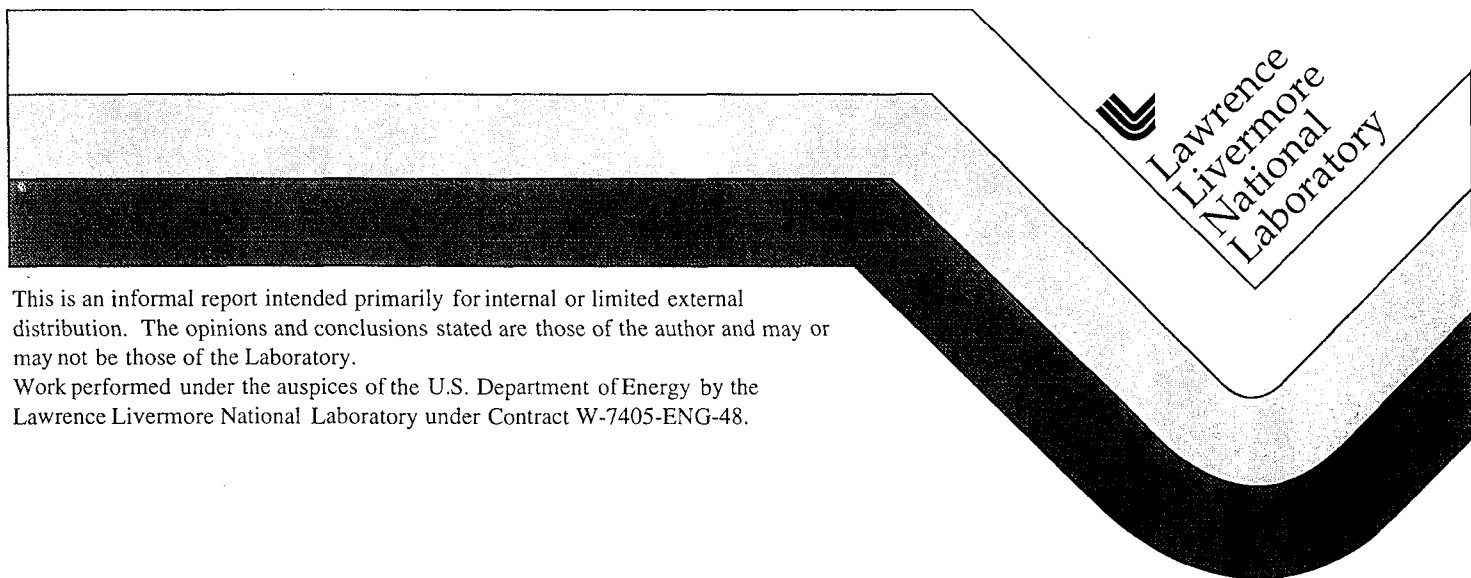


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A. F. Bello, T. Van Buuren, J. E. Klepeis, and T. W. Barbee, Jr.

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## ELECTRONIC EFFECTS AT INTERFACES IN Cu - Cr, Mo, W, Ta, Re MULTILAYERS

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### INTRODUCTION

In this study we characterize electronic effects in short-period ( $\approx 20$  Å) metallic multilayer films in which 40% of the atoms are at an interface using near-edge ( $L_{3,2}$ ) x-ray absorption. This study investigates Cu/TM where TM = Cr, Mo, W, Ta, Re. These immiscible elemental pairs are ideal to study as they form no compounds and exhibit terminal solid solubility. An interest in the charge transfer between elements in alloys and compounds has led to studies using x-ray absorption as described above. Near edge x-ray absorption fine structure (NEXAFS), a technique used for analyzing x-ray absorption near the absorption edge of the element, is especially suited to study the amount of unoccupied states in the conduction band of a metal. <sup>1</sup> The d-metals spectra show large peaks at the absorption edges called "white lines." These are due to the unoccupied d-states just above the Fermi level in these metals. A study <sup>2</sup> of the white lines in the 3d metals show that as the d-band is increasingly occupied the white lines decrease in intensity. Starting with Ti ( $3d^24s^2$ ), which has an almost empty d-band and shows strong white lines, the white-line intensities decrease across the Periodic Chart to Cu ( $3d^{10}4s^1$ ), which has a full d-band and no white lines. Systematic measurement of the  $L_{3,2}$  absorption spectra of bulk elemental Cu and Cu in the Cu/TM multilayers enabled measurement of the charge transfer.

NEXAFS on metallic multilayers has received less attention than alloys because of the difficulty in synthesizing multilayers with controllability up to the monolayer level and because there is little difference between the signal from the bulk and from longer period ( $> 30$  Å) multilayers <sup>3</sup>. For high-quality short period multilayers, however, the difference is clear. This is highlighted in a study of short period Co/Cu multilayers <sup>4</sup>, where the electronic density of states of Cu in Cu/Co greatly differed from that of bulk Cu. The difference was attributed to both charge transfer and band structure changes of the interface atoms. Short period Cu/Fe was the subject of another NEXAFS study <sup>4</sup>, where the signal from a periodic Cu(3 Å)/Fe(10 Å) multilayer was compared with that of a periodic Cu(10 Å)/Fe(3 Å) multilayer. The difference was attributed to the different structure of the Cu in each sample. Cu was BCC in one and was FCC in the other.

### EXPERIMENT

All films in our experiments were fabricated by dc magnetron sputtering. Base pressures were typically  $1 \times 10^{-7}$  torr, argon gas was used to sputter at a pressure of about  $2 \times 10^{-4}$  torr, and the sputtering power was set to around 300-400 watts. The set of samples, shown in Table I, are bilayers of Cu with another transition metal. In these samples, all layers were designed to have 5 monolayers (ML) each for a total period of about 21 Å. In Table I. each layer in the samples is composed of 5 ML of the constituent elements. For example, 5 ML of fcc Cu in the [111] direction is 10.435 Å. The total thickness of each sample is about 2000 Å. The bulk structure for the components are listed for reference, but the film layers may not necessarily have that structure. The charge transfer between the interfacial atoms are also listed, and will be discussed in the later sections.

Total Electron Yield (TEY) x-ray absorption experiments were conducted at Beamline 8-2 of the Stanford Synchrotron Radiation Laboratory (SSRL). In the range of 900 to 1100 eV, which is the region of interest for absorption in Cu, a resolution of 2000 was achieved. The experimental chamber vacuum was typically  $1 \times 10^{-9}$  torr. Samples were mounted so that the x rays were incident at  $45^\circ$ . A Au grid was placed in the incident x rays and its TEY signal was taken as proportional to the incident intensity. The TEY signal from both the sample and the Au grid were detected as current using a current amplifier. Data was acquired after annealing the sample to remove oxygen contamination on the surface. To anneal the sample, high current was passed through the film using Ta foil pressed against the outer edge of the sample. An optical pyrometer monitored the temperature, kept below 600 C to leave the film undamaged. In Table I. each layer in the samples is composed of 5 ML of the constituent elements. For example, 5 ML of fcc Cu in the [111] direction is 10.435 Å. The total thickness of each sample is about 2000 Å. The bulk structure for the components are listed for reference, but the film layers may not necessarily have that structure. The charge transfer between the interfacial atoms are also listed, and will be discussed in the later sections.

Table I. Bilayers of Cu With Other Transition Metals

Sample	bilayer thickness [Å]	bulk structure	Charge transferred from Cu atom (charge/interfacial atom)
Cu/Cu	10.435/10.435	fcc/fcc	
Cu/Cr	10.435/10.195	fcc/bcc	0.026
Cu/Mo	10.435/11.125	fcc/bcc	0.064
Cu/W	10.435/11.190	fcc/bcc	0.17
Cu/Ta	10.435/11.660	fcc/bcc	0.35
Cu/Re	10.435/11.145	fcc/hcp	0.23

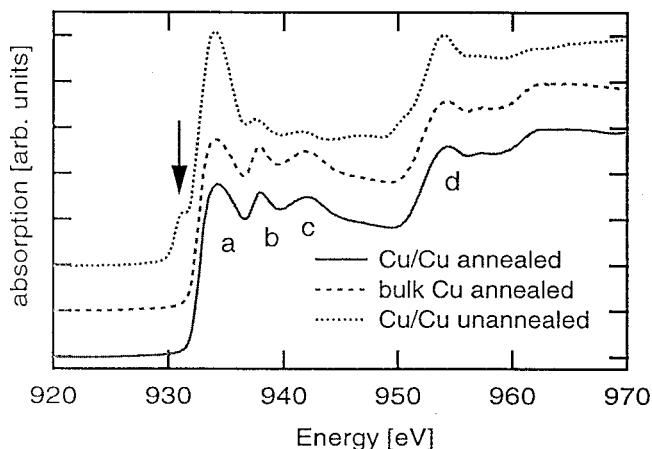


Figure 1. Absorption from the standards. The unannealed Cu<sub>5</sub>/Cu<sub>5</sub> multilayer show oxide phases — the shoulder at the absorption edge as denoted by the arrow, and the large peak relative to the annealed sample L<sub>3</sub> peak (a). An identical spectra between the annealed Cu<sub>5</sub>/Cu<sub>5</sub> and the annealed bulk Cu mean that the oxide from the multilayer has been completely removed at 300 C. The bulk sample was annealed to a high temperature of about 700 C to remove impurities, including oxides. The L<sub>2</sub> peak is labeled (d).

## RESULTS AND DISCUSSION

High-purity (99.999% pure) bulk Cu and a Cu<sub>5</sub>/Cu<sub>5</sub> multilayers sputtered from a 99.999% Cu target were used as L<sub>3,2</sub> Cu edge standards for pure copper. TEY is surface sensitive because of the short emission depth of photoelectrons in solids, so any oxide contamination of a sample surface is can drastically change the near-edge spectrum. Cu L<sub>3,2</sub> edge results from the standards were compared to published Cu oxide spectra.<sup>6</sup> CuO has a resonance peak at 931.3 eV; which is just below the Cu L<sub>3</sub> edge of 932.5 eV, and Cu<sub>2</sub>O has its absorption edge at 933.7 eV, which is just above the Cu L<sub>3</sub> edge. These experiments showed complete removal of the oxide phases from the bulk sample when it was annealed to a high temperature of roughly 700 C. The unannealed Cu<sub>5</sub>/Cu<sub>5</sub> clearly showed CuO contamination — the shoulder just before the absorption peak in Figure 1, which disappeared after annealing to a temperature higher than 300 C. Figure 1 shows the data for Cu<sub>5</sub>/Cu<sub>5</sub> before the anneal, after the anneal, and the annealed bulk Cu for comparison. An identical spectra from the high-temperature annealed bulk and the Cu<sub>5</sub>/Cu<sub>5</sub> mean that the oxide in Cu/Cu has been completely removed at about 300 C. Removal of the oxides is especially important since their signals are right at the L<sub>3</sub> Cu absorption edge, so their presence can lead to erroneous results in analyzing the near-edge absorption spectra. Figure 1 gives us confidence that on annealing the samples to 300C, the oxide phases vanish.

### Calculating the Charge Transfer from the White Lines

A method has been devised to calculate the charge transfer from the white lines. The basic idea is to fit the absorption spectrum by convolving a model of the unoccupied DOS with broadening functions. A complete model of the absorption spectra from the core level to the unoccupied states involve many factors. Ignoring some of these factors momentarily for a thought experiment, the absorption process is now examined. If there were no lifetime or instrumental broadening, no many-body (electrons) effects, and if the matrix elements were equal for all transitions, then the absorption spectra would equal the unoccupied DOS. A realistic model, however, must consider at least the largest of these effects. The lifetime and instrumental broadening are the two that are dominant in making the

spectra different from the unoccupied DOS. The broadening can be described by the Voigt function<sup>1</sup>, which is the convolution of a Gaussian (instrumental broadening) and a Lorentzian (lifetime broadening). To model the absorption, the Voigt function and the unoccupied DOS are convolved.

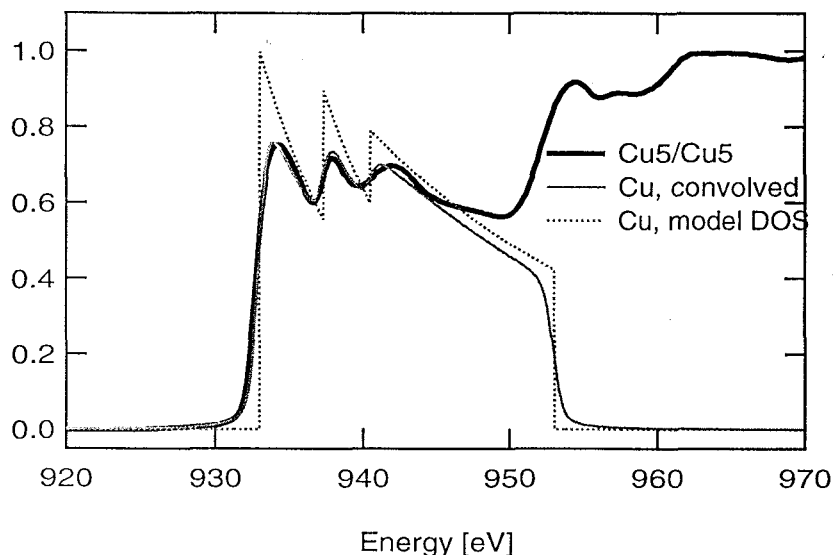


Figure 2. The Cu DOS is modeled by a set of exponentials, shown as the dotted curve. The model is convolved by the broadening function, shown by the thin curve, and a fit is made to the experiment data by optimizing the Cu DOS model.

To calculate the charge transfer, the unoccupied states are modeled as a series of exponentials because of the similarity between the DOS features past the Fermi energy and exponential functions. The dotted line in Figure 2 shows the example for Cu, where the first peak simulates the tail of the 3d- band, and the following two peaks correspond to the higher DOS at the Brillouin zone boundaries (van Hove singularities). Also in the figure is the convolution of the Voigt function with the modeled DOS, which is the thin solid line, and the x-ray absorption data, which is the thick solid line. The modeled unoccupied DOS is changed until a good fit between the absorption data and the convolved data is achieved. The excellent fit of the two curves in Figure 3 indicates that the modeled unoccupied DOS data fitting approach enables the development of an effective data analysis procedure.

The same procedure is followed for all the Cu/TM multilayers to obtain a quantitative measure of the unoccupied states in these multilayers: the results and experimental data for the series of Cu/X multilayer samples studied are shown in Figure 3. Again, the excellent fit between the convolved DOS and all the experimental data suggests that this data analysis procedure for the DOS is effective and can be generalized to other alloying and interfacial effects.

The Cu/Cr data shows a single peak between the  $L_2$  and  $L_3$  absorption edges, which is indicative of a BCC structure, contrary to the two peaks for Cu/Cu, which is indicative of FCC Cu. The single peak is due to higher DOS at the zone boundary of BCC Cu.<sup>5</sup> The prominence of this peak means that the BCC structure is very well defined and that the coherence of the BCC structure traverses over many periods in the sample. The rest of the samples show no such features.

Finally, the modeled DOS of Cu in the Cu/TM multilayers are compared to the modeled DOS of bulk Cu. Since the number of unoccupied states in bulk Cu is known, then direct normalization gives the amount of unoccupied states of Cu in the Cu/TM multilayers. Final results are in Table I, where the charge transferred is presented in units of electrons per interfacial atoms. The units allow these results to be related to interfaces in structures which contain bulk material and not limited dimensionality copper layers as studied here.

## DISCUSSION AND SUMMARY

The nature of the interactions at hetero-interfaces in bulk metals is an area of continuing scientific interest and technological importance. In many binary systems there are both well defined and not understood phenomena that are characteristic of hetero-interfaces in bulk metals. One of the least well understood areas is associated with electronic band structure effects. The binary material pairs studied here (Cu/TM) were specifically selected as examples of hetero-interface materials in which electronic band structure effects were expected to dominate the

hetero-interface interactions. This conclusion is based on the miscibility gaps in these binary systems, the terminal solubilities observed in the solid state of these binary systems and an unexpected wettability of the transition metals

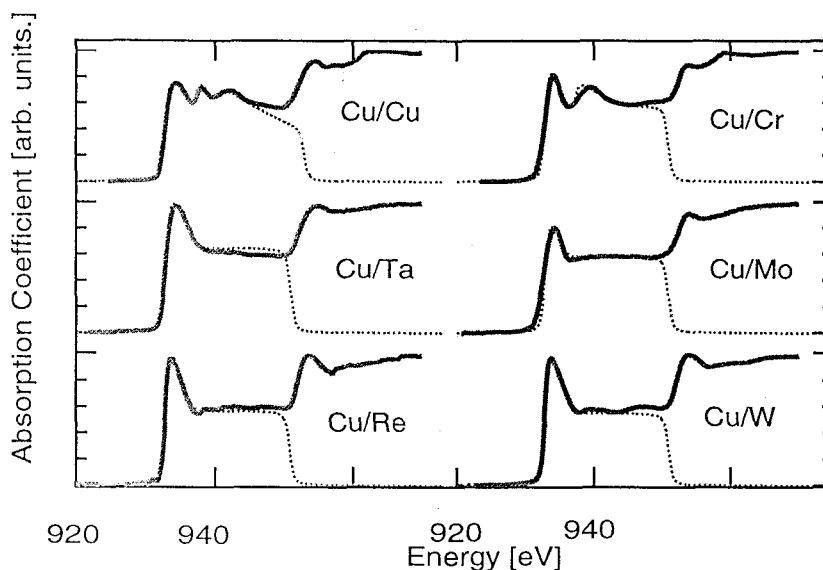


Figure 3. The absorption spectra and the fitted convolved data. Parameters for the modeled DOS are changed until there is a good fit of its convolution (with the broadening functions) to the x-ray absorption data.

and transition metal compounds by molten copper. There is also evidence that desorption energies of up to three monolayers of copper on a few of these transition metals are higher than the desorption energy/temperature of copper from copper. It is these general observations and the apparent localized nature of their causal effect which led to the conclusion that the hetero-interfacial interactions resulting in the decrease in the free energy of the interfaces between these dissimilar materials is electronic band structure based. It seemed most likely that the d state electrons at the Fermi level were strongly involved so that a study based on the determination of d state occupancy through quantitative measurements of the copper  $L_{3,2}$  "white line" intensities was undertaken. This study is reported here and shows that electron transfer at the hetero-interfaces in these Cu/TM multilayers does occur producing a dipole layer at the Cu/TM interface thus enhancing interfacial interactions and lowering the interfacial energy and the total energy of the multilayer system.

Charge transfer at hetero-interfaces between Cu and Cr, Mo, W, Ta and Re was quantitatively determined by fitting experimentally measured white line absorption resonance strengths on the  $L_{3,2}$  edges of Cu in multilayers with a phenomenological fitting model. These fitted curves could then be directly compared to a similarly fitted curve for bulk elemental Cu enabling increases in absorption and hence decreases in d band occupancy in the copper layers to be determined. In the L-edge XAS of bulk Cu metal, only weak white lines are observed since all the d-orbitals are filled. In the L-edge XAS of Cu in the Cu/TM multilayers, however, enhanced Cu white lines are observed. This is, as stated above, attributed to charge transfer from the interfacial Cu d-orbital to the transition metal layers. Analysis of the white line enhancement enables calculation of the charge transfer calculation from the Cu to the transition metal of about 0.03 electrons/interfacial Cu atom in Cu/Cr, 0.064 in Cu/Mo, 0.35 in Cu/Ta, 0.17 in Cu/W, and 0.23 in Cu/Re.

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