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A. Balzarotti, F. Comin, M. De Crescenzi, L. Incoccia, S. Mobilio
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EXAFS MEASUREMENTS ON Fe-B METALLIC GLASSES: ASYMMETRY OF THE RADIAL DISTRIBUTION FUNCTION.

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The EXAFS structure measured above the K-edge of Fe in the disordered Fe₈₀B₂₀ alloy is reported. Complete agreement is obtained with X-ray diffraction results in the position of the first neighbours coordination shell when the asymmetry of the Radial Distribution Function (R.D.F.) into the EXAFS formula is included. A Finney-like R.D.F. is used to describe the pair distribution of these metallic glasses. The weak temperature dependence of the spectra is discussed in terms of the structural properties of these amorphous alloys.

1.-Introduction

In the last few years a lot of experimental and theoretical work has been done on metallic glasses in order to understand their unusual electronic and structural properties /1/. It is well known that metallic glasses can be formed by several different atomic species whenever the alloying system shows a deep eutectic minimum in the phase diagram /2/. The series formed by a transition metal (as Fe, Ni, Cr,...) and a metalloid (as B, P, C,...) seems to be very promising for technical applications /3/.

The simplest atomic arrangement, which accounts for several mechanical and structural properties of these compounds, is the well-known D.R.P.H.S. (Dense Random Packing of Hard Spheres) model /4,5/. In this model the atoms, assumed like rigid spheres, are packed together in a cluster, dense because it does not contain voids large enough to accommodate another sphere and random because it lacks long range order. So far, the Radial Distribution Function (R.D.F.) - as obtained from this model - has been widely used to interpret X-ray and neutron diffraction data /6,7,8/.

More recently the EXAFS (Extended X-ray Absorption Fine Structure) technique has been applied to investigate the local disorder of these compounds /9,10,11/. The problems connected with the EXAFS analysis of disordered systems have been examined by Einsenberg and Brown /12/, who generalized the "classical" EXAFS formulation to take into account any asymmetry of the R.D.F.

In this communication we report on the EXAFS spectra of Fe₈₀B₂₀ taken at different temperatures. The main features of the spectra are:

- 1) the EXAFS amplitude changes only a few percent upon cooling the sample at 80 °K;
- 2) the nearest neighbours distance is 2.3 Å, in contrast with the value of 2.55 Å obtained by diffraction measurements /13/.

Both features are also found in a great variety of metal-metalloid glasses /9,14,15/. We show that 2) can be explained by assuming an asymmetric structural R.D.F. with a root mean square displacement, σ_D , about an order of magnitude greater than the thermal Debye-Waller factor σ_T .

2.-Experimental

The samples, in the form of a thin ribbon (Allied Chemical Metglas 2605), were reduced to about 10 μm in order to obtain the absorption spectrum around the Fe K-edge. The spectra were taken at the PULS facility at Frascati using the synchrotron radiation emitted by the ADONE storage ring. Details of the experimental apparatus have been published elsewhere /16/. Data were collected both at 300 $^{\circ}\text{K}$ and 80 $^{\circ}\text{K}$. The EXAFS signal was extracted from the absorption coefficient by subtracting a polynomial to remove the smooth atomic background /11/.

In Fig. 1 a) the oscillating part of the absorption coefficient, measured at $T=300$ $^{\circ}\text{K}$, together with its Fourier transform $F(R)$, is shown. $F(R)$ displays peaks up to about 5 \AA , suggesting an upper limit to the long range order in these alloys. The 80 $^{\circ}\text{K}$ spectrum is similar, and the amplitude of its $F(R)$ is only $\approx 10\%$ larger than the one at room temperature.

3.-Data Analysis

In the case of a gaussian pair distribution function, the EXAFS spectrum is given by a sum of contributions $\chi_j(k)$ from successive shells of atoms located at an average distance R_j from the absorbing atom /17, 18/:

$$\chi(k) \cdot k = \sum_j \frac{N_j A_j(k, \pi)}{R_j^2} e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda(k)} \sin(2kR_j + \phi_{\text{tot}}^j(k)). \quad (1)$$

Where N_j is the number of atoms in the j -th shell, σ_j^2 is their mean square displacement and $A_j(k, \pi)$ their backscattering amplitude. $\phi_{\text{tot}}^j(k)$ is the total phase shift for the considered atom pair and $\lambda(k)$ is the photoelectron k -dependent mean free path. Using eq. (1), we have calculated $\chi(k) \cdot k$ and its Fourier transform for the Fe-B and Fe-Fe first coordination shells. The theoretical phases and amplitudes of Teo and Lee /19/ and the bond lengths taken from X-ray diffraction data /13/ have been used. As can be seen from Fig. 1 b) the main peak of $F(R)$ is shifted of about 0.2 \AA towards higher R -values with respect to the experimental $F(R)$ of Fig. 1 a). In order to reproduce the experimental data, i.e. $\chi(k) \cdot k$ and $F(R)$, the following values for the distances $R_{\text{Fe-B}}^{\circ} = 2.05$ \AA , $R_{\text{Fe-Fe}}^{\circ} = 2.30$ \AA and an overall phase shift of $\pi/2$ over the whole k -range have been used. This result contrasts with diffraction data, density measurements and Teo and Lee's theoretical phase shifts.

The assumption of a symmetric pair distribution restricts the applicability of eq. (1) to systems having a high degree of crystalline order, but can lead to substantial errors in the determination of bond lengths in the case of anisotropic or disordered systems, as recently pointed out by Eisenberger and Brown /12/. They

have shown that, for arbitrary pair distributions, a more general formula holds:

$$\chi(k) \cdot k = A(k, \pi) e^{-2\sigma_T^2 k^2} \int_0^{\infty} \frac{e^{-2R/\lambda(k)}}{R^2} g(r) \sin(2kR + \phi_{\text{tot}}(k)) dR, \quad (2)$$

where the Debye-Waller term has been factorized since the thermal disorder is convoluted in R -space with the structural disorder /20/.

We have approximated the Finney's R.D.F. /22, 11/ with the following expression:

$$g(R) = \begin{cases} \frac{e^{-(R-R_j)/\sigma_D}}{\sigma_D} & \text{for } R \geq R_j \\ 0 & \text{for } R < R_j \end{cases} \quad (3)$$

By weighting R with the distribution $g(R)$ we get: $R = R_j + \sigma_D$, where $2R_j$ is the distance between the centres of two touching spheres. σ_D is the root mean square displacement giving the amount of structural disorder around each atomic site. This R. D. F. implies an overall phase shift correction to eq. (1) and an additional amplitude reduction term that, to the first order in $k^2 \sigma_D^2$, is $\exp(-2\sigma_D^2 k^2)$.

A fit to the experimental data using this generalized formula, Fig. 1 c), yields the following parameters:

$$R_j^{\text{Fe-B}} = 2.05 \text{ \AA} \quad R_j^{\text{Fe-Fe}} = 2.30 \text{ \AA}$$

$$\sigma_D^{\text{B}} = 0.25 \text{ \AA} \quad \sigma_D^{\text{Fe}} = 0.25 \text{ \AA}$$

Typical values of σ_T for crystalline bcc Fe /20/ are about an order of magnitude lower than σ_D for $\text{Fe}_{80}\text{B}_{20}$.

Should σ_T be in these amorphous alloys the same as in Fe, a 50% amplitude reduction of $\chi(k) \cdot k$ between 80 $^{\circ}\text{K}$ and 300 $^{\circ}\text{K}$ would result. Experimentally, only a 10-15% reduction is observed in this temperature range. This weak temperature dependence reflects the nearly constant thermal expansion coefficient /21/ of these compounds with respect to the crystalline metals.

The main implication of the R.D.F. of eq. (3) is that EXAFS responds to a frequency R_j in k -space rather than to R . The sharp rise at R_j in the R.D.F., which in k -space contributes at any k -value, will dominate on the exponential tail, which contributes at small k 's.

By inserting eq. (3) into eq. (2) and neglecting in the integral the R -dependence of the term $\exp(-2R/\lambda(k))/R^2$ we obtain:

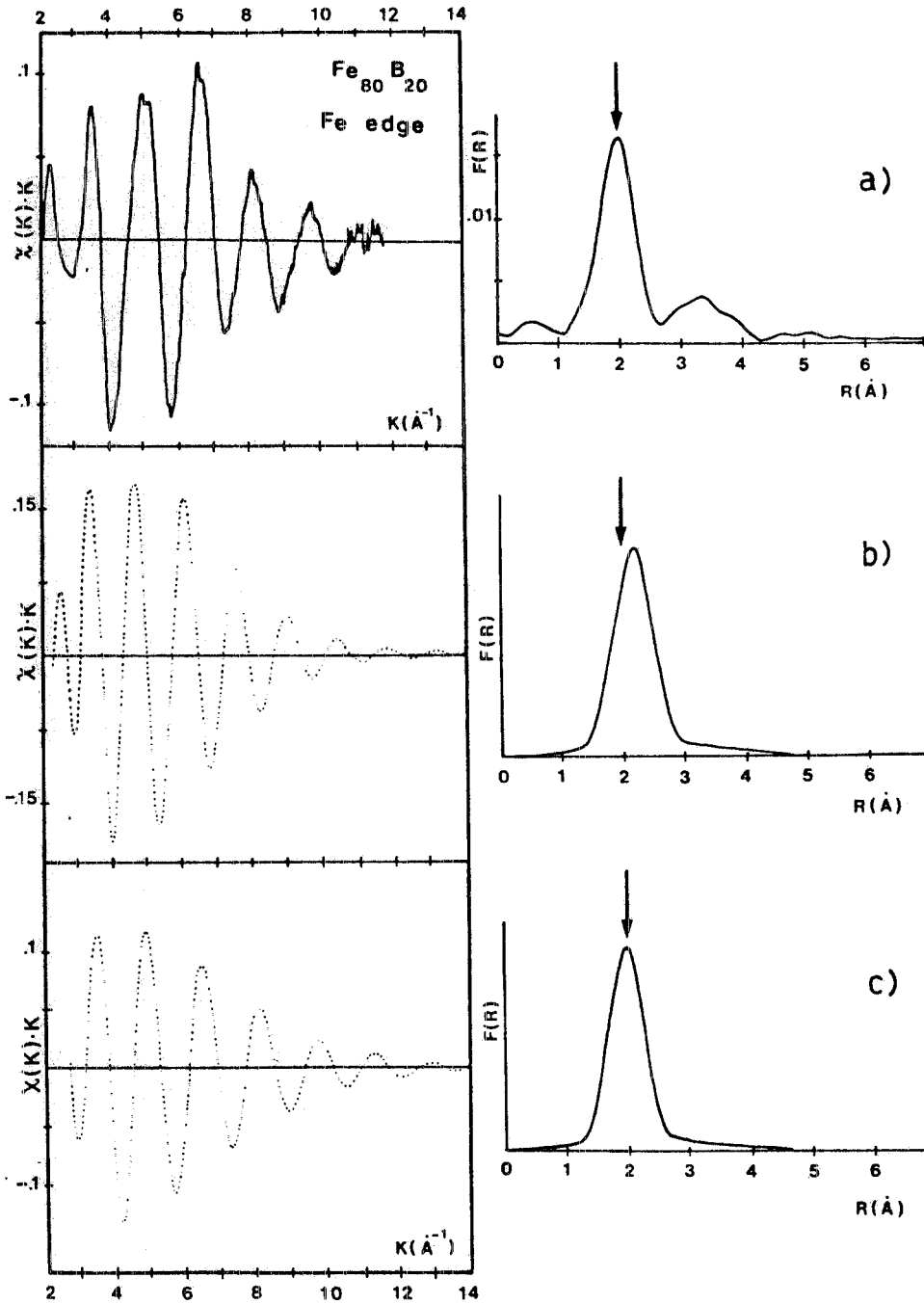


Fig.-1 a) $\chi(k) \cdot k$ of $\text{Fe}_{80}\text{B}_{20}$ above the Fe k-edge, and its Fourier transform $F(R)$. The peak value of $F(R)$ (nearest-neighbours distances from each Fe atom) occurs at 2.00 ± 0.02 Å and it is indicated by the arrow. b) $\chi(k) \cdot k$ and $F(R)$ computed using eq. (1) and assuming a gaussian R. D. F.. Amplitudes and phases are those of ref. /19/. Distances and coordination numbers are taken from X-ray diffraction data /13/. c) $\chi(k) \cdot k$ and $F(R)$ computed using eq. (2). The parameters are the same as in b) but the asymmetric pair distribution of eq. (3) is used.

$$X(k) \cdot k = A(k, \pi) \frac{e^{-2\sigma_D^2 k^2} e^{-2\bar{R}/\lambda(k)}}{\bar{R}^2} \frac{1}{\sqrt{1+4k^2\sigma_D^2}} \sin(2k\bar{R} + \phi_{\text{tot}}(k) + \Sigma(k)), \quad (4)$$

where:

$$\Sigma(k) = \arctg 2k\sigma_D - 2k\sigma_D. \quad (5)$$

In the limit of $\sigma_D \rightarrow 0$ eq. (4) reduces to eq. (1), since in this case one recovers a δ -like structural distribution function.

An interesting feature of our approximation is the understanding of the constant phase shift of $X(k) \cdot k$. As a matter of fact, in the k -range used for the Fourier transform ($3 \cdot 14 \text{ \AA}^{-1}$), the $\arctg 2k\sigma_D$ term in the total phase:

$$\Lambda(k) = \phi_{\text{tot}}(k) + 2k(\bar{R} - \sigma_D) + \arctg 2k\sigma_D \quad (6)$$

amounts to $\approx \pi/2$ and its k -dependence is negligible.

Accordingly, a constant phase shift of $\pi/2$ is required to fit the experimental $X(k) \cdot k$ spectrum with a gaussian R. D. F., as outlined above. It is also apparent from eq. (6) that, unlike X-ray diffraction which probes the average bond length \bar{R} , the EXAFS technique is sensitive to the frequency $R_j = \bar{R} - \sigma_D$.

In conclusion, we have shown that:

- a) a proper choice of the R. D. F. is crucial to understand the EXAFS spectra of metallic glasses, at least for transition metal-metalloid compounds;
- b) X-ray diffraction results have to be combined with EXAFS results in order to obtain a meaningful picture of the local ordering of these amorphous metals.

In principle the same approach should be used whenever an asymmetric R.D.F. is expected, as it is the case of liquids and solutions. A detailed analysis of the above model and its extension to other metal-metalloid alloys is in progress /23/.

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