A. Balzarotti, F. Comin, M. De Crescenzi, L. Incoccia, S. Mobilio and N. Motta: EXAFS MEASUREMENTS ON Fe-B METALLIC GLASSES: ASYMMETRY OF THE RADIAL DISTRIBUTION FUNCTION.
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 Fe_{80}B_{20} 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 in 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 accomodate 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 Eissenberger 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 Fe_{80}B_{20} 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 /9,18,15/. We show that 2) can be explained by assuming an asymmetric structural R.D.F. with a root mean square displacement, \sigma_1, about an order of magnitude greater than the thermal Debye-Waller factor \sigma^2.
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 °K and 80 °K. The EXAFS signal was extracted from the absorption coefficient by subtracting a polynomial to remove the smooth atomic background /17/.

In Fig. 1a the oscillating part of the absorption coefficient, measured at T = 300 °K, together with its Fourier transform P(R), is shown. P(R) displays peaks up to about 5 Å, suggesting an upper limit to the long range order in these alloys. The 80 °K spectrum is similar, and the amplitude of its P(R) is only 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 of the x(k) for successive shells of atoms located at an average distance R_j from the absorbing atom /17, 18/:

\[ X(k) = \sum_j \frac{N_j a_j(k) \sin(2\pi R_j e^{-\frac{1}{2} \sigma_j^2})}{R_j} e^{-\frac{2\pi R_j}{\lambda(k)}} \]

(1)

\[ X(k) \cdot k = A(k, \pi) e^{-\frac{2\pi^2 R^2}{\lambda(k)}} \]

(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:

\[ g(R) = \left\{ \begin{array}{ll}
    \frac{e^{-\frac{(R-R_j)^2}{2\sigma_j^2}}}{\sigma_j} & \text{for } R > R_j \\
    0 & \text{for } R < R_j
    \end{array} \right. \]

(3)

By weighting R with the distribution g(R) we get: R = R_j \cdot c_j, where 2R_j is the distance between the centers of two touching spheres. \( \sigma_j \) 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 \( k^2 \sigma_j^2 \), is exp(\(-2\sigma_j^2 k^2\)). A fit to the experimental data using this generalized formula, Fig. 1c), yields the following parameters:

- Fe-B: \( R_j = 2.05 \) Å, \( R_{Fe-Fe} = 2.30 \) Å
- \( \sigma_j = 0.25 \) Å, \( \sigma_{Fe-Fe} = 0.25 \) Å

Typical values of \( \sigma_j \) for crystalline bcc Fe /20/ are about an order of magnitude lower than \( \sigma_j \) for Fe-B /22/. However, Fe-B should have the same amorphous alloys, and the 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 \( \exp(-2R/k_j(k)) R/\lambda(k) \) we obtain:
Fig. 1 a) $X(k) \cdot k$ of Fe$_{80}$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) $X(k) \cdot k$ 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) $X(k) \cdot k$ 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.
\[ X(k) \cdot k = A(k, \pi) \frac{2a^2}{R^2} e^{-2 \pi k} / \Lambda(k) \cdot \frac{1}{\sqrt{1 + 4k^2 a_D^2}} \]

\[ \sin(2kR + \phi_{tot}(k) + \Sigma_k) \]

where:

\[ \Sigma_k = \arctg 2k a_D - 2k a_D. \]

In the limit of \( a_D \to 0 \) eq. (4) reduces to eq. (1), since in this case one recovers a 6-like structural distribution function.

A fascinating 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 \((3 \div 18 \text{ Å}^{-1})\), the \( \arctg 2k a_D \) term in the total phase:

\[ A(k) = \phi_{tot}(k) + 2k(R - a_D) + \arctg 2k a_D \]

amounts to \( \pi / 2 \) 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 \( R \), the EXAFS technique is sensitive to the frequency \( k = R - a_D \).

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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