LETTER TO THE EDITOR

XPS and UPS investigation of ordered and disordered equi-atomic CuAu

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Abstract. We report x-ray and UV photoemission measurements of the valence bands in equi-atomic CuAu in both the ordered (L1$_0$ structure) and disordered (FCC) phases. We find that there are large differences in the spectra, particularly in the region of the Au d states. The measurements also suggest that the valence bandwidth in the ordered phase is greater than that in the disordered phase.

In a recent paper we reported photoemission measurements of the valence bands and the core levels in CuAu I using x-ray photoelectron spectroscopy (XPS) [1]. Our interest in the electronic structure in equi-atomic CuAu is based on the fact that the alloy undergoes two transformations at elevated temperatures; an order–order transition from the CuAu I phase (L1$_0$ structure) to the CuAu II phase (a one-dimensional long period superlattice) at about 390 °C, and an order–disorder transition from CuAu II to disordered Cu-50%Au (FCC structure) at about 410 °C [2]. Our objective is to gain some fundamental understanding of the driving forces for these transformations. The latter depend on the competition between interatomic forces that, in turn, are intimately related to the underlying electronic structure [3]. Thus, ordering energetics may be investigated by considering the total electronic energies of the various phases and *ab initio* calculations along these lines are now a practicable proposition through the application of density functional theory. However, ordering energies are small (~ 0.05 eV) compared with total energies ($\sim 10^4$–10^5 eV) and so such calculations are a stiff test of theory. Furthermore, as has been pointed out by Temmerman *et al* [3], total energy calculations provide only limited insight into the mechanisms that drive the transitions, e.g., the role of the Fermi surface or the changes in band energies away from E_F. For more detailed information, therefore, one should aim to explore and characterize changes in the E and k dependence of the electronic structure.

The principal requirement for any electronic theory of phase stability is that it must provide an accurate description of the electronic structure in each phase. Photoemission is now accepted as the most useful experimental probe of the electronic structure in metallic alloys and when measurements are combined with a proper first-principles analysis, theory can be confronted in a most detailed and profound manner [4]. A particular advantage of the photoemission technique is that measurements can be carried out at different temperatures, i.e., with the sample in different states of order, etc.

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As a result, it is to be expected that photoelectron spectroscopy will play an important role in helping to establish an understanding of the electronic driving forces of phase transitions, see, for example [3]. The previous work [1] was carried out in order to elucidate details of the electronic structure in CuAu I. In this paper, we extend our studies to include measurements of the disordered phase using UV photoelectron spectroscopy (UPS) and XPS.

The measurements were carried out at normal emission from a polycrystalline CuAu sample using a VG BLADES500 spectrometer and He I ($h\nu = 21.2$ eV) and Mg Kα ($h\nu = 1253.6$ eV) radiations. The sample preparation, cleaning and ordering procedures were the same as described in [1]. The measurements were made at room temperature for the ordered CuAu I phase and at 460 °C for the disordered Cu–50%Au phase. The overall resolution was 0.25 eV and 0.88 eV for UPS and XPS, respectively. For clarity, the background has been removed from all of the experimental spectra; for XPS we used the scheme described by Shirley [5] and for UPS we used a fourth-order polynomial fit. Previously, we found that substantial Au enrichment occurs at the surface of the equi-atomic alloy—in agreement with the observations of Losch and Kirschner [6] and McDavid and Fain [7] —but that there was no significant change in surface composition across either of the transformations [1].
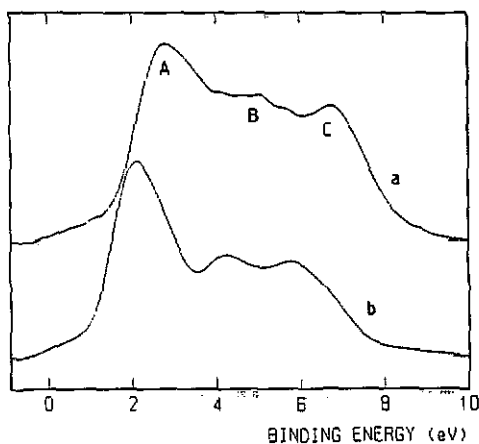

Figure 1. A comparison of: curve a, the experimentally measured x-ray photoemission spectrum from CuAu I using Mg Kα radiation incident at 42°, with curve b, the smoothed density of states from [7].

In figure 1, curve a, we show an x-ray photoemission spectrum from the valence bands of CuAu I. The spectrum is characterized by two relatively sharp peaks at ~ 2.8 eV (A) and ~ 6.7 eV (C) and several smaller and less distinct features between 4 and 6 eV (B); the largest appears at ~ 5.0 eV. Recent calculations by Kokko *et al* [8] of the densities of states in CuAu I—using the scalar relativistic, self-consistent field, linear muffin-tin orbital method within the atomic sphere approximation (SCF-LMTO-ASA)—indicate that in the region of peak A there is some overlap of Cu- and Au-related d states but that in the region of peaks B and C almost all of the weight in the electronic spectral density arises from Au-related d states. In order to provide some comparison between the experimental spectrum and the calculations we show in figure 1, curve b, a plot of the calculated density of states that has been cut off at E_F and convoluted with a Gaussian function with a FWHM of 0.88 eV to simulate

the experimental resolution. It must be stated that direct comparisons of curve a with curve b must be made with care for three main reasons. Firstly, electron–photon matrix elements are not included in curve b and so the relative intensities of the Cu and Au contributions will not be correct. For instance, data tables indicate that the cross section of Au is some three times larger than that of Cu for Mg $K\alpha$ radiation [9]. Secondly, the effects of the Au segregation are ignored in curve b; assuming a mean free path of 15 Å at these energies, the surface layer contributes $\sim$ 16% of the signal. These two points account for the relatively larger Au-related signal in the experimental spectrum. Thirdly, the spin–orbit interaction is not included in curve b. Nevertheless, the 'calculated' spectrum is quite similar to that measured experimentally in that it has three peaks, at $\sim$ 2.1 eV, $\sim$ 4.3 eV and $\sim$ 5.8 eV. The discrepancy of $\sim$ 0.6–0.7 eV between the experimental and calculated positions of (i) peak A, and (ii) the valley between A and B, is similar to that observed previously for Cu_3Au [10–12]. However, the experimental spectrum, curve a, is somewhat broader than curve b because of the effect of the spin–orbit interaction, particularly in the predominantly Au-related part of the spectrum—viz the situation in Cu_3Au [11–13]—which is not included in the calculation of the density of states.

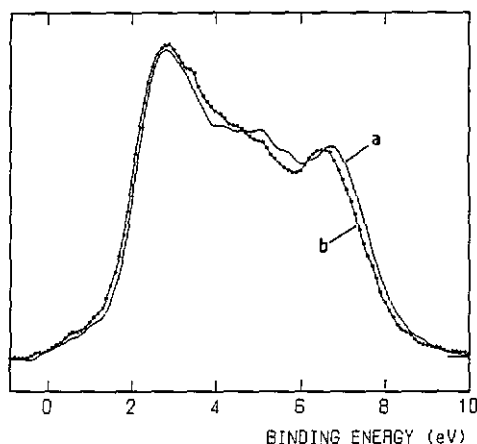**Figure 2.** A comparison of x-ray photoemission spectra from: curve a, ordered CuAu I with curve b, disordered Cu–50%Au, using Mg $K\alpha$ radiation incident at 42°. The spectra have been normalized in area.

In figures 2 and 3 we show spectra from the ordered phase (CuAu I) (curves a) and the disordered phase (Cu–50%Au) (curves b) using XPS and UPS, respectively. For convenience, the spectra have been normalized in area in each figure. Broadly speaking, the x-ray and UV photoemission measurements provide similar results. We identify three main differences between the spectra from the ordered and disordered phases.

(i) In both UPS and XPS the relatively sharp features characteristic of the ordered phase between $\sim$ 3–6 eV are 'smeared' out in the disordered phase. This behaviour is more obvious in UPS than in XPS because of superior resolution; the peaks at $\sim$ 3.25 eV, $\sim$ 4.2 eV and $\sim$ 4.8 eV in figure 3, curve a, are almost entirely 'lost' in figure 3, curve b.
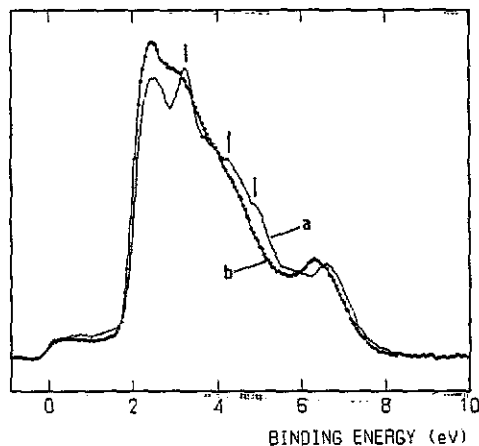
Figure 3. A comparison of UV photoemission spectra from: curve a, ordered CuAu I with curve b, disordered Cu–50%Au, using He I radiation incident at 35°. The spectra have been normalized in area.

(ii) The binding energy of the peak at 6.6–6.7 eV in the ordered phase is reduced by ~ 0.2 eV on disordering.

(iii) The overall width of the spectra is *smaller* in the disordered phase by ~ 0.1–0.2 eV.

We can interpret such behaviour if we consider the electronic structure in terms of a generalized Bloch spectral function, $A_B(k, E, S)$, that represents the density of electron states at energy E, reduced wavevector k and long-range order parameter S [3,4,14]. In the ordered state ($S = 1$) the spectral function is a sum of delta-function peaks whose loci in (E, k)-space trace the 'conventional' band structure. In the disordered state ($S = 0$) the spectral function corresponds to that of the random alloy and consists of peaks with heights and widths that vary in a complicated way with E and k [15]. Furthermore, as the space groups of the ordered ($P4/mmm$) and disordered structures ($Fm3m$) are different, additional effects will appear because of the change of symmetry. Thus, it is likely that there will be substantial differences between the spectral functions of the ordered and disordered states; see, for example, the analyses of the effects of order–disorder on the electronic structure in CuZn [3], AgZn [16], FeTi [17] and Pd_3Fe [18]. Since UPS and XPS from a polycrystalline sample *reflect* the density of states [19], given by

$$n(E, S) \propto \int_{BZ} A_B(k, E, S)\, dk$$

it is to be expected that these differences will be apparent in photoemission spectra. Indeed, such effects were observed over a decade ago in XPS studies of the effects of atomic order in α- and β-phase Ag–Cd alloys [20]. Thus, the smearing of the features we observe in curves b of figures 2 and 3 is due to disorder-broadening of the spectral function of the disordered alloy. However, the upper band edge remains sharply defined in both the ordered and disordered phases; the largest changes in the electronic structure appear not in the vicinity of the Fermi level but in the region of the Au d states. We speculate that the difference in the widths of the spectra in the different phases is due to two main factors. Firstly, there is a difference in symmetry

of the two phases and some degeneracies in the disordered FCC phase are lifted in the $L1_0$ (tetragonal) phase. Secondly, the volume of the unit cell of the ordered structure is $\sim 1\%$ less than that of the disordered structure [8, 21] and so the nearest neighbour bond lengths are greater in the latter. As a result, the valence bandwidth in the ordered phase is actually *greater* than that in the disordered phase.

We also measured the shift of the Au $4f_{7/2}$ core level on alloying in the ordered and disordered states. The shifts are 0.30 ± 0.05 eV and 0.22 ± 0.05 eV in CuAu I and Cu-50%Au, respectively, to increased binding energy. Thus, it appears that there is a small reduction between the ordered and disordered phases, as is the case for Cu_3Au [22], which we believe is due to the changes in the nearest neighbour environment of Au atoms. Although the precise mechanism of charge flow in Cu–Au is not clear [23], it would seem likely that there is more charge transfer per Au atom in the $L1_0$ structure since each Au atom has eight Cu neighbours (at a distance of 2.70 Å [8, 21]) whereas in the disordered FCC structure each Au atom has six Cu neighbours on average (at a distance of 2.74 Å [21]).

In summary, therefore, we find that there are considerable differences in the electronic structures of the valence bands in the ordered and disordered phases of an equi-atomic CuAu alloy. In particular, the largest changes occur in the region spanned by the Au-related d states. We note that this observation is consistent with the changes in the electronic structure in the ordered and disordered phases of Cu_3Au. In addition, we find that the valence bandwidth is greater in the ordered phase than in the disordered phase. We should point out that using AES we had previously found that there was no significant difference in surface composition between the ordered and disordered phases [1]. Thus, the changes we observe in the photoemission spectra are due to modifications in the electronic structure. In order to gain further insight into the electronic driving forces for the order–order and order–disorder transitions in equi-atomic CuAu, more detailed work is proposed; for example, k-resolved UV photoemission measurements and the appropriate, i.e., fully relativistic, band structure calculations for the different phases.

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