

An Auger electron spectroscopic investigation of the electron states of copper alloys

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MS received 28 July 1984

Abstract. L_3VV Auger transitions of copper alloys show a feature due to a band-like states, the shape and intensity of which depend on the composition. The energy separation between this feature and the $L_3M_{45}M_{45}$ peak increases progressively with Cu concentration.

Keywords. Auger transitions; electron states; copper alloy.

PACS No. 71·20; 79·20

1. Introduction

Unlike x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) has not been employed extensively to investigate electron states of metal alloys. AES should be specially useful in examining perturbations of the *d*-bands of transition metal alloys and to observe features due to band-like density of *d*-states. We have investigated several alloys of copper, both crystalline and glassy, and have obtained encouraging results.

2. Experimental

X-ray photoelectron spectra and x-ray induced Auger electron spectra were recorded using an ESCA 3 Mark II spectrometer (VG Scientific Ltd., UK), fitted with a sample preparation chamber, a gas handling manifold and Ar^+ etching facility (Rao *et al* 1979). The Au ($4f_{7/2}$) signal at 83·7 eV was used for energy calibration of the spectrometer.

Cu-Zr metglasses were prepared by rapid quenching from the melt (Sen *et al* 1984). Cu-Al and Cu-Mn alloys were prepared by induction melting under vacuum. Electron beam melting was employed for the Cu-Pd system and the remaining alloys were prepared in an induction furnace in argon atmosphere.

All the samples were first cleaned and polished mechanically before introduction into the vacuum (2×10^{-10} Torr) of the sample preparation chamber of the spectrometer. Subsequently, the samples were cleaned by scraping them *in situ* with a stainless steel file. Surface compositions of samples were determined by XPS. All the studies were carried out at room temperature (298K).

3. Results and discussion

In figure 1, we show the L_3VV region of Cu in Cu metal and glassy $Cu_{50}Zr_{50}$. The $L_3M_{45}M_{45}$ Auger structure appearing between 912 and 923 eV, clearly shows five distinct features (marked A, B, C, D and E) similar to those noticed by earlier workers (Antonides *et al* 1977). These features arise from quasi-atomic two-hole excitations in the d -level and double ionization processes. We have decomposed these multiplets in terms of five gaussian peaks by a least-squared-error procedure after subtracting the background. This analysis shows that the central intense peak (C) contributes 45% of the total intensity in Cu metal and 42–44% in the other alloys studied, with the exception of the two metglasses, $Cu_{50}Zr_{50}$ and $Cu_{30}Zr_{70}$, where the contribution of peak C is only 30–32%. The intensity of C increases up to 48% on depositing potassium on Cu metal. Such variations in the relative intensities of the component peaks suggest that the $L_3M_{45}M_{45}$ transition of Cu in these alloys involves band-like states. Besides the $L_3M_{45}M_{45}$ structure, figure 1 also shows a broad feature (F) between 924 and 930 eV. We assign this feature to the band part of the $L_3M_{45}M_{45}$ spectrum. This assignment finds support from the studies of Weightman and Andrews (1979) as well as of Sawatzky (1977).

We have investigated the F peak around 927 eV, assigned to band-like density of d -states convoluted with itself, in several crystalline alloys of Cu with Mn and Ni as well as in the metglasses with Zr and find that its shape and intensity change from alloy to alloy (see figure 2a). In Cu-Zr alloys, the feature becomes narrower with decreasing Cu concentration, suggesting an increased atomic impurity-like behaviour of Cu in the matrix of Zr. These changes are likely to arise from a narrowing of the Cu(3d) level due

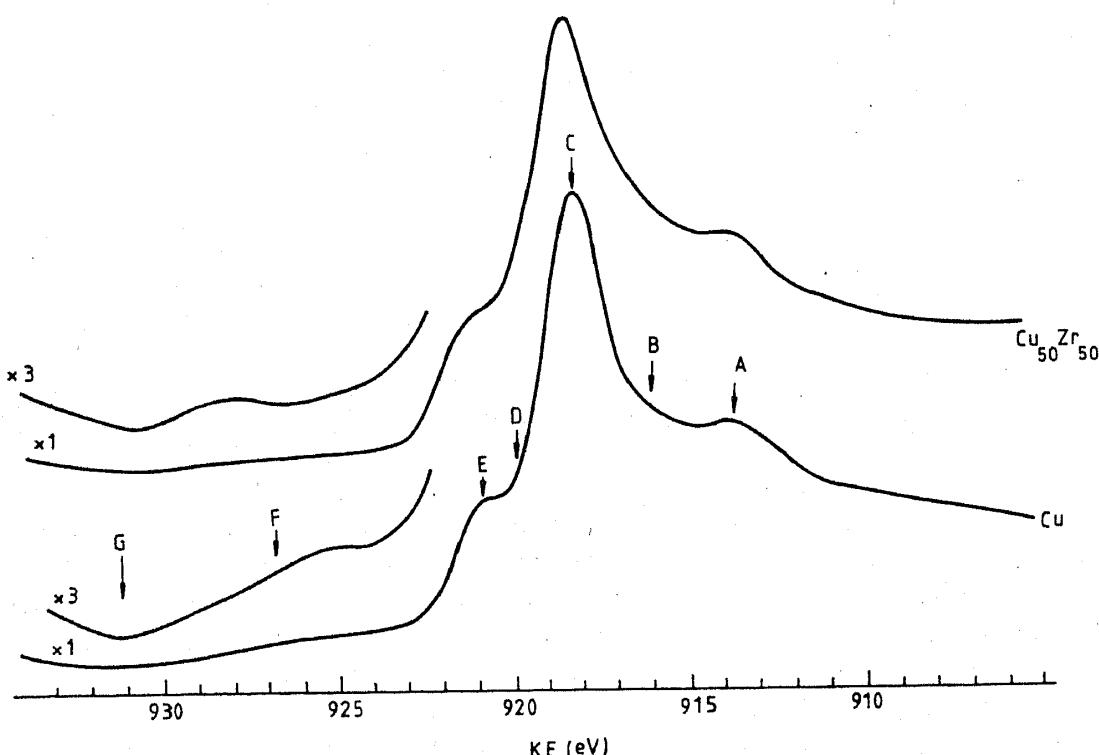


Figure 1. X-ray induced L_3VV ($L_3M_{45}M_{45}$) Auger spectra of Cu in Cu metal and $Cu_{50}Zr_{50}$ metglass. The high energy side of the signal has been expanded to show the band part of L_3VV transition.

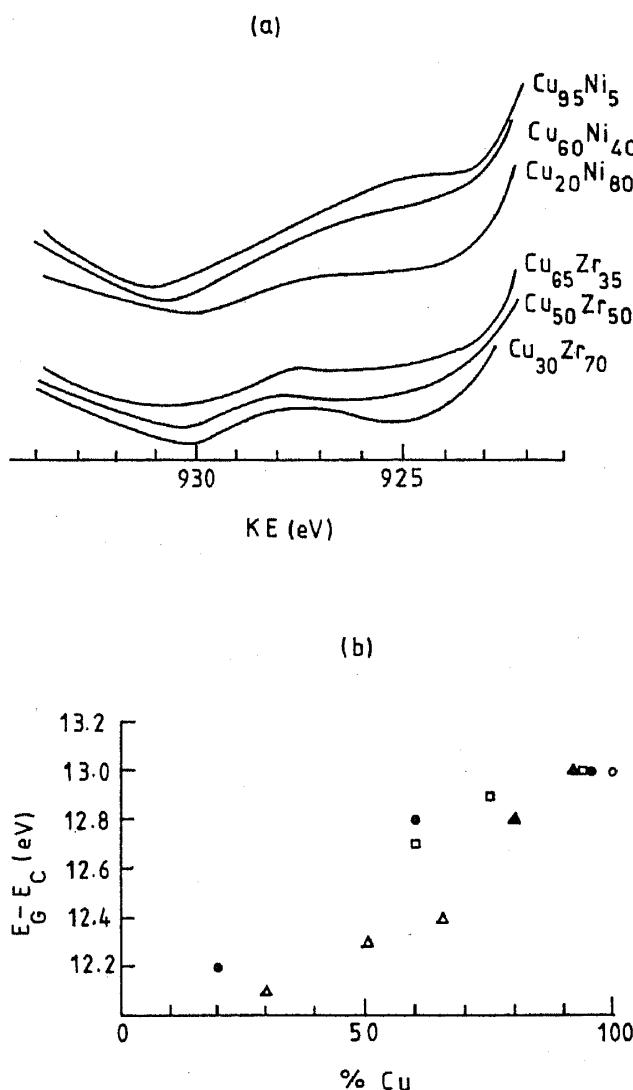


Figure 2. a) Band part of $\text{Cu}(\text{L}_3\text{VV})$ Auger transition in crystalline Cu-Ni alloys and Cu-Zr metglass. b) Plot of $E_G - E_C$ against atomic % of Cu in Cu alloys: Cu (open circles); Cu-Ni (full circles); Cu-Zr (open triangles); Cu-Al (full triangles) and Cu-Mn (open squares).

to increase in $3d$ - $4d$ overlap. In Cu-Ni alloys however, the intensity of the feature decreases with decreasing Cu concentration with no evidence of s -band localization. We have found similar changes in Cu-Al and Cu-Mn alloys.

In figure 1, we also see a dip (marked G) in intensity around 931 eV appearing between the rising parts of the band-derived $\text{L}_3\text{M}_{45}\text{M}_{45}$ feature (F) and the smoothly decaying part of the $\text{L}_2\text{M}_{45}\text{M}_{45}$ transition. We may point out here that G would have appeared at L_3 binding energy, had there been no decaying tail of the $\text{L}_2\text{M}_{45}\text{M}_{45}$ transition. The presence of the latter makes G appear as a dip and pushes it to lower kinetic energy, the magnitude of the energy shift depending on the intensity of the band part of the $\text{L}_3\text{M}_{45}\text{M}_{45}$ transition. The energy difference between G and the most intense peak C, $E_G - E_C$, decreases progressively with the decreasing Cu concentration irrespective of the alloy systems (figure 2b). It is noteworthy that the Cu-Zr system exhibits a more pronounced decrease in $E_G - E_C$ compared to other alloys. This is in accord with the fact that the Cu($3d$) signal in XPS shifts away from E_F when alloyed with Zr.

In Cu-Pd alloys, we find that the Pd($M_{45}N_{45}N_{45}$) transition energy shifts to lower kinetic energy by ~ 1.5 eV in going from Pd to $Cu_{92}Pd_8$ indicating an increase in the U_{eff} value for dilute Pd alloys. This observation suggests a narrowing of the Pd(4d) level on dilution.

Acknowledgement

The authors thank the DST, Government of India and the UGC for support.

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