ISTITUTO NAZIONALE DI FISICA NUCLEARE

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D. Bacci, A. Balzarotti, F. Comin, M. De Crescenzi,
L. Incoccia and S. Mobilio: EXAFS SPECTROSCOPY
OF AMORPHOUS Fe-Ni STEELS.

# EXAFS SPECTROSCOPY OF AMORPHOUS Fe-Ni STEELS.

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ABSTRACT. - We have investigated the local disorder of the $Fe_{80}B_{20}$ and $Fe_{40}Ni_{40}B_6P_{14}$ glasses. The asymmetric peak of $F(r)$ obtained from EXAFS (Extended X-Ray Absorption Fine Structure) studies is believed to be due to a sizeable backscattering contribution of the metal-metal pairs. The metal-metalloid arrangement cannot be definitely assigned using the EXAFS data alone. Near-edge K-absorption spectra support a strong hybridization involving the d-p bands of metal and B (or P).

## 1. - INTRODUCTION.

Amorphous metals $Fe_1-B_{1-x}$ and $Ni_1-P_{1-x}$ and their alloys have interesting metallurgical properties, such as low corrosion, high elasticity and low oxidation rate. Whether (and to what extent) these properties are determined by the lattice disorder has been the subject of a number of theoretical and experimental investigations[1].

The dense random packed-hard sphere model (DRPHS) originally proposed for the liquid state hes been applied to monoatomic amorphous and liquid transition metals and has provided a description of the radial distribution function (RDF) obtained from X-ray diffraction measurements (ref. (2,3)). This technique, when applied to Pd-Si glasses, gave rise to a splitting of the first peak of the RDF. Gaskell[4] developed an extended version of the DRPHS model and interpreted this separation as due to metal-metal and metal-metalloid coordination spheres. This splitting is not observed when Fe or Ni is alloyed with B or P[5, 6] probably because of the reduced ionic radius of the metal and/or of the low scattering factor of the metalloid.

The EXAFS technique has also been used to investigate the local environment of several binary glasses. In the case of the Pd-Ge[7] system convincing evidence was obtained that the chemical bonding of germanium with palladium is not substantially altered in the amorphous phase. This result does not fit a random packing model which requires approximately two nearest neighbours Ge atoms to palladium. The Fe-Ni metallic glasses and their alloys with B and P were studied by Wong et al.[8] by EXAFS. From their results it is not easy to discriminate between a random and a chemically ordered distribution of metalloid atoms around the metal. Some indications of a preferred P-Fe and B-Ni bonding is provided by the thermal behaviour of the RDF. Supplemental investigations are thus needed to elucidate the point. The present paper is concerned with measurements of both near-edge and EXAFS absorption for $Fe_{80}B_{20}$ and $Fe_{40}Ni_{40}B_6P_{14}$ metallic glasses. The observed asymmetry of the first peak of RDF in these compounds is compatible with a beating between two metallic scattering shells surrounding the excited metal atom (Fe or Ni). The metalloid shells may contribute to the weak satellites of the main peak in agreement with the DRPHS model.

## 2. - EXPERIMENTS AND RESULTS.

The samples in the form of thin ribbons obtained by the splat cooling technique were reduced to a final thickness of $\simeq 10\,\mu$ in order to achieve the best signal-to-noise ratio. The measurements were performed at the PULS X-ray facility using the ADONE storage ring of Frascati La boratory. Details of the experimental set up and data processing will be reported elsewhere[9]. Fig. 1 shows the K-edge absorption of the alloy $Fe_{40}Ni_{40}B_6P_{14}$. In the following we analyze this one as representative of data processing. The K-edges of Fe and Ni are sufficiently well separated to allow the EXAFS structure of both edges to be isolated with great accuracy. The structural information is contained in the reduced function $K \cdot \chi(K) = \left[ \mu(K) - \mu_0(K) \right] / \mu_0(K)$ which is plotted in Fig. 2 for Fe.
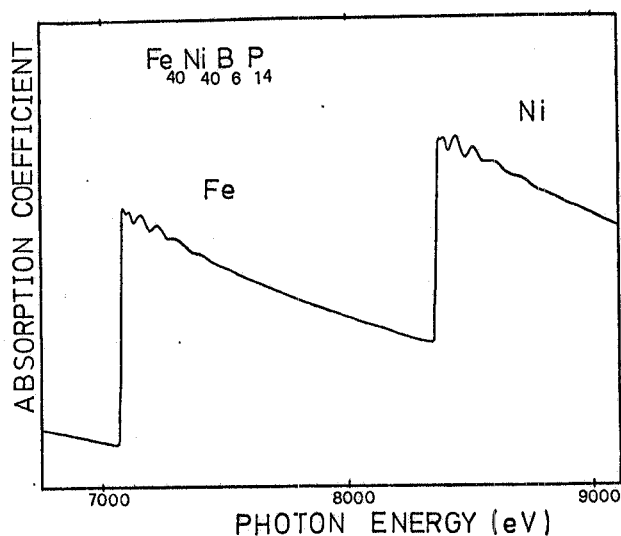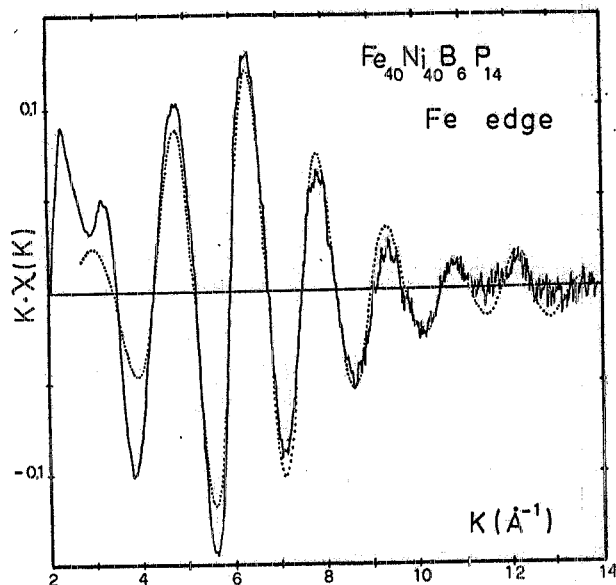
FIG. 1 - Absorption spectrum of $Fe_{40}Ni_{40}B_6P_{14}$.

FIG. 2 - $K \cdot \chi(K)$ for the $Fe_{40}Ni_{40}B_6P_{14}$; the dotted line is the backfourier transform of the first peak of $F(r)$.

$\mu_0(K)$ represents the monotonic atomic absorption of the isolated atom. The corresponding $F(r)$, as calculated by Fourier transforming $K \cdot \chi(K)$, are reported in Fig. 3. It is apparent that $F(r)$ consists of a large asymmetric peak centered at $2.00 \pm 0.02$ Å and of minor satellite structure lying between 3 and 4 Å. X-ray diffraction[10] measurements yield a value of 2.54 Å, which may imply a substantial phase shift correction for the metal-metal bond length. By inverting the RDF between 1.1 and 2.8 Å we have isolated the $\chi(K) \cdot K$ contribution of the first neighbouring shells. The envelope functions $\tilde{A}(K) \cdot K$, Fig. 4, for both Fe and Ni display minima at $K_{min} \simeq 11$ Å$^{-1}$
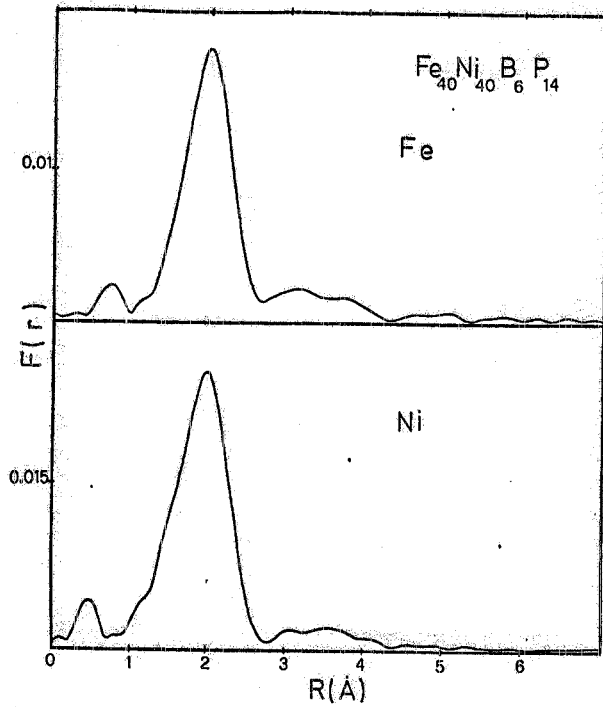
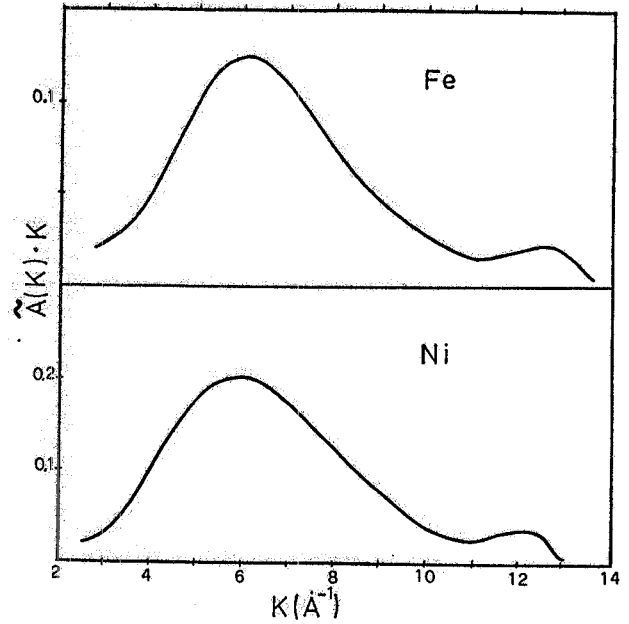FIG. 3 - Fourier transform F(r) for Fe and Ni in $Fe_{40}Ni_{40}B_6P_{14}$.

FIG. 4 - Backscattering amplitude obtained from the backfourier transform of the first peak of F(r) for Fe and Ni in $Fe_{40}Ni_{40}B_6P_{14}$.

which are characteristic of a beating process[11]. It can be readily shown[18] that the difference in the bond length of two inequivalent shells, $\Delta R$, is given by:

$$\Delta R = (n\pi - \Delta\Phi)/2K_{min} \qquad (1)$$

where $\Delta\Phi = \Phi_1 - \Phi_2$ is the corresponding total phase difference of the beating neighbours. By inserting the theoretical backscattering phases calculated by Teo and Lee[12], the $\Delta R$'s appropriate to two different atom pairs are calculated and listed in Table I.

TABLE I

| $Fe_{80}B_{20}$ | $Fe_{40}Ni_{40}B_6P_{14}$ | |
|---|---|---|
| | Fe edge | Ni edge |
| $\Delta R_{Fe-B} = 0.43$ Å | $\Delta R_{Fe-B} = 0.44$ Å | $\Delta R_{Ni-B} = 0.46$ Å |
| $\Delta R_{Fe-Fe} = 0.15$ Å | $\Delta R_{Fe-P} = 0.27$ Å | $\Delta R_{Ni-P} = 0.29$ Å |
| | $\Delta R_{Fe-Ni} = 0.12$ Å | $\Delta R_{Ni-Fe} = 0.15$ Å |
| | $\Delta R_{Fe-Fe} = 0.14$ Å | $\Delta R_{Ni-Ni} = 0.13$ Å |

Combining X-ray and neutron scattering measurements in Ni-P and Co-P alloys, Sadoc and Dixmier[13] found a Co-P distance of 0.23 Å. From these data Polk and Boudreaux[14] estimated a Ni-P first neighbours distance of 0.29 Å. These results support the DRPHS structure of Polk, made up by placing the P in the voids of a dense random packing arrangement of metal atoms.

Our $\Delta R_{Ni-P}$ and $\Delta R_{Fe-P}$ bond lengths (Tab. I) are not too different from the above values. Furthermore $\Delta R_{Fe-B}$ and $\Delta R_{Ni-B}$ agree rather well with the Fe-C average distance determined in crystalline $Fe_3C$[15] where the C atoms are known to be the nearest neighbours to Fe. A metal-metalloid beating is, however, unlikely since the weighted backscattering amplitude of the light components vanishes at large K. Indeed, a direct model calculation of $\chi(K) \cdot K$ based on theoretical phases[12] and averaged coordination spheres is capable of reproducing a beating for the metal-metal pairs only. Hence, in this case it is difficult to construct the definite structural model for the Fe atom first sphere using EXAFS information, at least within the limits of the present analysis. The doublet appearing at 3.15 and 3.75 Å for Fe and less clearly for Ni has been repeatedly reported for amorphous metallic alloys using diffraction methods[10]. The interpretation based on the DRPHS model for hard spheres gives an average doublet splitting of $0.65 \pm 0.05$ Å for the $Fe_{40}Ni_{40}B_{20}$ and $Fe_{40}Ni_{40}P_{20}$ alloys[8]. Our value of $0.60 \pm 0.05$ Å for $Fe_{40}Ni_{40}B_6P_{14}$ agree well with the above estimates.

Figs. 5 and 6 shows the K absorption edge fine structure for the amorphous alloys compared with that for crystalline Fe. It is evident that the addition of B or P causes a strong reduction in intensity of the first peak at the edge. This intensity reduction may be attributed to a charge transfer from metalloid to Fe atom causing a decrease of the empty density of states of the metal[16]. The detailed calculations of Szmulowicz and Pease[17] indicate a p-like character for these electronic states just above the Fermi level.
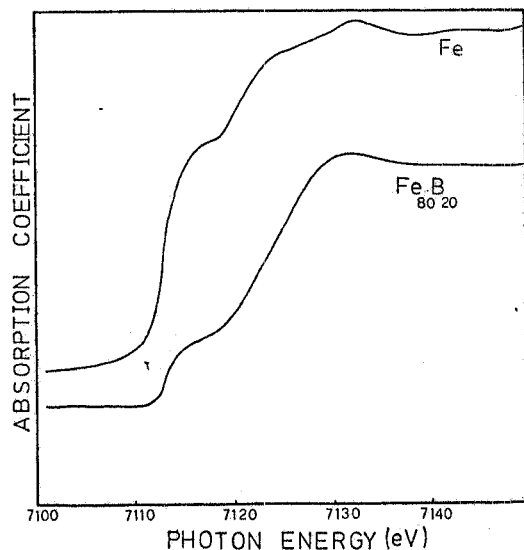

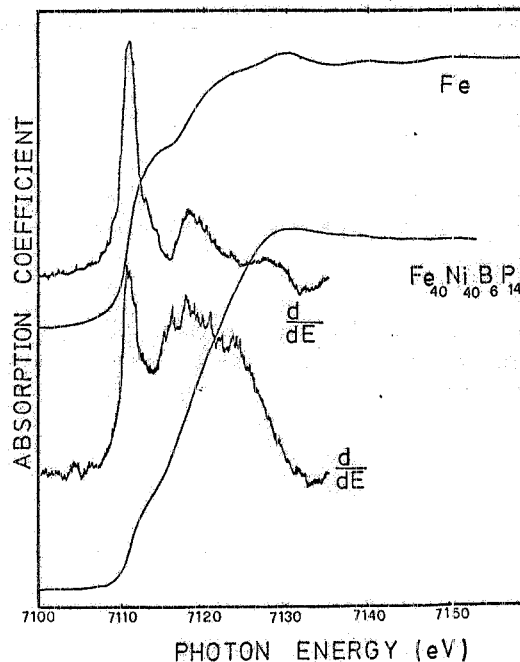
FIG. 5 - K absorption edges of bcc Fe and $Fe_{80}B_{20}$.



FIG. 6 - K absorption edges and first derivatives in pure Fe and $Fe_{40}Ni_{40}B_6P_{14}$.

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