

## XANES and EXAFS in Cu-Ti and Ni-Zr glasses

K B GARG, K S JERATH, H S CHAUHAN, U CHANDRA,  
R K SINGHAL and K V R RAO

Department of Physics, University of Rajasthan, Jaipur 302 004, India

MS received 19 October 1987; revised 2 June 1988

**Abstract.** X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements have been done at the K-edge of Cu in Cu-Ti glasses and on the K-edges of Ni and Zr in Ni-Zr glasses using a synchrotron radiation source. The results are discussed in terms of the shape shift and intensity of the absorption edge as well as the principal absorption maximum. The values of bondlength calculated by the one-electron multiple scattering XANES theory as well as the graphical analysis EXAFS technique show good agreement.

**Keywords.** XANES; metal-metal glasses; bond distance; near-neighbour environment; synchrotron radiation.

PACS No. 78-70

### 1. Introduction

Interest in the physical properties of metallic amorphous alloys has been greatly stimulated by the wide range of their potential applications. Indeed, their mechanical, electrical and magnetic properties have remarkable features. These properties are linked to the electronic and structural arrangement and information concerning their structures in particular necessary to understand their characteristics. The information contained in a set of partial radial distribution functions is sufficient to express many bulk properties such as the equation of state and the chemical short range order, though the local structure of metallic glasses still gives rise to some controversy. One of the controversial points is the existence of chemical ordering similar to that in the crystalline state. Many techniques such as X-ray scattering (Chen *et al* 1982), neutron scattering (Nold *et al* 1981), electron scattering (Paasche *et al* 1982) and Mössbauer spectroscopy (Dubois and Le 1982) have been used to study the structure of these glasses. During the past few years the X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) techniques have been applied in the determination of the local structure of metallic and metal-metalloid glasses (Hayes *et al* 1978; Raoux *et al* 1981; Haensel *et al* 1981). The contribution of EXAFS is to show the asymmetry of the radial distribution function of some pairs of atoms. Furthermore, EXAFS can answer questions about the nature and extent of the short range order along with the extent of chemical ordering. On the other hand, XANES, being a microscopic probe, measures the local density of the unoccupied state of a particular symmetry and as a result of recent developments in the theory, it is now possible to exploit the region of the X-ray absorption spectrum around 50 eV of a K shell threshold

to provide structural information on the local atomic environment of the absorbing species (Durham *et al* 1981).

In this paper we present a XANES and EXAFS study of copper-titanium and nickel-zirconium glasses at their copper, nickel and zirconium edges respectively. The local chemistry of these glasses has been explained in terms of hybridization, edge shift and charge transfer. Bond lengths have been evaluated by the graphical analysis method (Lytle *et al* 1975) of EXAFS theory and the new multiple scattering approach (Bianconi *et al* 1983) for XANES calculation.

## 2. Experimental

Ribbons of metallic glasses ( $\sim 30\ \mu\text{m}$  thick) were gifted to us by Prof. G Hallam of Leeds University, UK and prepared by the melt spinning technique. These were thinned down to about  $\sim 10\ \mu\text{m}$  for measurements. In the Cu-Ti glasses the Cu percentage varied from 43–66% and in Ni-Zr glasses the Ni content varied from 24–34%. XANES and EXAFS measurements were performed at the K-edge of Cu in Cu-Ti glasses and at the K-edges of Ni and Zr in the Ni-Zr glasses at the EXAFS 5.1 station at Daresbury (UK) using the synchrotron radiation source operating at 1.8 GeV and 200 mA in the multibunch mode at a Si (220) channel-cut monochromator. Spectral resolution was better than 0.2 eV. All the spectra were recorded at room temperature.

## 3. Results and discussion

The spectra recorded after proper calibration and normalization to the main peak are shown in figures 1–4. Figure 1 shows the XANES part of the Cu K-edge in Cu-Ti glasses and Cu metal. Figure 2 shows the XANES part at the Ni and Zr K-edge in Ni-Zr glasses with their respective metals. Similarly figures 3 and 4 show their corresponding EXAFS region. Figures 5 and 6 show the  $n$  vs  $k$  plots of EXAFS at Cu K-edge in Cu-Ti glasses and at Ni and Zr K-edges in Ni-Zr glasses.

### 3.1 XANES

Figures 1 and 2 show that the edge structure in Cu-Ti glasses and Cu metal as also in Ni-Zr glasses and their corresponding metals looks almost similar. A clear kink observed midway in the spectra or at the end of the first rise of metal and glasses, loses its intensity in glasses indicating an increase in hybridization of the  $4p$  states with  $3d-4s$  states due to glass formation resulting in a decreased density of pure symmetric states. Similarly the clearly discernible decrease in the prominence of the kink (figure 2) in the Zr edge in Ni-Zr glasses may be due to decrease in the  $5s-5p$  hybridization. Although the first increase appears to be coincident in Cu-Ti and Ni-Zr glasses with their corresponding metals, the second and the main peak in the glasses shifts towards the lower energy region with respect to the metal. A small shift of about  $\sim 0.5\ \text{eV}$  is observed (table 1) in Cu-Ti and Ni-Zr glasses at the Cu and Ni edges with respect to metals. Results on Zr indicate an edge shift of  $\sim -2.0\ \text{eV}$  and a shift of about  $-12.5\ \text{eV}$  in glasses with respect to metals. The same order of chemical shift was reported by Garg *et al* (1988), Raoux *et al* (1980) and studies of dysprosium by Stern *et al* (1978) in  $\text{DyFe}_2$ .

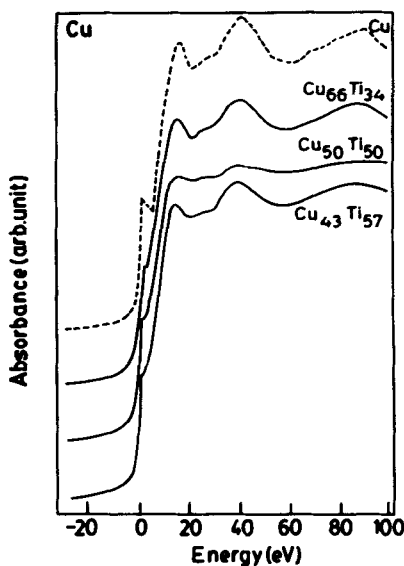


Figure 1. Cu K-XANES spectra from Cu foil and Cu-Ti glasses.

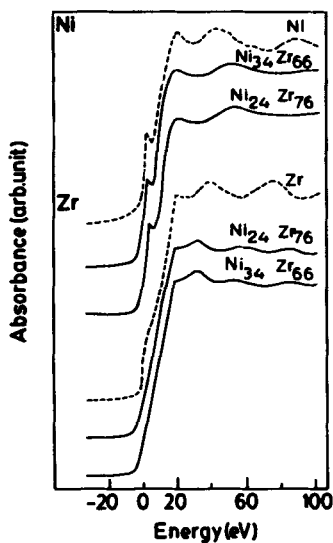


Figure 2. XANES spectra at the Ni and Zr K-absorption edges in Ni and Zr foil and Ni-Zr glasses.

It is also interesting to note (figures 1, 2 and table 1) that these shifts in Cu-Ti glasses increase with decrease in the Cu-content (or increasing Ti content) whereas in Ni-Zr glasses it decreases progressively with decreasing Ni content (or increasing Zr content) both in Ni and Zr spectra. The observed shifts to lower energies could be ascribed either to a charge transfer (Agarwal and Verma 1970) between the two components to the

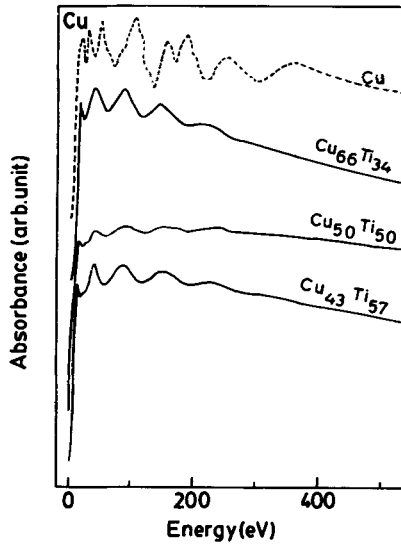


Figure 3. Cu K-EXAFS spectra from Cu foil and Cu-Zr glasses.

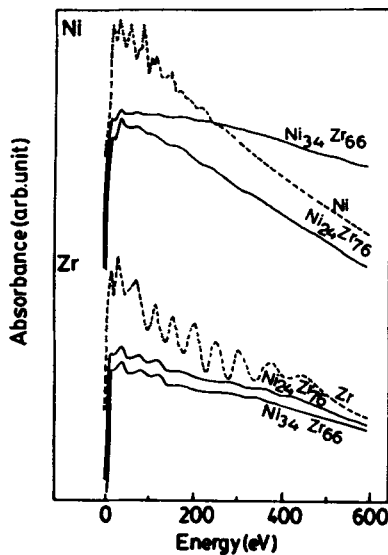


Figure 4. EXAFS spectra at the Ni and Zr K-absorption edges in Ni and Zr foil and Ni-Zr glasses.

changes in the near-neighbour distances (Garg *et al* 1986) or to the changes in effective radius of the atomic valence shell (Hageman *et al* 1974). It is difficult to attribute the shifts to any particular factor though a counter-balancing interplay in these effects appears to be the cause of such shifts. In the XANES at the Ni edge (figure 2), however, this could be explained by a charge transfer from the Zr 4*d* orbitals to the unfilled Ni 3*d* shell in the alloy (Visnov *et al* 1982). The shift in the first peak of Zr is too high and

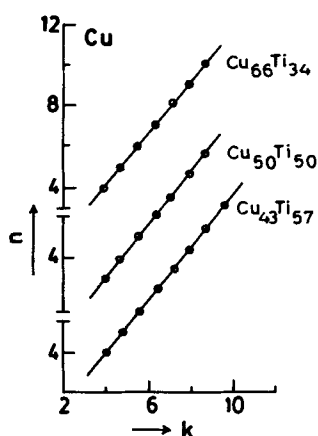


Figure 5.  $n$  vs  $k$  plots of EXAFS at Cu K edge in Cu-Ti glasses.

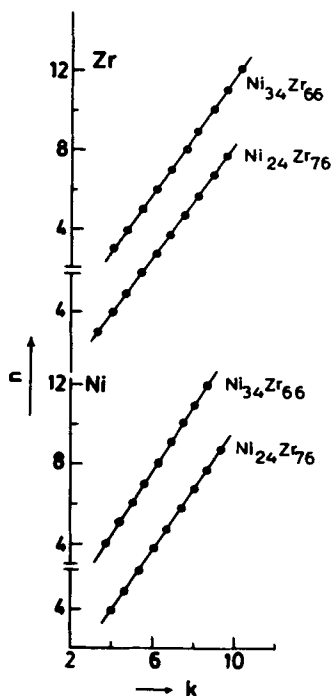


Figure 6.  $n$  vs  $k$  plots of EXAFS at Ni and Zr K-edge in Ni-Zr glasses.

probably due to changes in the near-neighbour environment of charge transfer though the mode and direction of this may not be easily envisaged (Garg *et al* 1986). Based on the above argument the shift in Cu-Ti glasses is more likely to arise due to charge transfer from Ti(3d) to Cu(3d), Cu being more electronegative.

Another important feature is the intensity of the main peaks in these glasses which varies with copper percentage. The intensity of the peak first appears to decrease

**Table 1.** Data on chemical shifts ( $\Delta E_F$ ), shift of the main peak ( $\Delta E_A$ ), the energy of the ejected photoelectron ( $E_r$ ), and the bond-distance ( $R$ ) in Cu-Ti and Ni-Zr glasses at the Cu, Ni and Zr edges respectively.

Sample	$\Delta E_F$ (eV)	$\Delta E_A$ (eV)	$E_r = E_A - E_F$ (eV)	$R(\text{XANES})$ (Å)	$R(\text{EXAFS})$ (Å)
Cu ( $E_F = 8971.54 \text{ eV}$ ; $E_A = 8987.01 \text{ eV}$ )				$\bar{V} = 72.60$	$\alpha = 0.48$
Cu66Ti34	-0.26	-0.24	15.49	2.53	2.53
Cu50Ti50	-0.46	-0.51	15.42	2.52	2.53
Cu43Ti57	-0.74	-1.51	14.70	2.51	2.50
Ni ( $E_F = 8331.2 \text{ eV}$ ; $E_A = 8349.5 \text{ eV}$ )				$\bar{V} = 84.89$	$\alpha = 0.15$
Ni34Zr66	-0.67	-1.21	17.76	2.60	2.63
Ni24Zr76	-0.47	-0.23	18.55	2.62	2.60
Zr ( $E_F = 17996.0 \text{ eV}$ ; $E_A = 18022.66 \text{ eV}$ )				$\bar{V} = -69.24$	$\alpha = 0.52$
Ni34Zr66	-2.91	-13.44	16.12	2.75	2.76
Ni24Zr76	-1.93	-12.79	15.79	2.75	2.78

(Cu66Ti34, Cu50Ti50) and then increases in (Cu43Ti57) (figure 1). Similar behaviour was observed by Garg *et al* (1988) in Cu-Zr glasses where multiple resonances get weakened with decrease in copper content attaining a minimum at 50% Cu and then again in strength with further decrease in the Cu content. This holds true for Cu-Ti glasses as Ti and Zr belong to the same group. This is also supported by photoemission data in which valence band structure nearly remains unchanged when the Zr atom was substituted by the Ti atom (Oelhafen *et al* 1980).

In figure 2 the main peak at the Ni and Zr edges in glasses seems to lose its intensity as the Ni and Zr percentage decreases though the change is not so drastic. Probably the charge transfer from Zr to Ni in Ni34Zr66 is less as compared to Ni24Zr76, hence the density of the unoccupied states at the Ni atom in Ni34Zr66 is greater than that in Ni24Zr76. This is also true of the main peak at Zr edge while going from Ni24Zr76 to Ni34Zr66.

Table 1 incorporates our quantitative measurements on the shift of Fermi level ( $\Delta E_F$ ), main peak ( $\Delta E_A$ ) in the glasses with respect to that in the metal, the energy of the ejected photoelectron ( $E_r = E_A - E_F$ ) and the bond length ( $R$ ) as calculated by the Bianconi's method (Bianconi *et al* 1983). In the case of Cu-Ti glasses the volume average potential ( $\bar{V}$ ) was calculated using the bond length ( $R$ ) and the photoelectron energy ( $E_r$ ) values in Cu<sub>2</sub>Ti (Raoux *et al* 1980) and Cu90Zr10 (Garg *et al* 1988). Due to absence of data for Cu-Ti glasses, Cu90Zr10 was used as a second reference material as Zr and Ti, belonging to the same group as discussed earlier, yield good values of bond length ( $R$ ) which are in accordance with bond length values evaluated by the EXAFS method (table 1). Similarly the bond length values were calculated for Ni and Zr in the case of Ni-Zr glasses using Ni33.3Zr66.7, Ni24.1Zr75.9 (Frahm *et al* 1984), Cu33Zr67 (Sadoc 1984) as standard reference materials.

### 3.2 EXAFS

Figures 3 and 4 show our EXAFS spectra in Cu-Ti and Ni-Zr glasses above K edges of Cu, Ni and Zr and the corresponding metal spectra for comparison. As can be seen

from these figures, the metal spectrum in each case displays a much more finer structure than the spectra of the corresponding glasses. The spectra appear to possess a sinewave form indicating how the first near-neighbour shell dominates in the back-scattering of the photoelectron wave which is mainly due to the amorphous nature of these samples. On the other hand, the EXAFS spectra of the metals have contributions coming from a number of near-neighbour shells owing to their high crystallinity and thus show a lot of fine structure. The interpeak separations along with the amplitude of the peaks were almost similar to each other in Cu-Ti as well as in Ni-Zr glasses. However, in the case of Cu<sub>50</sub>Ti<sub>50</sub> there was a slight reduction in the peak amplitude which rapidly dampened out at higher energies. This reduction in peak amplitude was partly due to the interference effect and partly due to the inherent structural disorder. Kobayashi and Takenchi (1982) reported similar results in Cu<sub>57</sub>Zr<sub>43</sub>. The Zr EXAFS in Ni<sub>34</sub>Zr<sub>66</sub> and Ni<sub>24</sub>Zr<sub>76</sub> looked virtually the same even though the Ni EXAFS in the same alloys did not resemble each other.

The Fourier transformation technique was not used because of certain limitations resulting from non gaussian pair distribution function for which an asymmetric distribution function has to be introduced. These limitations were discussed in the case of Cu-Zr and Fe-B glasses (Garg *et al* 1986, 1988). To overcome this we have used the graphic analysis method of EXAFS (Lytle *et al* 1975; Islam *et al* 1985) which would suffice for amorphous materials since the back-scattering was dominated by the first near-neighbour shell. The interpretation of the oscillating part term  $\sin [2Kr_j + \phi_f(k)]$  governs the analysis. Using this method a plot of  $n$  vs  $k$  was made where  $n = 0, 2, 4 \dots$  for EXAFS maxima and  $n = 1, 3, 5 \dots$  for EXAFS minima,  $K$  is the corresponding wave vector given by  $K = (0.263E)^{1/2}$ . Figures 5 and 6 show these plots and the slope  $m$  of  $n$  vs  $k$  is then related to bond length by

$$R - \alpha = m\pi/2,$$

" $\alpha$ " being constant is evaluated from the standard reference material. For Cu-Ti glasses the Cu<sub>2</sub>Ti amorphous material (Raux *et al* 1980) was employed as the standard reference material with Cu-Cu distance 2.53 Å. Similarly for Ni-Zr glasses Ni<sub>33</sub>Zr<sub>66</sub>·7 (Frahm *et al* 1984) with Ni-Ni distance 2.63 Å and Zr-Ni distance 2.76 Å were employed as the standard reference material. The bond distances thus calculated (table 1) show very good agreement with bond distances calculated by us using the XANES method and with those reported by others (Raoux *et al* 1980; Sadoc *et al* 1982).

#### 4. Conclusion

XANES and EXAFS features have yielded interesting results about the local atomic structure of glasses. XANES spectra provide qualitative information on the chemical interactions between the Cu and Ti and between Ni and Zr in these Cu-Ti and Ni-Zr glasses and also complement the structural data from the EXAFS region. The changes observed in their local chemistry have been explained in terms of hybridization, charge transfer and changes in near-neighbour environment. In these EXAFS region the broadened peaks in all glass spectra with respect to their corresponding metals are due to the inherent structural disorder. Along with this, the value of bond distances calculated by the XANES technique shows good agreement with values obtained by us from the EXAFS method as well as those obtained by other authors.

## Acknowledgements

One of us (KBG) thanks the Royal Society and the SERC (UK) and the DST (India) for financial assistance and D Norman for valuable assistance.

## References

- Agarwal B K and Verma L P 1970 *J. Phys.* **C3** 535
- Bianconi A, Dell'Araccia M, Gargano A and Natoli C R 1983 *EXAFS and near edge structure* (eds) A Bianconi, L Incoccia and S Stipcich (Berlin: Springer Verlag) p. 57
- Chen H S, Fujiwara T and Waseda Y 1982 *J. Mater. Sci.* **17** 1337
- Dubois J M and Le C G 1982 *J. Phys. (Paris)* **43** **C9** 67
- Durham P J, Pendry J B and Hodges C H 1981 *Solid State Commun.* **38** 159
- Durham P J, Pendry J B and Hodges C H 1982 *Comput. Phys. Commun.* **25** 193
- Frahm R, Haensel R and Rabe P 1984 *J. Phys.* **F14** 1029
- Garg K B, Jerath K S, Chauhan H S and Chandra U 1986 *Pramana – J. Phys.* **27** 821
- Garg K B, Jerath Kavita S, Chauhan H S and Chandra U 1988 *Indian J. Phys.* **A62** 107
- Haensel R, Rabe P, Tolkeihn G and Werner A 1981 *Proc. NATO Adv. Study Inst. liquid and amorphous materials* (eds) E Luscher and D Reedel (Dodrecht D. Reidel) 467
- Hageman H J, Gudat W and Kunj C 1974 *Solid State Commun.* **15** 655
- Hayes T M, Allen J W, Tauc J, Giesson B C and Hauser J J 1978 *Phys. Rev. Lett.* **40** 1282
- Islam M S, Deshpande A P, Mande C and Hovestreydt 1985 *Indian J. Phys.* **A59** 194
- Kobayashi S and Takenchi S 1982 *J. Phys.* **F12** 1273
- Lytte F W, Sayers D E and Stern E A 1975 *Phys. Rev.* **B11** 4825
- Nold E, Lamparter P, Olbrich H, Rainer-Harbach G and Steeb S 1981 *Z. Naturforsch.* **A36** 1932
- Oelhafen P, Hauser E and Guntherodt H J 1980 *Solid State Commun.* **35** 1017
- Paasche F, Olbrich H, Raener-Harbach G, Lamparter P and Steeb S 1982 *Z. Naturforsch.* **A37** 1215
- Raoux D, Sadoc J F, Lagarde P, Sadoc A and Fontaine A 1980 *J. Phys. (Paris)* **C8** 207
- Raoux D, Sadoc A, Lagarde P and Fontaine A 1981 *Proc. of the Daresbury study week on EXAFS for inorganic systems*, compiled by C D Garner and S S Hasnain
- Sadoc A 1984 *J. Non-cryst. Solids* **61, 62** 403
- Sadoc A, Flank A M, Raoux D and Lagarde P 1982 *J. Phys. (Paris)* **C9** 43
- Visnov R, Ducaslelle F and Treglia G 1982 *J. Phys.* **F12** 441