

## Empty and occupied electronic states of $\text{Cu}_x\text{Y}_{1-x}$ amorphous alloys as probed by inverse and direct photoemission spectroscopies

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The densities of the unoccupied states of  $\text{Cu}_{90}\text{Y}_{10}$  and  $\text{Cu}_{74}\text{Y}_{26}$  alloys have been probed by inverse photoemission in the ultraviolet range and compared with those of pure Cu and Y. This, along with direct photoemission spectra, allows for the determination of Cu  $3d$ - and Y  $4d$ -band energy positions and widths in the joint density of empty and occupied states. From these data an increase of empty  $d$ -like states along with a resulting decrease of empty  $sp$ -like states is revealed as well as a hybridization of the Cu  $3d$  and Y  $4d$  levels.

### INTRODUCTION

To describe the electronic structure of solids, it is necessary to investigate the density of states both below and above the Fermi level ( $E_F$ ). The density of occupied states of amorphous metallic alloys has been studied thoroughly, as reviewed by Oelhafen,<sup>1</sup> but experimental studies of unfilled states are still scarce.<sup>2-4</sup> Calculations of densities of such states are nevertheless available.<sup>5-10</sup>

The empty states play an essential role in excitation processes and in numerous physical properties, such as optical properties. Thus it is well justified to attempt to map them. We have previously presented photoemission results of  $\text{Cu}_x\text{Y}_{1-x}$  amorphous alloys, describing the occupied electronic states dominated by the Cu  $3d$  band.<sup>11</sup> The Y  $4d$  band was nearly empty and thus we are urged to probe the unoccupied electronic states. We present here the first inverse photoemission measurements on amorphous  $\text{Cu}_x\text{Y}_{1-x}$  alloys.

### EXPERIMENT

The inverse photoemission (IPE) spectra are obtained with an inverse photoemission spectrometer in the ultraviolet range.<sup>12</sup> This apparatus is connected to a photoelectron spectrometer (VG Esclab), operating at a residual gas pressure in the low  $10^{-9}$ -Pa range.

The samples are prepared as before<sup>11</sup> in a chamber attached to the spectrometer, by sputtering Cu-Y targets

with an  $\text{Ar}^+$ -ion gun operating at a voltage of 4 kV and a current of  $50 \mu\text{A}$ , onto a tantalum substrate. The films are transferred directly into the spectrometer without exposure to the atmosphere. X-ray photoelectron spectroscopy (XPS) studies have demonstrated the very high reactivity, mainly towards oxygen, of these alloys. A possible contamination is not easily located by IPE measurements, and thus the chemical analysis facility of XPS is used to determine the contamination free time of the samples. The cleanliness of the samples is also checked by ultraviolet photoelectron spectroscopy (UPS) which is even more sensitive to contamination; the O  $2p$  band appears around 6-eV binding energy and is well separated from the proper electronic structures of the alloys.

He II radiation is used for the UPS measurements at 40.8 eV. For the IPE measurements, the initial kinetic energy of the impinging electrons is 34.6 eV (with respect to the Fermi level of the sample). Under these conditions, the electron mean free path is nearly the same for both UPS and IPE experiments, and therefore, the analyzed depth as well. The IPE excitation current is estimated at  $300 \mu\text{A}/\text{cm}^2$ .

### RESULTS AND DISCUSSION

The inverse photoemission spectra of pure Y,  $\text{Cu}_{74}\text{Y}_{26}$ ,  $\text{Cu}_{90}\text{Y}_{10}$ ,  $\text{Y}_2\text{O}_3$ , and pure Cu are shown in Fig. 1. For the purpose of comparison of their shape, all spectra are nor-

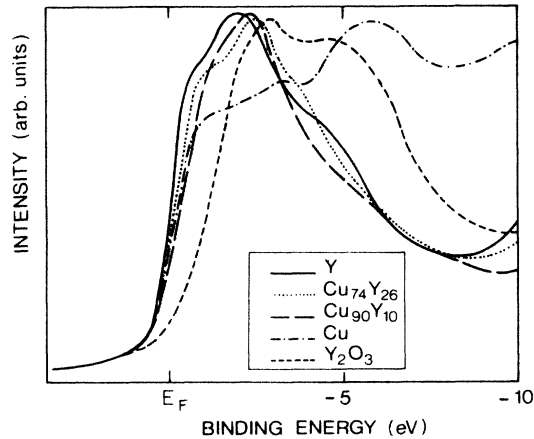


FIG. 1. Inverse photoemission measurements of  $\text{Cu}_{74}\text{Y}_{26}$ , and  $\text{Cu}_{90}\text{Y}_{10}$  amorphous alloys and of the pure constituents. The spectrum of  $\text{Y}_2\text{O}_3$  is added because Y is easily oxidized on the surface. Notice that all the spectra are normalized at their maximum height.

malized at their maximum height. Although the spectrum of Cu is similar to those reported previously,<sup>13,14</sup> by contrast the spectrum of Y differs from that of Speier *et al.*<sup>15</sup> In this latter experiment electrons up to 1486.6-eV kinetic energy were used. The main difference arises for the structure at 5 eV above  $E_F$ , which is more apparent in the spectrum of Speier *et al.*, and may be attributed to cross-section effects, as previously discussed for Ni and Pd.<sup>16,17</sup> The spectrum of  $\text{Y}_2\text{O}_3$  is shown to determine the spectral range influenced by the presence of an oxidation layer, which could distort the density of states (DOS) of the alloys.

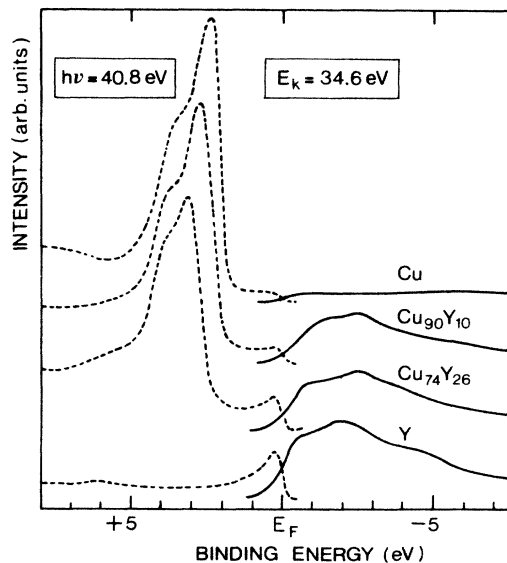


FIG. 2. Occupied and unoccupied electronic levels of two  $\text{Cu}_x\text{Y}_{1-x}$  amorphous alloys and of pure Cu and pure Y, matched with respect to the Fermi level. ( $E_k$  is the initial kinetic energy of the impinging electrons relative to the Fermi level of the sample.)

The alloys and pure Y have quite similar spectra. They are dominated by  $\text{Y } 4d$ -like states. However, a modification of the spectra can be seen as a function of the composition. The maximum located at 1.9 eV above  $E_F$  for pure Y is shifted away from  $E_F$  by about 0.5 eV in the alloys. Furthermore, the DOS at  $E_F$  [ $D(E_F)$ ] is smaller in the alloys than in pure Y, relative to the DOS at the maximum. The empty-band width is almost constant around 8 eV. In order to follow the gradual change of the width with concentration, the instrumental resolution, which is about 0.7 eV, can be neglected.

A general view of the DOS both below and above  $E_F$  is provided by Fig. 2, and the corresponding data summarized in Table I. Occupied and unoccupied states are matched at the Fermi level which is measured in both UPS and IPE experiments. We have used Cu to locate  $E_F$ . The steplike function of Cu at  $E_F$ , convoluted with the spectrometer response, puts the experimental Fermi level at the middle of the step for both UPS and IPE measurements. When the position of  $E_F$  is correctly determined, the matching of UPS and IPE spectra is realized with respect to the intensity at  $E_F$ . The relative DOS intensities of the alloys and their pure constituents are determined from their measurements by IPE. The IPE intensities are simply divided by the time and the current in order to be normalized.

The photoemission spectrum of  $\text{Cu}_{90}\text{Y}_{10}$  has not been reported previously. This spectrum closely follows the

TABLE I. Binding energy with respect to the Fermi level and total width in eV of  $d$  bands of pure Cu, pure Y, and  $\text{Cu}_x\text{Y}_{1-x}$  amorphous alloys with IPE emission intensity and area. The last row indicates the normalized area as calculated from the concentration of the alloys. An increase of the density of unoccupied  $d$  states is found in the IPE spectra of the alloys by comparing the last two rows.

	Cu	Y	$\text{Cu}_{74}\text{Y}_{26}$	$\text{Cu}_{90}\text{Y}_{10}$
$\epsilon_{\text{Cu } 3d}$ (eV)	3.0		3.5	3.2
Total width (eV) (UPS)	3.2		2.75	3.10
$\epsilon_{\text{Y } 4d}$ (eV)		-2.25	-2.60	-2.95
Total width (eV) (UPS & IPE)		10	9.5	9.0
Intensity normalized at the maximum of empty states	15	100	70	70
Normalized area of unoccupied band $A_{\text{Cu}_x\text{Y}_{1-x}}$	25	100	72	63
Weighted area				
$\frac{x A_{\text{Cu}} + (100-x) A_{\text{Y}}}{100}$	25	100	44	32

general trends observed for the other  $\text{Cu}_x\text{Y}_{1-x}$  alloys.<sup>11</sup> The copper 3*d* band shifts to higher binding energy with respect to pure Cu, the high-binding-energy side being located at the energy observed in the Y-rich alloys. On the other hand, as in the case of the other alloys, the low-binding-energy side of this band is not as steep as in pure Cu. This observation could be indicative of increasing *s-d* hybridization in this energy range.<sup>6,18</sup> Furthermore, the direct photoemission spectrum of  $\text{Cu}_{90}\text{Y}_{10}$  exhibits a higher density of states at the Fermi level, as well as between the Fermi level and the onset of the Cu 3*d*-like band, than in pure Cu. This shape cannot be explained by a simple superposition of the density of states of the pure constituents.

The total width of the Y 4*d*-like band shows a narrowing of less than 10% from Y to  $\text{Cu}_{90}\text{Y}_{10}$ . The width stays at about 10 eV, roughly divided between 8 eV in the empty states and 2 eV in the occupied states. The bandwidth is determined by both the number of Y-Y pairs, which decreases in the alloys, leading to a narrowing of the *d* band, and the number of Y-Cu interactions which tends to widen this band. The small observed *d*-band narrowing may then be related to strong interactions between Y and Cu states.

In the  $\text{Cu}_{90}\text{Y}_{10}$  amorphous alloy, as in the  $\text{Cu}_5\text{Y}$  crystal-line compound,<sup>19</sup> the Y atoms do not have Y nearest neighbors; therefore, our results for  $\text{Cu}_{90}\text{Y}_{10}$  can be compared with impurity-type calculations. Calculations for Y impurities embedded in an ordered Cu matrix<sup>20</sup> show a large hybridization between Y and Cu levels. The results of these calculations and our  $\text{Cu}_{90}\text{Y}_{10}$  measurements for empty states are in good agreement as far as the general shape and width are concerned (Fig. 3). A significant difference appears, however, at 4–5 eV above  $E_F$ . The resonance shown by the calculations, and indicated by an

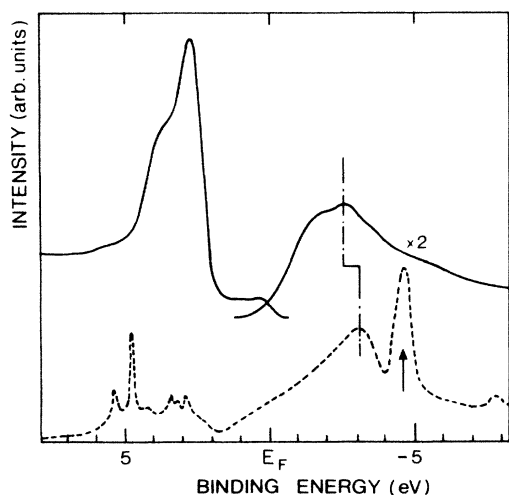


FIG. 3. Solid line represents the UPS and IPE measurements of the DOS of a  $\text{Cu}_{90}\text{Y}_{10}$  amorphous alloy. The dashed line shows calculated local DOS of Y impurities embedded in a Cu ordered matrix (courtesy of R. Zeller). The arrow indicates a structure which results from an interference between the Y empty states and the *L7* high-symmetry point of the Cu matrix.

arrow in Fig. 3, results from an interference of the virtual Y bound state with the Cu empty states at the *L7* high-symmetry point. The topological disorder of the amorphous alloys is expected to be responsible for the disappearance of this resonance.

An important quantity influencing a number of properties is the density of states at  $E_F$ ,  $D(E_F)$ . Apart from the fact that  $D(E_F)$  decreases relative to the intensity of the maximum of empty states, as observed in Fig. 1, we find in Fig. 2 an absolute decrease of  $D(E_F)$ , in agreement with calculations for Cu-Zr alloys<sup>8,9</sup> and Cu-Y alloys.<sup>21</sup>

Our measurements as a whole are therefore in favor of a hybridization between the Cu 3*d* and the Y 4*d* states; occupied Cu 3*d*-derived states must be present on Y sites, as shown by x-ray emission spectroscopy, on parent  $\text{Cu}_x\text{Zr}_{1-x}$  alloys,<sup>22</sup> and reciprocally we must find empty Y 4*d*-derived states on Cu sites. This is due to the fact that the centroid of the Y 4*d* band is located above  $E_F$  (Table I). A confirmation of this statement is given by appearance potential spectroscopy measurements,<sup>3</sup> which show *d*-like empty states on Cu sites in  $\text{Cu}_{60}\text{Zr}_{40}$  and  $\text{Cu}_{40}\text{Ti}_{60}$  amorphous alloys. More detailed information can be gained from the evaluation of the areas of the measured spectra of the empty density of states. As observed in Table I, the area measured for  $\text{Cu}_x\text{Y}_{1-x}$  alloys is greater than the value obtained by weighting the area of the pure metals, indicating an apparent excess of *d*-like empty states in the alloys. An increase of empty *d*-like states at the expense of empty *sp*-like states on the Cu sites (i.e., an intra-atomic electron transfer from *d* to *sp* states) may therefore explain this apparent excess. An unambiguous interpretation of our results necessitates a better knowledge of the *d* and *sp* IPE cross sections.

Previous XPS measurements<sup>11</sup> on the Cu 2*p*<sub>3/2</sub> core-level asymmetry in the same  $\text{Cu}_x\text{Y}_{1-x}$  alloys, have shown an increase in the asymmetry parameter when going from pure Cu to the alloys, suggesting an increase of the local DOS at  $E_F$  on the Cu sites. From the analysis of our IPE measurements, these states are expected to be *sp*-like.

## CONCLUSION

We have reported for the first time a direct picture of the density of empty states in metallic glasses, given by inverse photoemission.

In combination with previous photoemission measurements on the same alloys, these results allow for a realistic description of the electronic structure of noble-metal-early-transition-metal alloys.

These alloys cannot be viewed as split-band-limit alloys; on the contrary, strong interactions between the Cu 3*d* and Y 4*d* bands can be inferred from the following observations: (i) a smaller than expected variation of the Y *d*-band width by alloying, (ii) an excess of *d*-like empty states in the alloys, and (iii) the gradual change of the density of states at the Fermi level.

In the case of Cu-Y alloys, the interaction is particularly important because the difference between the bandwidth of pure Cu and Y, together with the difference between their atomic energy levels, are important.<sup>23</sup>

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