribution in the nearest neighbor distance,[25,30] and many theoretical studies[17,19,31] have predicted a change of the electronic structure, due to this local lattice relaxation. For example, in the case of disordered Cu-Pd alloys, the lattice relaxation effect has been credited as the source of the observed low spectral weight of the bonding states found in the synchrotron radiation photoemission[32] or Auger electron spectroscopy (AES) (Ref. 30) studies. But we have shown in previous studies[28,29] that the Cu-Pd disordered alloy system is not a good example of the influence of the lattice relaxation on electronic structures, because of the strong matrix element effect and the lifetime broadening, which obscure the bonding states even in the x-ray photoemission spectra. Because the local lattice relaxation at the Au impurity site in the Cu host is larger than that at the Pd impurity site in the Cu host,[25] we can expect that the influence of the lattice relaxation will be more significant in Cu-Au alloy system. Furthermore, the bandwidth of Cu-Au alloys can be easily determined. In the case of Cu-Pd alloys, it is very difficult to determine precisely the bandwidth of pure Pd 4d band from the experimental photoemission spectra. In contrast, the valence band of pure Au has a very sharp peak composed of the $d_{3/2}$ states, due to the Γ_{8+} point on the band along Q, Λ, and Σ lines, and a prominent shoulder, due to the X_{7+} point, which forms the bottom of the entire d band, as well as a sharp peak composed of the $d_{5/2}$ states, due to the $L_{4,5+}$ point, which forms the top of the d band.[33] Since the dispersion of bonding states is not too large in $\mathrm{Cu_3Au}$,[10,16,20] the Au-related $d_{3/2}$ states are anticipated to preserve their sharp structures even in alloys provided the broadening of the states due to disorder is not so severe.

An outline of this paper is as follows. Section II gives the experimental details, including the sample preparation. In Sec. III, we present the photoemission spectra at different photon energies, and using the Cooper minimum phenomenon of the Au 5d states, we deduce the experimental partial spectral weights (PSW's). For this purpose, we use the experimentally determined ratio of Au 5d and Cu 3d photoionization cross sections using synchrotron radiation, and take proper account of the photoionization matrix element effect following the procedure discussed in Refs. 28 and 29. We then compare the thus determined PSW of $\mathrm{Cu_{75}Au_{25}}$ with the existing theoretical results. In Sec. IV, we obtain the spectra of ordered and disordered $\mathrm{Cu_{50}Au_{50}}$ and $\mathrm{Cu_{75}Au_{25}}$ with ultraviolet PES (UPS) to elucidate the importance of the lattice relaxation effect on the precise determination of the electronic structure of disordered Cu-Au alloys.

II. EXPERIMENT

Polycrystalline alloys $\mathrm{Cu}_x\mathrm{Au}_{1-x}$ (x=0.10, 0,25, 0.50, 0.75, and 0.90) were prepared by arc melting of constituents in an atmosphere of argon on water-cooled copper hearth. X-ray diffraction (XRD) measurements with Cu $K\alpha$ lines confirmed homogeneous face-centered-cubic (fcc) solid solutions. The Cu-Au alloy system has well-defined ordered structures when properly annealed ($\mathrm{Cu_3Au}$ has a $L1_2$ structure below 390 °C, CuAu I has a $L1_0$ structure below 385 °C and CuAu II is a long-period superlattice at 385–410 °C, and $\mathrm{CuAu_3}$ has a $L1_2$ structure below 217 °C).[34] No ordered phases were observable in our samples.

The spectra of disordered alloys at soft x-ray regime were taken at National Synchrotron Light Source (NSLS) Beamline U4A of Brookhaven National Laboratory equipped with 6m/160° toroidal grating monochromator. The total resolution at the Fermi level was less than 0.3 eV in full width at half maximum (FWHM), for photon energies below 160 eV, but at 160 eV, the total resolution was broadened to 0.45 eV, to obtain enough photon flux. The photon energies ranged from 40 eV to 200 eV. The measurement of photocurrents was performed by Vacuum Scientific Workshop (VSW) HA100 concentric hemispherical analyzer (CHA), with a single channel electron multiplier and a pressure in the low 10^{-10} torr range. UPS spectra with unpolarized He II lines ($h\nu$ = 40.8 eV) from a gas discharge lamp were taken with VSW ESCA/Auger system at Seoul National University equipped with HA150 CHA and multichannel detector. The total resolution for this measurement at the Fermi level was 0.22 eV in FWHM. During the measurement, the pressure was in the low 10^{-8} torr range.

The surfaces were cleaned by sputtering with neon or argon ions with 1 keV kinetic energy for about 20 min. To remove the damages at the surface induced by sputtering, the samples were annealed at 240 °C for 20 min. Such an annealing condition is far from sufficient for the surface to become ordered, and no difference in peak positions was observed between the spectra taken before and after annealing. The surfaces were found to be free of contamination after this sputter-annealing treatment.

Ordered phases were obtained by heating $\mathrm{Cu_{50}Au_{50}}$ at 350 °C for 30 min and $\mathrm{Cu_{75}Au_{25}}$ at 350 °C for 60 min. The ordered structures were confirmed by x-ray diffraction, and the surface ordering could also be confirmed by the difference in the photoemission spectra. In fact, we found that when the surfaces of ordered phases were sputtered, the photoemission spectra became those of disordered phases. It was reported that the time required for $\mathrm{Cu_3Au}$ to restore a substantially ordered condition after a disordering anneal is of the order of 10^6 s,[35,36] but the coarsening of the ordered domain starts after ~2000 s of ordering anneal.[35] So the structure of $\mathrm{Cu_3Au}$ that we obtained from the above treatment can be regarded as composed of ordered phases with small domain size.

III. RESULTS

A. Raw spectra

Figure 1 shows the photoemission spectra of $\mathrm{Cu}_x\mathrm{Au}_{1-x}$ (x = 0.1, 0.25, 0.50, 0.75, 0.90), along with those of pure Au and Cu taken with 60 eV photon energy, where the calculated ratio of atomic photoionization cross sections[37] between Cu 3*d* and Au 5*d* is 0.8. The higher binding peak in pure Au spectra around $E_B \simeq$ 6 eV, which is mainly composed of the $5d_{3/2}$ states, seems to shift slightly toward higher binding energy as Au content decreases. Also, the peak around $E_B \sim 4$ eV in pure Au, which mainly consists of the $5d_{5/2}$ states, seems to shift toward higher binding energy rapidly as Au content decreases. This observation prompted some investigators[4] to conclude that the spin-orbit splitting of Au 5*d* band decreases from 2.7 eV in Au metal to 1.3 eV in $Cu_{90}Au_{10}$, which is close to but smaller than the atomic Au spin-orbit splitting. The analysis of the $Cu_{75}Au_{25}$ spectrum led them to conclude that the band formation of Cu-Au disordered alloy system is the split-band type and that there is only a small density of Au 5*d* states at $E_B = 2$–4 eV as the result of weak hybridization between Cu 3*d* and Au 5*d* states. However, as we will see in the following, this interpretation is very doubtful.

Figure 2 shows the photoemission spectra of the same samples at 160 eV, where the calculated cross section ratio[37] between Cu 3*d* and Au 5*d* is 22. Since this cross section ratio is very large due to the Cooper minimum of the Au 5*d* states, the spectra can be regarded as the Cu PSW's at this photon energy. We can see that the Cu partial DOS becomes narrow as Cu content decreases, due to the decrease in the number of Cu neighbors on adjacent sites. The lower edge of the Cu 3*d* band is not changed, but the centroid of Cu 3*d* DOS is shifted by about 1 eV toward the Fermi level. This shift could be due to the band repulsion between the two different *d* bands, but the more probable cause in dilute Cu alloys is the difference in the chemical potentials of pure Au and Cu, which is estimated to be about 0.5 eV from the difference of their work functions.[38]

From Figs. 1 and 2, it is clear that the PSW's of this alloy system must be obtained with great accuracy in order to gain an understanding of the shapes of the partial DOS and of the mechanisms that determine the electronic structure of disordered binary alloys, in general.

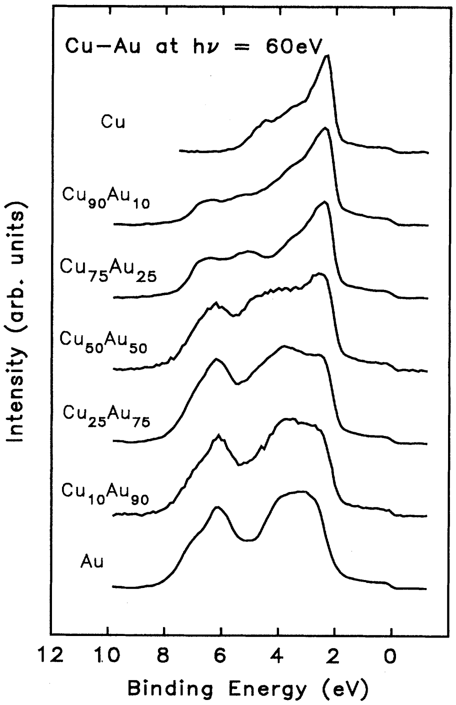

FIG. 1. Photoemission spectra of Cu, $Cu_{90}Au_{10}$, $Cu_{75}Au_{25}$, $Cu_{50}Au_{50}$, $Cu_{25}Au_{75}$, $Cu_{10}Au_{90}$, and Au with photon energy $h\nu = 60$ eV, where the calculated photoionization cross section ratio between the Cu 3*d* and the Au 5*d* state is 0.8 (Ref. 37). The data are normalized by the photon flux and then drawn to have the same height. The inelastic background is removed and the analyzer transmission function is corrected assuming $1/E$ behavior.

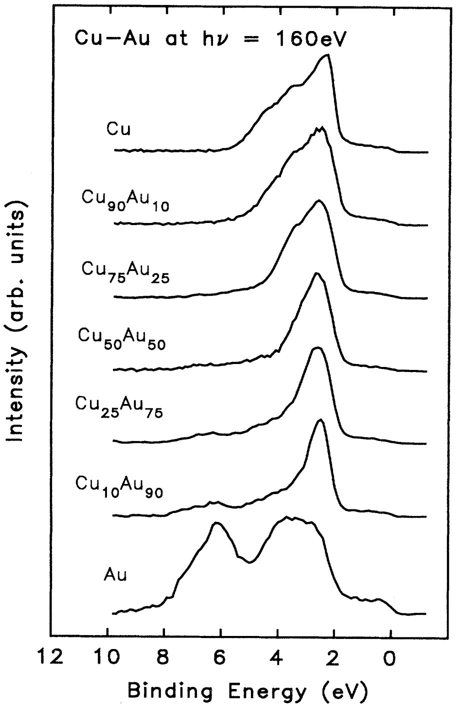

FIG. 2. Photoemission spectra of Cu-Au alloys with photon energy $h\nu = 160$ eV, where the calculated photoionization cross section ratio between the Cu 3*d* and the Au 5*d* state is 22. The details are the same as in Fig. 1.

B. Photoionization cross section

In order to obtain reliable PSW's of alloys using the Cooper minimum phenomenon, it is important to determine photoionization cross section ratios accurately. We have shown, in previous work,[29] that it is possible to determine the ratio of photoionization cross sections (σ) at photon energies in the soft x-ray regime (from 40 eV to 200 eV in this work) experimentally from the ratio of intensities of valence bands at various incident-photon

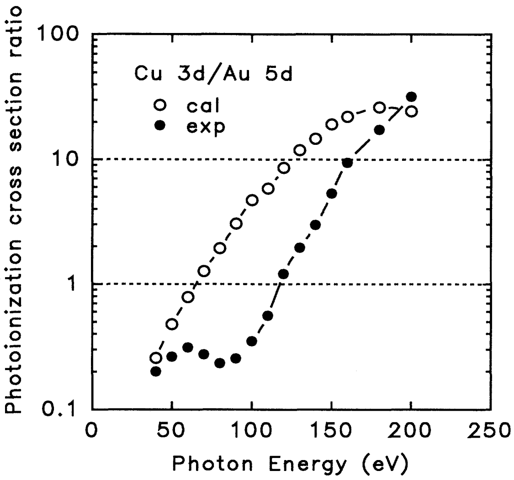

FIG. 3. Ratio of the photoionization cross section of the Cu 3*d* to that of the Au 5*d* at $h\nu$ = 40 eV∼ 200 eV, both the experimental solid-state (filled circles) and the calculated atomic case (open circles) (Ref. 37).

energies. This is accomplished using the intensity ratio of two core-level x-ray photoemission spectroscopy (XPS) peaks, one from each element, with comparable binding energies as a reference. This is based on the fact that the intensity ratios of valence-band photoemission spectra taken at different photon energies are related to their cross section ratios. To fix the proportionality constant, the intensity ratios of core levels and valence bands are measured with XPS and with ultraviolet PES (UPS) under the same conditions. Then these ratios are connected with the valence-band intensity ratios measured with synchrotron radiation. For Cu-Au alloys, the Cu 3*p* (E_B = 75 eV for $p_{3/2}$) and the Au 4*f* (E_B = 84 eV for $f_{7/2}$) levels were used as the reference core levels, because they have similar binding energies. This procedure assumes that the calculated atomic cross section values for core levels remain valid in solids, since the core-level wave functions are not much changed in a solid compared with those in atoms. The experimental result for the cross section ratio between Cu 3*d* and Au 5*d* states (Fig. 3) shows monotonically increasing behavior above $h\nu$ = 80 eV, for $\sigma_{3d}^{\rm Cu}/\sigma_{5d}^{\rm Au}$, in agreement with the atomic calculation.[37] So, within the limit of good statistics and reasonable resolution, we chose to use low photon energy of 60 eV and high photon energy of 160 eV to determine the partial DOS of Cu-Au alloys.

C. Partial spectral weights of disordered alloys

The procedure for extracting the partial DOS of binary alloy systems, using these cross section ratios employed in this work, was discussed in detail in Ref. 29. In this procedure, the photoemission spectrum is represented as the sum of contributions from different species of atomic sites weighted by their photoionization matrix elements, which are dependent both on *photon* energy and on *binding* energy. Because of the variation of matrix element with binding energy, the photoemission spectrum or the component from different species is not exactly equal to the total or the partial DOS of alloy system. That is, it is necessary to include the matrix elements correctly for extracting PSW, from the measured photoemission spectra, for comparison with calculated partial DOS. If we can determine the matrix elements of constituents or at least the ratio of the matrix elements between different photon energies, then it is possible to extract the PSW's. Here, we represent the change in matrix elements at two different photon energies by the ratio of the spectra of pure metals.

Since the experimental value of cross section ratio of the Cu 3*d* to the Au 5*d* state is 9.4 at $h\nu$ = 160 eV, we can regard the PES spectra, at that photon energy as the Cu PSW's, as a first approximation. Using the measured cross section ratio and the divided spectra representing the change in the matrix elements of pure Cu between different photon energies, the Au PSW at $h\nu$ = 60 eV can be obtained. With this approximate Au PSW, a better Cu PSW at $h\nu$ = 160 eV can be determined by a similar method, and the process is iterated until we obtain self-consistent results. In this procedure, we neglect the possible wave vector **k** dependence of the matrix element, because we treat only the angle-integrated spectra. The required spectral ratio for transforming the Cu PSW's at different two photon energies is the spectrum of pure Cu at $h\nu$ = 60 eV divided by the spectrum at $h\nu$ = 160 eV, which are normalized to have the same area. In this work, we have smoothed this divided spectrum with the Gaussian broadening of 0.5 eV to remove some of the noise in the spectrum. We have also broadened the spectra at $h\nu$ = 60 eV, in order to match the instrumental broadening of the spectra at 160 eV.

The compositions of Cu-Au alloys used in the analysis cannot be assumed to be those of the bulk, because of the strong surface segregation at low Au concentration.[39,40] We, therefore, used the compositions of the annealed surfaces at 200 °C measured with AES,[39] which were determined from Cu (58/60 eV) and Au (66/69 eV) transitions. The values used as surface compositions are Au 17%, 32%, and 57% for $\rm Cu_{90}Au_{10}$, $\rm Cu_{75}Au_{25}$, and $\rm Cu_{50}Au_{50}$, respectively. We can indeed see that the spectra after annealing have less weight at E_B = 2–4 eV than the spectra before annealing, where most of the Cu partial DOS will remain. This confirms the Au segregation during annealing, because sputtering does not yield segregated surfaces for Cu-Au alloys.[41] Since our measurement was done at room temperature and the AES measurement was at 200 °C, the surface composition may be slightly different. Also, the electron mean free paths in solids at 60 eV and 160 eV are different, and, in principle, we have to use different surface compositions at different photon energies, but, in practice, a slight change in surface composition does not make any serious change in the deduced PSW.

The results of the analysis can be seen in Figs. 4 and 5, which show the experimentally determined Cu and Au PSW's, respectively. As anticipated, the bandwidth

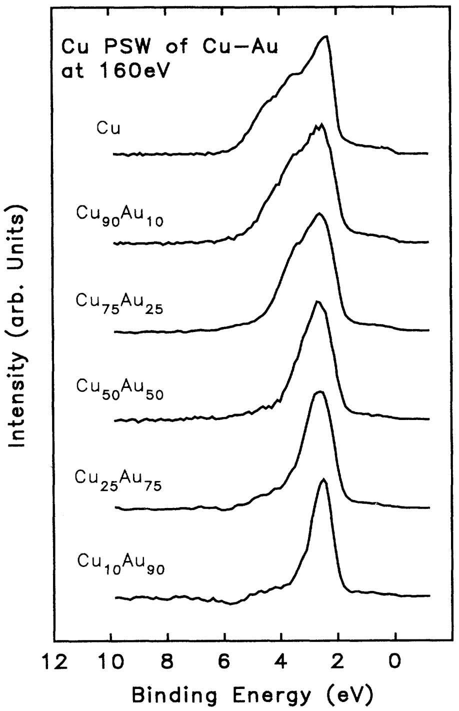

FIG. 4. Experimental Cu partial spectral weights of Cu-Au alloys of various compositions at $h\nu = 160$ eV, using the experimentally determined cross section ratio.

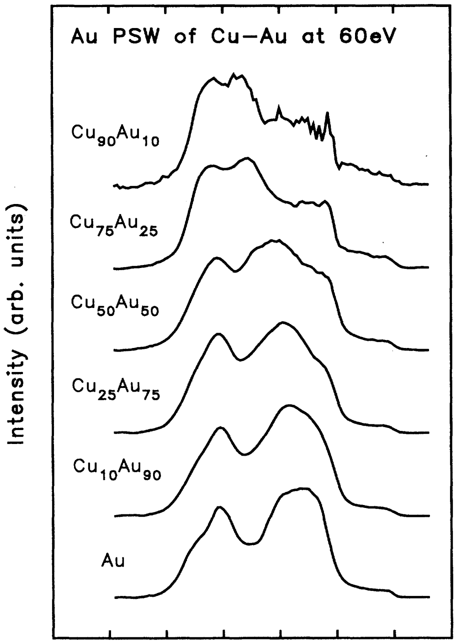

FIG. 5. Experimental Au partial spectral weights of Cu-Au alloys of various compositions at $h\nu = 60$ eV, using the experimentally determined cross section ratio. Note the lower binding structures, which are not negligible even in Cu$_{90}$Au$_{10}$.

of the anti-bonding Cu PSW gets reduced from its pure metal value of 4 eV to less than 2 eV for Cu$_{10}$Au$_{90}$. The Cu partial DOS in Cu-Au alloys can be interpreted as a result of two competing factors, band narrowing, due to the decrease in the number of Cu near neighbors and band broadening due to the mixing with electronic states of Au atoms. The narrowed Cu partial DOS is not broadened much by the hybridization with the Au 5*d* states, partly due to the small number of the Au 5*d* states that can mix with the Cu 3*d* states, and partly due to the dilated Cu atomic site in the Au host, which results in the weak hybridization with the host band.

For the case of Au PSW shown in Fig. 5, a large amount of the Au 5*d* states are confined within $E_B =$ 4–7 eV for Cu$_{90}$Au$_{10}$ and for Cu$_{75}$Au$_{25}$ forming bonding states. At $E_B = 2$–4 eV, the density of the Au 5*d* states is decreased as Au is diluted and they form anti-bonding states with most of the Cu 3*d* states. But the intensity of these states is by no means negligible. In fact, we can say that Fig. 5 shows that the width of the Au partial DOS is not reduced much from its pure metal value. This result is in contrast to the band repulsion picture for this alloy, which could result in two separated *d* bands. This is also in accord with the band calculation results,[8,11] which show the Au 5$d_{5/2}$ states form common band with Cu 3*d* states, and part of the 5$d_{5/2}$ states is pushed out of the host band, due to strong hybridization forming a broad peak near the Γ point at $E_B \sim 5.2$ eV. Only the Au 5$d_{3/2}$ states are predicted to show split-band behavior.

It has sometimes been argued that the spin-orbit splitting of the Au 5*d* states in Cu-Au alloys is greatly narrowed as Au is diluted by focusing only on the structure at high binding energy, between 5 and 7 eV, which is composed of two peaks.[4] Band calculation predicts that the higher one is mainly composed of the $d_{3/2}$ states and the lower one of the $d_{5/2}$ states, and, thus, if the Au PSW's were confined within this binding energy region, it would be correct to say that the spin-orbit splitting of the Au 5*d* states in Cu rich Cu-Au alloys is close to or smaller than that of the atomic value 1.5 eV. For disordered Cu$_{90}$Au$_{10}$ alloy and for ordered Cu$_3$Au alloy, the results of band calculations[16,21] show nearly no dispersion of the Au 5*d* states, especially for the Δ directions. However, this can only be true for the bonding states that form the higher binding structure of the spectra. There is increasingly more Au 5*d* character in mixed states as the wave vector **k** moves from the Γ_{8+} critical point to such points at the zone boundary as X_{7+} or L_{6+}, which form the hybridized $j = 5/2$ states.[21] These states make up the structure between 2 and 3 eV, which is relatively small in intensity, but not at all negligible in the Au partial DOS of Cu$_{90}$Au$_{10}$ and Cu$_{75}$Au$_{25}$. If we define the spin-orbit splitting of the Au partial DOS as the splitting between the centroids of Au $d_{3/2}$ and $d_{5/2}$, the value will be larger than the separation of the Au-derived peaks at the binding energy region between 5 and 7 eV. In addition to this common band structure, the dispersion of the Au-related high binding states was observed along the Λ direction for ordered Cu$_3$Au (Ref. 20). Thus, we conclude that the assertion of a narrow, nondispersive, and split Au 5*d* partial DOS is not valid.

D. Comparison with the band calculation: $Cu_{75}Au_{25}$

It is essential to compare PES spectra with the band calculation to check the validity of the calculation scheme. There have been many results of band calculations on ordered Cu_3Au (Refs. 1–3, 7–9, 11, 17 and 20) and on disordered $Cu_{75}Au_{25}$ (Refs. 3, 8, 11, 14, 17 and 19). For the ordered phase, the results do not differ very much from each other, except in the region from 5 to 7 eV, which contains Au-related high binding states which are affected by the spin-orbit splitting. Calculations with fully relativistic or semirelativistic schemes both predict three peaks in this region, which have been found experimentally on many crystallographic faces.[12,16] It is known that the crystal field splitting is very important in determining these structures. As pointed out in Ref. 7, the lowest binding energy peak (at 5.1 eV) has Γ_1 symmetry in simple cubic structure and, thus, has nothing to do with the spin-orbit splitting. Of the other two peaks, the highest binding energy peak (at 6.9 eV) is an e_g state, which is not split by the spin-orbit interaction. Only the middle peak (t_{2g} state at 6.0 eV) is split by 0.35 eV by this interaction, as observed with angle-resolved PES.[20] But this small splitting does not mean that the spin-orbit splitting parameter is small, because the spin-orbit interaction and the crystal field splitting are comparable.[7]

For the disordered phase, such three-peak structure is absent, because of different crystal structure and large lifetime broadening resulting from the disorder (the difference in the phase shifts of the Au and the Cu $d_{3/2}$ states is large). Thus, the fully relativistic calculations show only two broad peaks for high binding energy structures, composed of the $d_{3/2}$ (at around 6.9 eV) and the $d_{5/2}$ (at around 5.5 eV) related states, respectively. Even a smeared one-peak structure was predicted by the scalar relativistic calculation, which shows no splitting for the high binding structure.[14] The early Korringa-Kohn-Rostocker–coherent potential approximation (KKR-CPA) results showed too large a bandwidth compared with that of the ordered phase, which is not in accord with the PES spectra.[3,12] More reasonable results, based on the correct calculation scheme,[11,14] predict bandwidth that are smaller, but still larger than those observed experimentally. Especially, Ginatempo *et al.* argue that disordering only broadens the Bloch spectral function of the ordered phase, but produces no shift in most of the peak positions between two phases.[11] However, the calculation based on the special quasirandom structure (SQS), which has a distribution of distinct environments, the average of which corresponds to the random medium, predicts a reduced bandwidth relative to the CPA result when lattice relaxation is included.[19]

The direct comparison of PES spectra with the calculated DOS can produce problems, because band calculations do not include many-body effects and are in some cases not at all equal to the $(N-1)$ body quasiparticle spectra. For the alloy systems under consideration, two factors must be included in the process of analysis, i.e., the lifetime broadening, which is due to many-body interaction and the binding energy dependence of the matrix element in photoemission process discussed in detail in earlier work.[28,29] Some caution must be paid to the lifetime broadening of pure Au. As suggested in Ref. 42, it seems that the states near Γ_{8+} and near X_{7+} experience different lifetime broadening. So it is difficult to obtain the experimental matrix element, which is defined as the spectrum of the pure Au divided by the folded Au DOS assuming simple Fermi liquid behavior. Since the pure Au spectrum at $h\nu = 60$ eV resembles that at $h\nu = 1486.6$ eV, we assume that the matrix element resembles that calculated in Ref. 43, the value of which at the Fermi level is about 1.5 times the value at $E_B = 10$ eV. The lifetime broadening is carried out with a Lorentzian half width of 0.49 eV at $E_B = 7$ eV (near the bottom of the Au 5d band), which decreases quadratically, vanishing at the Fermi level. This lifetime broadening value is smaller than the one used for the fit of pure Au XPS spectra.[43] Gaussian broadening is also performed to match the experimental width at the Fermi level.

As shown in Fig. 6, the experimental Au PSW of $Cu_{75}Au_{25}$ is in good agreement with the theoretical Au PSW, using the result of Ref. 14, except for the total width and the separation between the two prominent structures at the high binding energy. Good agreement on the overall structure reflects the fact that the Au partial DOS of $Cu_{75}Au_{25}$ is not narrowed, and most probably the same is true for the Au partial DOS of ordered Cu_3Au. This is consistent with the results of the recent x-ray photoelectron diffraction study[13] on Cu_3Au. Hence the previous argument that the Au partial DOS of Cu_3Au is narrowed due to band repulsion[4] is incorrect. Even though the high binding structures are reported to have nearly no dispersion, $Cu_{75}Au_{25}$ and Cu_3Au clearly have common-band behavior at least for the Au $5d_{5/2}$ states.

The experimental Au PSW in Fig. 6 has more inten-

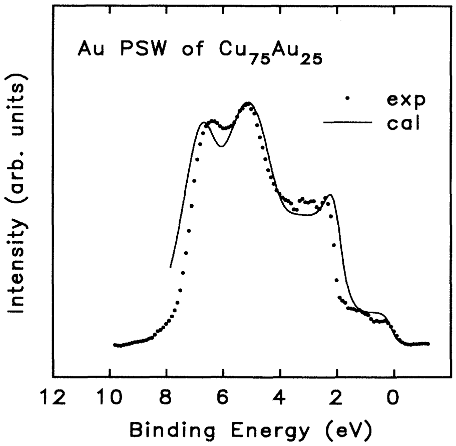

FIG. 6. Comparison of the experimental (dots) and the theoretical (line) Au partial spectral weight of $Cu_{75}Au_{25}$. The calculated Au partial DOS is from Ref. 14.

sity in between the two prominent structures near $E_B =$ 6 eV than the theoretical curve. This is probably due to the emissions from the surface, since the photoemission spectrum is surface sensitive at this photon energy and a slight segregation of Au atoms to the surface occurs for this alloy. Although the surface density of states of the disordered $Cu_{75}Au_{25}$ alloy has not been determined experimentally, this interpretation is supported by the experimental study of ordered $Cu_3Au(100)$ surface[5,9] and the theoretical calculation on layer-dependent electronic structure of disordered $Cu_{75}Au_{25}$ alloy,[44] both of which identified surface Au 5*d* features in this energy region. Because of this surface contribution, an exact agreement between the experimental and theoretical bulk Au PSW is not expected.[45] However, the contribution from the surface band does not prevent the determination of the bulk bandwidth or the peak positions of the bulk states from our experimental spectra, because even the surface sensitive photoemission spectra contain both bulk and surface features[9] and the surface band is well inside the bulk band with less prominent structures in this case.[5,12] Hence the above conclusion on the bandwidth of $Cu_{75}Au_{25}$ alloy and its common-band behavior still hold. The same is true for the discussion of lattice relaxation effects presented in the following section.

IV. LATTICE RELAXATION EFFECTS

Because Au impurity sites in a Cu host experience strong lattice relaxation, we perform UPS of disordered and ordered $Cu_{50}Au_{50}$ and $Cu_{75}Au_{25}$ to see the lattice relaxation effect on the alloy electronic structures. Figure 7 shows the results of measurement on $Cu_{50}Au_{50}$ and CuAu I. When we define the bandwidth as the width between the half maxima of the highest and the lowest energy sharp structures, the reduction of the bandwidth in the disordered phase is about 0.1 eV, but this value will be about 0.2 eV if the change of the bandwidth is determined from the change in the deepest peak position as in Ref. 46.

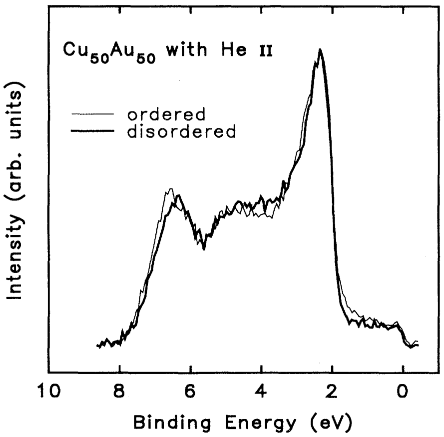

FIG. 7. Spectra of ordered CuAu I (thin line) and disordered $Cu_{50}Au_{50}$ (thick line) with He II lines. They are normalized to the same area. The shift of the deepest binding peak is only about 0.2 eV for relaxed disordered phase.

Since it was argued that disorder does not shift the states of disordered alloys,[11] we can determine the amount of the reduction in bandwidth, due to lattice relaxation from the position of the deep bonding states. However, because CuAu I has different lattice constant from disordered phase, it must be borne in mind that the bandwidth can be reduced by the total volume change. CuAu I has tetragonal structure with $a = 3.966$ Å and $c = 3.673$ Å and $Cu_{50}Au_{50}$ has fcc structure with $a = 3.876$ Å.[47] The tetragonal deformation, which results from the strain between Cu and Au planes, is predicted to change the bandwidth only by 1 mRy,[48] and thus can be neglected in this discussion. Hence the decrease in total bandwidth must have its origin in the total volume change and the lattice relaxation. The volume change due to disordering is 0.8%, which can give rise to 1.3% decrease in total bandwidth, assuming that the bandwidth is inversely proportional to the fifth power of the average nearest neighbor distance.[49]

The influence of the lattice relaxation on the electronic structure of $Cu_{50}Au_{50}$ can be appreciated via the band calculation result of CuAu II, which has a modulated long period ordered structure. The unit cell of CuAu II is obtained by stacking five CuAu I unit cells in a row in the direction of one of the long cell edges and then repeating this unit at five cell intervals, with a simultaneous out-of-step shift at the boundary through the lattice vector $\frac{1}{2}(a+c)$. Near antiphase boundary, lattice relaxation and substitutional disorder have been observed by XRD.[50] The interatomic distance between two Au atomic sites at the antiphase boundary is 2.777 Å, and that between two Cu atomic sites is 2.579 Å, relaxed from the regular lattice constant 2.706 Å. These differences are comparable to the calculated differences between the Au-Au or the Cu-Cu bond length and the average nearest neighbor distance of CuAu I, 0.08 Å, and 0.05 Å, respectively.[19] With the experimentally observed atomic positions, Kokko[51] calculated the partial DOS of ten different atomic sites in CuAu II and found that the bandwidth of the DOS within a layer is reduced by 10 mRyd, due to lattice relaxation as the distance from the antiphase boundary is decreased. This means that the lattice relaxation effect can also play some role in the reduction of bandwidth of the disordered $Cu_{50}Au_{50}$. But the reduction, due to the lattice relaxation in the disordered phase, will be about 0.1 eV, judging from the above calculation on CuAu II. Thus, the experimentally observed reduction of the bandwidth in the disordered phase is the sum of the amount expected from the lattice relaxation and that from the total volume change, which are comparable in magnitude.

Figure 8 shows the experimental results for disordered $Cu_{75}Au_{25}$ alloy and ordered Cu_3Au along with the results of the band calculations of Ref. 11. If the bandwidth is defined as the energy between the half maxima of the highest and the lowest binding structures, the change in the bandwidth is negligible. But if we regard the shift of

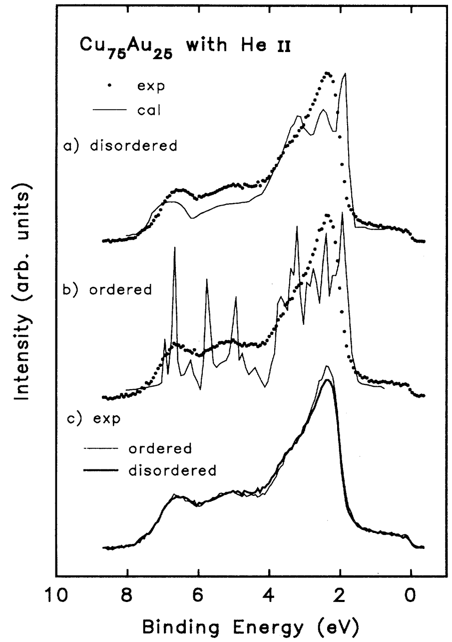

FIG. 8. Spectra with He II lines (dots) and band calculation results (thin lines : Ref. 11) of (a) disordered $Cu_{75}Au_{25}$ and (b) ordered Cu_3Au. The spectra are normalized to the same area and then compared in (c). The bandwidth of the disordered phase (thick line) is reduced by 0.2–0.3 eV from that of the ordered phase (thin line), partly due to the larger lattice constant and partly due to the lattice relaxation effect.

the Γ_{8+} states as the change in the bandwidth, the total bandwidth is decreased in the disordered phase by 0.2–0.3 eV. Again, a volume change of $Cu_{75}Au_{25}$ occurs at the order-disorder transition and must be considered. Disordered $Cu_{75}Au_{25}$ has $a = 3.7671$ Å, while ordered Cu_3Au has $a = 3.7594$ Å (Ref. 3) and the volume difference is 0.6%. For this amount of volume change, a 1.0% of reduction in bandwidth (about 0.05 eV) is expected at the order-disorder transition of $Cu_{75}Au_{25}$, and the observed reduction of about 0.2 eV must be the result of lattice relaxation, which is stronger than in $Cu_{50}Au_{50}$. Thus, the influence of the lattice relaxation on the electronic structure will not be negligible in determining such properties as the heat of formation of the disordered alloy. However, its effect does not seem so critical in determining the overall band structure.

The comparison of the experimental results with the band calculation requires some caution, because relativistic effects must be included to treat the Au $5d$ states. The results of the band calculation with tight-binding linear muffin tin orbital–CPA (LMTO-CPA) method,[17] which can include the lattice relaxation effect, predict that the bandwidth of disordered $Cu_{75}Au_{25}$ decreases by ~0.7 eV when the lattice relaxation is taken into account. But such a reduction in bandwidth is too large compared with the SQS calculation[19] and with our experimental result in Fig. 8. Since the detailed structure cannot be compared directly with the experimental data, due to the scalar-relativistic treatment of Ref. 17, the origin of this overestimate is not clear.

Some KKR-CPA calculations with inaccurate numerical schemes tend to predict a larger bandwidth and much smoothed structure for bonding states.[8] So, here we compare the spectra of disordered $Cu_{75}Au_{25}$ and ordered Cu_3Au with the band calculations of Ref. 11, which employ self-consistent-field fully relativistic LMTO, for ordered Cu_3Au and KKR-CPA, for disordered $Cu_{75}Au_{25}$ with the same potentials. After shifting the Fermi level of the calculated results, there is excellent overall agreement between theory and experiment for the ordered phase. The ordered phase spectrum does not have the three-peak structure for the Au-related deep bonding states, in agreement with the previous XPS measurement[15] on polycrystalline ordered Cu_3Au. For the disordered phase, the bandwidths are somewhat different in theory and experiment, but other than that, the overall structure is again in good agreement.

Lu *et al.*[19] argued from the calculation based on the SQS that the lattice relaxation reduces the total bandwidth of $Cu_{75}Au_{25}$ by about 1 eV when comparing their unrelaxed and relaxed SQS. But their conclusion seems somewhat exaggerated. Their unrelaxed SQS was neither a real random alloy nor a favorable ordered structure, and although the DOS difference curve between the relaxed and the unrelaxed disordered phase shows a dip of about 1 eV width at the deep bonding states, the difference in the centroid binding energy of the deepest structure is only 0.3 eV. If the comparison is made with the unrelaxed result of KKR-CPA,[11] the reduction is again only about 0.3 eV. Furthermore, they chose the PES spectra for comparison[12] which shows the maximum difference of the bandwidth between disordered and ordered phases. The spectra in Ref. 12 with $h\nu = 26$ eV on the (001) surface show the fairly large difference as about 0.5 eV, but the spectra on the (110) surface show only about 0.1 eV difference. Hence, we can expect that the angle-integrated spectra will show a smaller difference than Lu *et al.* had cited. We can conclude from these considerations that the observed reduction of the bandwidth of $Cu_{75}Au_{25}$ comes partly from the volume change and partly from the lattice relaxation, whose contributions seem comparable.

V. CONCLUSION

We performed photoemission spectroscopy on a disordered Cu-Au alloy system with synchrotron radiation. By the benefit of the Cooper minimum phenomenon of the Au $5d$ states, we obtained PSW's of these alloys, using the experimentally determined cross section ratio. Then we analyzed the PSW's of both components in order to obtain information about the band formation of Cu-Au alloy system. The band narrowing plays an important role in all Cu partial DOS to give reduced bandwidth. The Au partial DOS in Cu-rich Cu-Au alloys have sometimes been regarded as the results of band narrowing, which shifts and confines the partial DOS at higher binding energy than in pure Au metal. But we have shown from the observed Au PSW's that Cu-rich Cu-Au alloys form a common band, due to the strong band mixing originating from the compressed Au atomic sites.

Finally, we have shown that the lattice relaxation effect in Cu-Au alloys, which is stronger than in Cu-Pd alloys, influences the electronic structures a little, but not critically. In particular, we have discussed the previous studies treating the lattice relaxation, and concluded that the lattice relaxation effect had been somewhat overestimated. The lattice relaxation effect must be included in a detailed calculation for ground state properties, but it does not seem so important in determining the overall electronic band structures.

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