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Electronic structure of ternary Y-Cu-Fe metallic glasses

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X-ray photoemission spectroscopy (XPS) measurements are reported on metallic glasses of the form $Y_{65}(Cu_{1-x}Fe_x)_{35}$. For $Y_{65}Cu_{35}$, the spectrum consists of two peaks: an intense, relatively sharp band at -2.8 eV corresponding to the Cu 3*d* band, and a weaker band near the Fermi level related to the Y 4*d* band. For $Y_{65}Fe_{35}$, a single broad feature is observed in the XPS spectrum at the Fermi edge that contains contributions from both the Fe 3*d* and Y 4*d* subbands. Separate Fe 3*d* and Cu 3*d* subbands are found in the intermediate compositions whose intensities but not positions change with the [Cu]/[Fe] ratio. Models for the electronic structure of these ternary metallic glasses are discussed.

INTRODUCTION

Previous measurements of the electronic structures of metallic glasses have concentrated primarily on binary alloys. In this work, the changes in the electronic density of states as the [Cu]/[Fe] ratio is varied in Y-Cu-Fe ternary alloys is investigated. This glassy system is particularly well suited to a study of this type since the Cu 3*d* and Fe 3*d* subbands are well separated and the Y 4*d* subband makes a small contribution to the valence-band states. Metallic glasses can easily be prepared in the form of $Y_{65}(Cu_{1-x}Fe_x)_{35}$ for all values of x. Cu and Fe have about the same metallic radii and in the context of a dense random packing of hard-spheres model (DRPHS) one would expect the glasses Y-Cu and Y-Fe to have similar atomic structures. Results of Mössbauer-effect experiments on the glasses of this study have been reported[1] and will be discussed in the context of the present electronic-structure measurements.

EXPERIMENTAL PROCEDURE AND RESULTS

Metallic glass alloys having the compositions $Y_{65}(Cu_{1-x}Fe_x)_{35}$ ($x = 0.0, 0.30, 0.50, 0.70, 1.00$) were prepared by the splat-cooling technique.[2] The sample preparation is the same as that described in Ref. 3. The x-ray photoemission spectroscopy (XPS) measurements on the metallic glass foils were performed using a Kratos XSAM 800 spectrometer. A Mg $K\alpha$ (1253.6-eV) anode was used as the excitation source operated at 300 W. The instrument resolution for valence-band data was 1.1 eV and for core-level data was 0.6 eV. The samples were mounted on stainless-steel pins using silver paste. The surface of each of the samples was sputtered using an argon-ion beam (25 $\mu A/cm^2$) to remove any metal oxides that had formed. The core levels of the components of the alloys were monitored to ensure that all of the oxide coating had been removed.

Figure 1 shows the valence-band spectra of the glasses of this study. At $x = 0.00$ ($Y_{65}Cu_{35}$) the spectrum consists of a single relatively sharp feature located at about -2.8 eV from the Fermi edge (E_F). This is the Cu 3*d* subband and it is clearly seen in all the samples except $x = 1.00$ ($Y_{65}Fe_{35}$). In the $x = 0.00$ spectrum, the states near 0 eV

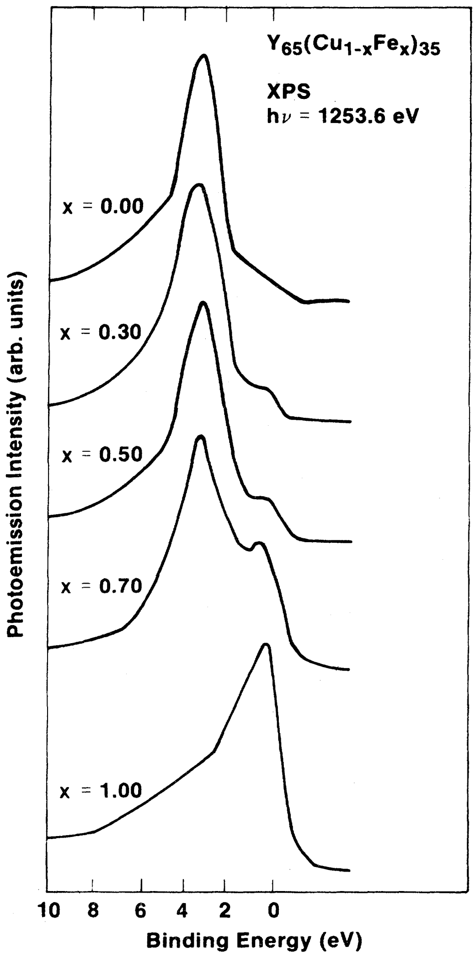

FIG. 1. X-ray photoemission spectra of $Y_{65}(Cu_{1-x}Fe_x)_{35}$ metallic glasses. The zero of energy is with respect to E_F.

TABLE I. Binding-energy positions of the Cu $3d$ subband in $Y_{65}(Cu_{1-x}Fe_x)_{35}$ metallic glasses. Values are relative to the Fermi energy ($E_F=0$).

x	Cu $3d$ (eV)
0.0	2.8
0.30	2.8
0.50	2.6
0.70	2.7

($E_F=0.0$) come primarily from the Y $4d$ subband. This contribution to the density of states is relatively small due to the fact that the Y $4d$ subband is almost empty (Y has nominally two $4d$ electrons). The replacement of Cu by Fe results in the appearance of a feature near the Fermi level that is associated with the Fe $3d$ subband. The increase in intensity of this subband is monotonic with increasing Fe concentration. Unlike the Cu $3d$ subband, the Fe $3d$ is not fully occupied and its centroid is located near E_F. As the $x=1.00$ spectrum shows, $D(0)$ is dominated by Fe $3d$ electronic states in $Y_{65}Fe_{35}$. For a given [Cu]/[Fe] ratio the contribution from the Cu $3d$ subband is enhanced due to its larger cross section (roughly a factor of 4 greater) for XPS compared to that of the Fe $3d$ subband.[4] This fact is responsible for the relatively small contribution the Fe $3d$ subband makes to the spectra of the Cu containing samples. The energy positions of the Cu $3d$ subband are listed in Table I for the various compositions. The position of this subband is independent of composition. The compositional dependence of the XPS, shown in Fig. 1, appears to result from a superposition of the end-point spectra ($Y_{65}Fe_{35}$ and $Y_{65}Cu_{35}$).

The results of the measurements of the core-level positions are listed in Table II. Similar to the Cu $3d$ subband position, these values appear to be independent of the [Cu]/[Fe] ratio. Also of interest are the differences between the respective core-level positions in the alloy and those of the pure metals [$\Delta E_B=E_B(\text{alloy})-E_B(\text{metal})$]. The values for the Y-Cu-Fe glasses are $\Delta E_B(Y)=0.0$, $\Delta E_B(Fe)=+0.17$, and $\Delta E_B(Cu)=+0.20$. These values are similar to those reported in Ref. 5 for $Zr_{76}Fe_{24}$ and $Zr_{70}Cu_{30}$ metallic glasses. The increase in binding energies of the core levels has been interpreted in Ref. 6 in terms of the heat of formation of the glassy alloys. A similar analysis is not attempted here due to the difficulty in locating the energy position of the centroids of the Y $4d$ and Fe $3d$ subbands. Similar to the results of core-level measurements on Zr-based glasses,[5] a change in the degree of asymmetry of the core lines is observed. The Fe core line is more symmetric in the alloy while the Cu core line is more asymmetric in the alloy compared to the pure metals. Oelhafen *et al.*[5] deduced from this behavior in the Zr-based glasses that the contribution to the electronic states at the Fermi energy [$D(0)$] was greater for the case of Fe in Fe metal compared to the alloy and smaller for Cu in Cu metal compared to the alloy. The same kind of reasoning appears to hold for the Y-based glasses of this study.

TABLE II. Core-level binding-energy positions observed in $Y_{65}(Cu_{1-x}Fe_x)_{35}$ metallic glasses.

x	Y $3d_{5/2}$ (eV)	Cu $2p_{3/2}$ (eV)	Fe $2p_{3/2}$ (eV)
0.0	155.8(2)	933.0(2)	
0.30	155.7	933.0	707.2(2)
0.70	155.8	933.0	707.3
1.00	155.7		707.3

DISCUSSION AND CONCLUSION

The first model to describe the electronic structure of crystalline transition-metal alloys (such as Cu-Ni) was the Mott and Jones rigid-band model.[7] This model describes the electronic structure of a transition-metal alloy as consisting of a common d band. Varying the composition of the alloy has the effect of shifting the Fermi energy to accommodate the proper number of valence electrons. The behavior of the $3d$ subbands of the Y-Cu-Fe glasses does not agree with that expected from a rigid-band model. Instead, the present results appear to be well described by a coherent-potential-approximation (CPA) method. In contrast to the rigid-band model, the CPA theory assumes that the charge exchange between the constituents of the alloy is small and that the electronic states of an ion are not significantly changed on going from the metal to an alloy.[8] CPA calculations have been very successfully applied in the past to crystalline alloys such as Cu-Ni.[8] In cases such as Cu-Ni, the CPA predictions and the experimental observations agree that the positions of the individual subbands do not change much with composition.[8] A CPA prediction for a Y-Cu-Fe alloy would involve three separate d subbands: Cu $3d$, Fe $3d$, and Y $4d$. The positions of these subbands would not change with a change in the [Cu]/[Fe] ratio. Although the subband positions do not change significantly in a CPA picture, the subband width and shape is expected to depend on composition. In Ref. 9, the subband widths of Zr-based metallic glasses were assumed to vary as the square root of composition. In the case of well-separated subbands this is the proper dependence.[8] In the alloys considered here, the Cu and Fe subbands strongly overlap and this simple behavior is not expected. A complete CPA calculation can resolve this matter, but the present considerations, it is sufficient to say that the width of the individual subbands should increase as the concentration of that element increases in the alloy. Experimentally, this is difficult to see in Fig. 1 due to the overlap of the Fe and Cu subbands and the finite resolution of the measurements. Concentrating on the Cu $3d$ subband, it does appear that it is increasing in width as the Cu content is increased in the glassy alloys. In summary, in the spirit of a CPA calculation, a qualitative description of the electronic structure of Y-Cu-Fe metallic glasses can be given. It consists of the three separate subbands whose intensities, shapes, and widths, but not positions, depend on composition. The experimentally observed XPS are in good agreement with this description.

From the results on the electronic structure of the Y-Cu-Fe glasses, it is possible to comment on their expected

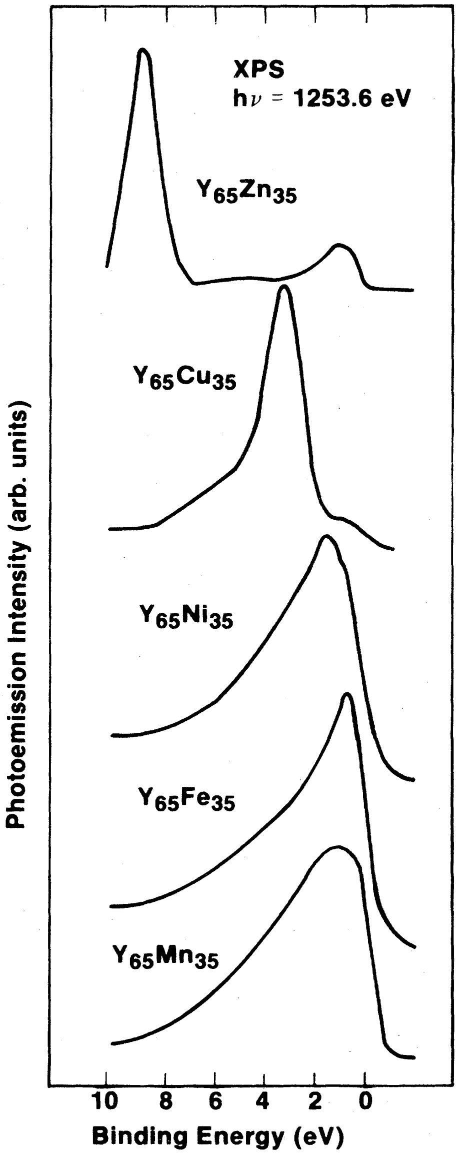

FIG. 2. X-ray photoemission spectra of $Y_{65}M_{35}$ metallic glasses.

magnetic and superconducting properties. Based on the analysis of superconductivity in Zr—transition-metal glasses, $Y_{65}Cu_{35}$ would seem to have too low a density of states at the Fermi energy $[D(0)]$ to have a superconducting transition temperature (T_c) above 1.2 K.[9] Comparing $Zr_{70}Cu_{30}$ $(T_c = 2.8\ \mathrm{K})$ to $Y_{65}Cu_{35}$, the common feature is that the states that constitute $D(0)$ come primarily from the Zr and Y $4d$ subbands. $D(0)$ is smaller for the Y case due to the greater bandwidth of Y (Ref. 10) and the smaller occupancy of the Y $4d$ subband. The T_c of the Zr $3d$ glasses was found to increase as states of the $3d$ transition-metal components began to overlap the Fermi level. For $Zr_{70}X_{30}$ (X=Co,Fe,Mn,Cr,V) a strong depression of T_c was observed that was attributed to the formation of localized magnetic moments and spin fluctuations. In the Y-Cu-Fe glasses of the present study, $D(0)$ does appear to increase as the [Cu]/[Fe] ratio is decreased. However, the increase in $D(0)$ comes from Fe $3d$ states which will also result in the formation of magnetic moments and thus will not lead to an increase of T_c in the alloys. The Fe $3d$ states retain their identity in the alloy and are prone to magnetic interactions. Whether an Fe atom forms a magnetic moment in the Y-Cu-Fe glasses and its magnitude depends on the details of its local environment in the glassy structure. From the present XPS measurements it is clear that the electronic states are positioned in a favorable manner for a magnetic moment to form.

It was mentioned in the Introduction that Mössbauer-effect measurements have been reported on the glasses of this study. These measurements indicated that $Y_{65}Cu_{35}$ and $Y_{65}Fe_{35}$ glasses are not isostructural, despite the similar metallic radii of Cu and Fe. Reference 1 summarizes the Mössbauer measurements and discusses the origin of this deduction. In this work it was found for $Y_{66}M_{34}$ glasses that M=Mn,Fe,Co,Ni glasses are similar in atomic structure while the structure in M=Cu,Zn glasses are different from the others. One of the key measurements of this work was that of the quadrupole splitting of Fe-doped glasses. The differences between the M=Mn,Fe,Co,Ni and M=Cu,Zn glasses were related to the importance of d-band binding in the M=Mn,Fe,Co,Ni glasses and the lack of it in the M=Cu,Zn glasses. Figure 2 shows the XPS of the Y-M glasses. The point to note here is that for M=Mn,Fe,Co,Ni, the $3d$ band is partially occupied, while for M=Cu and Zn it is full and separated from the states at the Fermi level. Thus, the XPS results provide support for the ideas of Ref. 1 concerning the differences in bonding for the Y-M glasses. This subject will be discussed in more detail in an upcoming report on the electronic structure of Y-M glasses.[11] Of importance for the present study is the possibility that the atomic structure of Y-Cu-Fe glasses is also a function of the [Cu]/[Fe] ratio. XPS measurements do not seem capable of detecting the subtle changes in atomic structure reported in the Mössbauer-effect measurements.

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