

## Measurements of 3*d* occupancy from Cu $L_{2,3}$ electron-energy-loss spectra of rapidly quenched CuZr, CuTi, CuPd, CuPt, and CuAu

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We used electron-energy-loss spectrometry to measure the intensities of the Cu white lines found at the onsets of the  $L_2$  and  $L_3$  absorption edges of rapidly quenched CuZr, CuTi, CuPd, CuPt, and CuAu. Enhancements of the white lines in the alloys as compared to elemental Cu were correlated with changes in the 3*d* occupancy of Cu atoms upon alloying. We found that the Cu atoms lost  $0.2 \pm 0.06$  *d* electrons when alloyed with Ti or Zr,  $0.0 \pm_{0.0}^{0.06}$  *d* electrons when alloyed with Au or Pd, and  $0.03 \pm_{0.03}^{0.06}$  *d* electrons when alloyed with Pt. We found no strong correlation between measured 3*d*-occupancy changes and heats of formation of the alloys, consistent with expectations that outer *s* electrons play an important role in the alloying of Cu with Pt, Pd, and Au.

Sharp peaks known as "white lines" are observed at the  $L_2$  and  $L_3$  absorption edges in the electron-energy-loss spectra (EELS) and x-ray-absorption spectra (XAS) of transition metals. These white lines originate from excitations of 2*p* core electrons to unoccupied *d* states about an atom.<sup>1,2</sup> While a number of EELS and XAS studies have investigated the ratios of the  $L_3$  and  $L_2$  white lines<sup>3-10</sup> other studies have attempted to relate the total intensities of the white lines to the occupancies of the corresponding outer *d* states.<sup>11-21</sup> Because of the limited spatial extent of the 2*p* electrons, such measurements sample the *d*-electron density near the core of the atom. In this paper we examine Cu 3*d* occupancies from EELS measurements for a number of rapidly quenched Cu alloys whose electronic structures have been of recent interest.<sup>20,21,22-32</sup> Changes in the 3*d* occupancies were determined by integrating the white lines above the Cu  $L_3$  and  $L_2$  absorption edges and using a correlation between white-line intensity and 3*d* occupancy reported previously.<sup>33</sup>

Alloys of CuZr, CuTi, CuPd, CuPt, and CuAu in 1:1 atomic proportions were prepared from elemental metals of at least 99.99% purity either by induction melting on a water-cooled silver hearth in an argon atmosphere or by arc melting on a water-cooled copper hearth in an argon atmosphere. The ingots were inverted and remelted several times to ensure homogeneity, and mass losses after melting were found to be negligible. Thin alloy foils were then prepared by quenching molten droplets of the alloys between Cu disks using an Edmund Buhler Ultra Rapid Quencher. X-ray powder-diffraction patterns of the rapidly quenched splats were measured with an INEL CPS 120 x-ray diffractometer using Co  $K\alpha$  radiation. The CuTi and CuZr alloys were found to be amorphous, and the CuPd, CuPt, and CuAu alloys were found to be disordered fcc.

Specimens for transmission electron microscopy (TEM) were prepared from the CuZr, CuTi, CuPd, and CuAu foils by electrochemical polishing with a Fishione twin-jet electropolisher. The CuPt specimen was prepared by dimpling with a VCR Dimpler followed by ion-milling in a VCR dual-gun argon ion mill. The chemical composi-

tions of the TEM specimens were measured with an EDAX 9900 energy-dispersive x-ray (EDX) analyzer attached to a Philips EM 430 TEM and were found to be stoichiometric to within the 5% uncertainty in the EDX analysis.

Electron-energy-loss spectra were obtained with a Gatan 666 parallel acquisition energy-loss spectrometer attached to a Philips EM 430 TEM operated at 200 kV in image mode at magnification of 3560 $\times$  to 5070 $\times$  with no objective aperture. A spectrometer collection aperture of 3 mm and a dispersion setting of 0.5 eV/channel were used. The spectra were positioned by placing the onsets of the  $L_3$  edges at 931 eV. No attempt was made to measure chemical shifts of the absorption edges due to alloying which are expected to be small (<1 eV). All spectra were examined for oxygen edges and samples were ion-milled briefly to remove surface oxides when necessary.

As the Gatan 666 spectrometer collects only 1024 channels of data simultaneously, the low-loss and core-loss spectra were acquired separately. In addition, these spectra required additional processing owing to the response and gain fluctuations of the linear photodiode array detector.<sup>34</sup> Ten spectra were collected for both the low-loss and core-loss regions, each shifted by three data channels from the previous spectrum. Each spectrum was then divided by the response function of the detector, determined by uniformly illuminating the photodiode array with no sample in place. The individual spectra were then realigned to a common feature in the spectrum and added. The core-loss spectra were then stripped of their pre-edge backgrounds and deconvoluted by the Fourier-ratio method to remove multiple inelastic-scattering effects.<sup>35</sup>

In previous work on the 3*d* transition metals,<sup>33</sup> it was shown that changes in normalized white-line intensities could be used to measure changes in the occupancies of the associated 3*d* states. The normalized white-line intensity was defined as the integrated intensity of the  $L_2$  and  $L_3$  white lines divided by the integrated intensity in a normalization window 50 eV in width beginning 50 eV past the  $L_3$  edge onset. When the normalized white-line intensities for the 3*d* metals were divided by appropriate

matrix-element factors, which were calculated for each atomic species and which included both white-line and normalization-window contributions, a linear correlation with  $3d$  occupancy was obtained with a fit given by

$$I'_{3d} = 10.8(1 - 0.10n_{3d}). \quad (1)$$

In Eq. (1),  $I'_{3d}$  is the normalized white-line intensity divided by the appropriate matrix-element factor, and  $n_{3d}$  is the  $3d$  occupancy in electron/atom. Note that for pure Cu, the  $3d$  states are full ( $n_{3d} = 10$ ), and no white lines are observed ( $I'_{3d} = 0$ ). More details may be obtained by consulting the original paper.<sup>33</sup>

Equation (1) provides a relatively straightforward procedure for estimating changes in  $3d$  occupancy upon alloying given an observed change in the normalized white-line intensity. One first evaluates the change in the normalized white-line intensity from the data and divides by the appropriate matrix-element factor from tabulated values,<sup>33</sup> yielding  $\Delta I'_{3d}$ . In the case of Cu, for example, the matrix-element factor is 0.172. Equation (1) then gives  $\Delta n_{3d} = (-1/1.08)\Delta I'_{3d}$ . The negative sign indicates that an enhancement of the white lines corresponds to a depletion of electrons from the  $3d$  states.

It has been pointed out that care should be taken to define the concept of  $d$  occupancy in the context of absorption spectra measurements.<sup>36,37</sup> Although dipole selection rules allow  $p$  electrons to couple to final states with both  $d$  and  $s$  character, the absorption to  $s$  states is usually negligible in comparison to the absorption to  $d$  states. In this context, therefore,  $d$  occupancy specifically refers to the number of electrons with  $d$  character.

Energy-loss spectra for the alloys are shown in Figs. 1–5. In each case an absorption spectrum from pure Cu (dotted line), which has no white lines, has been aligned at the  $L_3$  edge for reference. In order to use the spectra from pure Cu to isolate the white lines in the alloys, the spectra have been scaled such that their average intensities between 960 and 990 eV are unity. The spectrum obtained from amorphous CuZr in Fig. 1 exhibits enhanced white lines compared to pure Cu, indicating that some

electrons have left Cu  $3d$  states upon alloying. Similar enhancements are observed for CuTi in Fig. 2. Adding the intensity above the pure Cu spectrum from 931 to 936 eV and from 951 to 956 eV (shaded regions) and dividing by the integrated intensity in the normalization window from 981 to 1031 eV yields a normalized white-line intensity of 0.0382 for CuZr. Dividing by the matrix-element factor of 0.172 and using  $\Delta n_{3d} = (-1/1.08)\Delta I'_{3d}$  gives  $\Delta n_{3d} = -0.21 \approx -0.2$  electron/atom for CuZr. Thus the enhanced white lines in amorphous CuZr correspond to a depletion of about 0.2 electron/atom from  $3d$  states. Measurements from the white lines of CuTi yield  $\Delta n_{3d} = -0.19 \approx -0.2$  electron/atom. An estimate of the uncertainty in these measurements may be obtained by considering the extended energy-loss fine structure present in the Cu spectra past the  $L_2$  edge. While we have scaled the spectra to an average intensity of unity between 960 and 990 eV, other energy ranges or methods could be chosen, leading to different heights of the Cu reference spectrum and, therefore, to different values for the white-line intensities. Choosing an uncertainty of  $\pm 0.05$  (absolute intensity) in the scaling of the Cu reference spectrum due to fine-structure variations and integrating this uncertainty over the energy ranges of the white lines leads to an estimated uncertainty of  $\pm 0.06$  electron/atom in the final measurement. It is worth noting that the measured depletion of  $0.2 \pm 0.06$  electron/atom from Cu  $3d$  states upon alloying for CuZr compares favorably with local density-of-states calculations which predict a depletion of 0.31 electron/atom.<sup>30</sup>

Data obtained from disordered fcc CuAu, CuPd, and CuPt are shown in Figs. 3–5. There appears to be a slight enhancement of the white lines for CuPt and essentially no enhancement of the white lines for CuAu and CuPd. Measurements of the white lines for CuPt yield a depletion of  $0.03^{+0.06}_{-0.03}$  electron/atom from Cu  $3d$  states due to alloying. The lower uncertainty bound of 0.03 electron/atom reflects the fact that the maximum  $3d$  occupancy cannot exceed 10 electrons/atom. In addition, although a small white line is observed at the  $L_3$  edge for CuPt, almost none is observed at the  $L_2$  edge. This effect

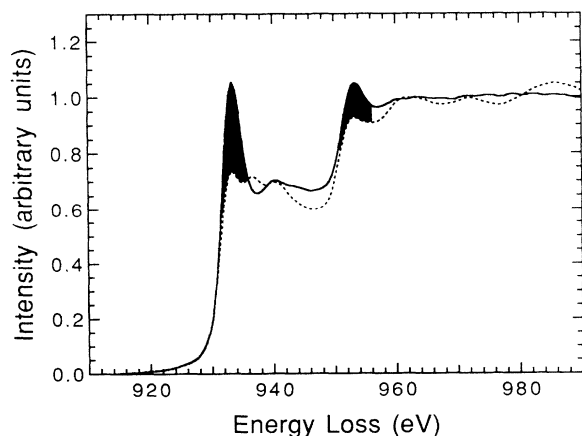


FIG. 1. Cu  $L_{2,3}$  absorption edge for amorphous CuZr and pure Cu (dotted line). Shaded regions correspond to a depletion of electrons from Cu  $3d$  states.

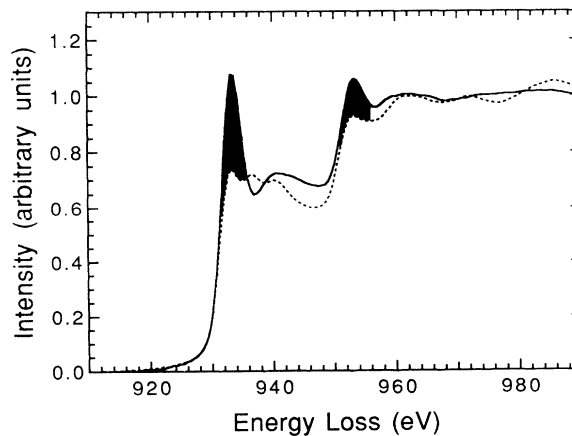


FIG. 2. Cu  $L_{2,3}$  absorption edge for amorphous CuTi and pure Cu (dotted line). Shaded regions correspond to a depletion of electrons from Cu  $3d$  states.

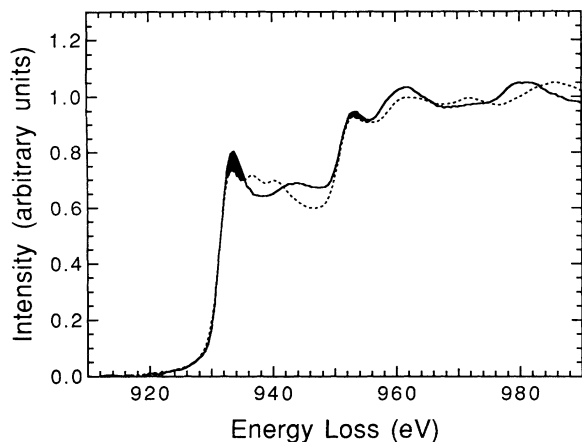


FIG. 3. Cu  $L_{2,3}$  absorption edge for disordered fcc CuPt and pure Cu (dotted line). Shaded regions correspond to a depletion of electrons from Cu  $3d$  states.

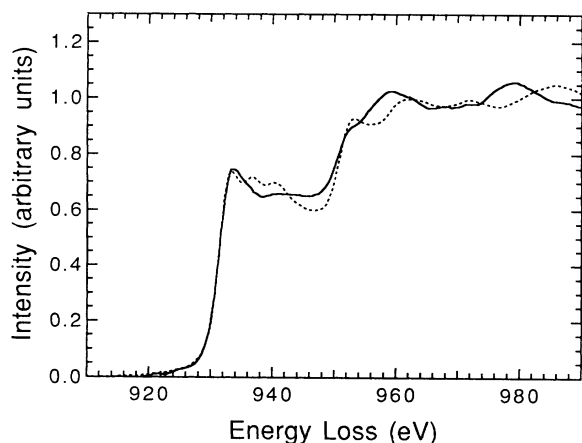


FIG. 4. Cu  $L_{2,3}$  absorption edge for disordered fcc CuAu and pure Cu (dotted line). No enhancement of the white lines is observed in the alloy.

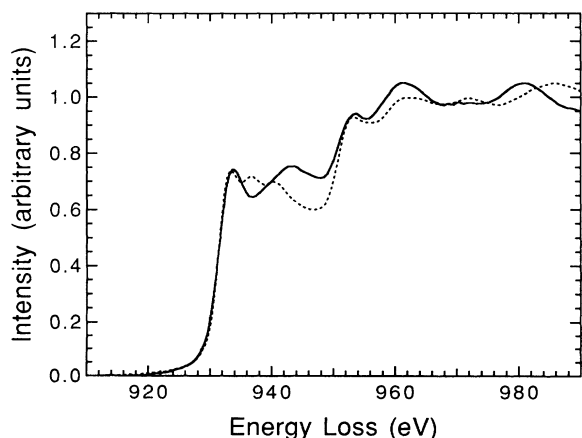


FIG. 5. Cu  $L_{2,3}$  absorption edge for disordered fcc CuPd and pure Cu (dotted line). No enhancement of the white lines is observed in the alloy.

may be an indication that the unoccupied  $3d$  states in CuPt mainly possess  $j = \frac{5}{2}$  character, as has been reported for pure Pt.<sup>17,18</sup> It is worthwhile to note that density-of-states calculations for CuAu (Ref. 31) and for disordered fcc CuPd (Ref. 32) show the  $3d$  states to be full, in agreement with the absence of white lines in these cases.

We also examined the heats of formation of these alloys in order to investigate any empirical relationships between the heats of formation and the changes in Cu  $3d$  occupancy. Pettifor's "rectangular  $d$ -band" model of alloying between transition metals, which combines the  $d$  bands of the constituent metals into a common  $d$  band for the alloy while ignoring  $s$ - $d$  hybridization effects, predicts that the amount of electron transfer from outer  $d$  states of one atom type to another should scale approximately with the heat of formation, although a strict proportionality is not expected.<sup>38-41</sup> The reported heats of formation of  $-2.2$  kcal/mol for CuZr,<sup>42</sup>  $-2.3$  kcal/mol for CuTi,<sup>42</sup>  $-1.6$  kcal/mol for CuPt,<sup>43</sup>  $-1.8$  kcal/mol for CuAu (Ref. 43) and  $-2.6$  kcal/mol for CuPd (Ref. 44) are clearly not proportional to the measured Cu  $3d$  depletions of 0.2 electron/atom for CuZr and CuTi, 0.03 electron/atom for CuPt, and 0.0 electron/atom for CuAu and CuPd. This observation is not surprising considering the role of the  $d$  electrons in these alloys. For alloying between late transition metals and early transition metals, such as in CuZr and CuTi, Pettifor's model assigns a substantial role to the outer  $d$  electrons due to the large differences between the  $d$ -band occupancies and band-center energies of the elemental metals and predicts relatively large  $d$ -electron transfers between constituent atoms and large heats of formation, in qualitative agreement with experiment.<sup>38-41</sup> For alloying of Cu with noble metals, such as Pd, Pt, and Au, the  $d$  bands of the elemental metals are nearly or completely full, and the Pettifor model is not a good description due to the neglect of  $s$ - $d$  hybridization and  $s$  charge transfer effects in such alloys.<sup>22</sup> Thus, although substantial heats of formation are observed in CuPd, CuPt, and CuAu, significant depletions of electrons from Cu  $3d$  states are not necessarily expected for these alloys. In addition, one might question whether the large depletions of electrons from Cu  $3d$  states in CuZr and CuTi are related to their amorphous structure as compared to CuPd, CuPt, and CuAu which are polycrystalline. In previous work we examined the effects of crystallization and ordering on white lines for several transition-metal alloys and found the effects to be less significant than those due to alloying.<sup>19</sup> Those results and theoretical implications as discussed above suggest that the large electron depletions from Cu  $3d$  states in CuZr and CuTi stem more from the fact that Zr and Ti lie at the left-hand sides of the  $3d$  and  $4d$  transition series, away from Cu, while Pd, Pt, and Au lie at the right-hand sides, near Cu.

In conclusion, we measured the intensities of the Cu  $L_{2,3}$  white lines in EELS spectra for rapidly quenched CuTi, CuZr, CuAu, CuPt, and CuPd. From these data we determined depletions in  $3d$  occupancy due to alloying of  $0.2 \pm 0.06$  electron/atom for CuZr and CuTi,  $0.03^{+0.06}_{-0.03}$  electron/atom for CuPt, and  $0.0^{+0.06}_{-0.0}$  electron/atom for CuAu and CuPd. In addition, we

found no correlation between measured  $3d$ -occupancy changes and heats of formation for these alloys, consistent with expectations that outer  $s$  electrons play an important role in the alloying of Cu with Pd, Pt, and Au.

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