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To cite this version:
M. Maurer, A. Mehdaoui, J. Friedt. LOCAL SYMMETRY AT THE 3d METAL SITE AND CHEMICAL ORDER IN AMORPHOUS AND CRYSTALLINE Ni1-xBx. Journal de Physique Colloques, 1985, 46 (C8), pp.C8-217-C8-221. <10.1051/jphyscol:1985831>. <jpa-00225174>
LOCAL SYMMETRY AT THE 3d METAL SITE AND CHEMICAL ORDER IN AMORPHOUS AND CRYSTALLINE Ni$_{1-x}$B$_x$

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Résumé - La structure locale des phases amorphes $^{57}$Fe:Ni$_{1-x}$B$_x$ ($18 < x < 40$at%) est explorée au moyen de la spectroscopie Mössbauer de $^{57}$Fe sous champ externe et de l'EXAFS. Les effets d'ordre chimique et la symétrie locale autour du métal de transition confirment l'existence d'un ordre local voisin de celui des phases cristallines dérivant de prismes trigonaux, en excellent accord avec la symétrie locale autour de $^{11}$B. Toutefois, le désordre autour de l'élément majoritaire (Ni) est plus fort qu'autour du minoritaire (B) ce qui est vraisemblablement relié à la connection des prismes trigonaux adjacents.

Abstract - The local order of amorphous $^{57}$Fe:Ni$_{1-x}$B$_x$ ($18 < x < 40$at%) is investigated with help of EXAFS and $^{57}$Fe Mössbauer spectroscopy under an external field. The chemical order and the local symmetry around the 3d metal support an ordered local structure similar to that observed in crystalline phases and built from trigonal prisms, in agreement with $^{11}$B NMR results. The disorder around the 3d metal is larger than around boron, since 3d metal belong to several interconnected trigonal prisms.

I - INTRODUCTION

The partial radial distribution functions of binary amorphous alloys are accessible from scattering experiments (neutrons scattering on isotopically substituted alloys, EXAFS, anomalous X-ray scattering ...)/1,4/. On the other hand, little experimental information is available regarding higher order correlation functions, although they represent crucial quantities for test of structural models. To this respect, the quadrupolar hyperfine interactions probe the local symmetries (2nd order) which are directly correlated with many-atoms correlation functions /5,7/.

The aim of the present work is to compare the local symmetry at the transition metal sites in amorphous Ni$_{1-x}$B$_x$ alloys ($18 < x < 40$at%) and in the crystalline counterparts Ni$_3$B, Ni$_4$B$_3$, NiB (all orthorhombic) and Ni$_2$B (tetragonal). Information on the electric field gradient parameters $q_{zz}$ and $\eta=(q_{xx}-q_{yy})/q_{zz}$ is gained from Mössbauer spectroscopy (0.5 at % of $^{57}$Fe) by applying an external magnetic perturbation to quadrupolar levels. The results provide a valuable complement to $^{11}$B NMR investigations of the EFG at the metalloid sites /5/ and to partial radial distribution functions deduced form neutron scattering and EXAFS /1-3,10/. Moreover, the ability to vary the metalloid content over a broad range covering several crystalline phases permits to improve the comparison with the crystalline local order. In this series of crystalline alloys, trigonal prismatic units centered at the B atoms are particularly stable, likely due to both steric and chemical effects. Depending on the boron composition, the mode of interconnecting
the units is changing. Ni₂B (tetragonal Cu₃Al₂-like) is an exception where the B coordination unit is represented by a square antiprism.

II - EXPERIMENTAL DETAILS

Amorphous ribbons of composition $^{57}$Fe₀.₀₀₅Ni₀.₉₉₅₋ₓBₓ, x=0.18; 0.32; 0.38 were obtained by melt-spinning in inert atmosphere. The non-crystallinity was checked by X-ray diffraction. The Mössbauer experiments were performed in H=0 and H=7T external field, parallel to the γ-ray axis versus a $^{57}$Co:Rh source. For each sample, the temperature was chosen high enough (80 < T < 300K) to ensure negligible local susceptibility at Fe atoms.

Analysis of zero field spectra was done following a standard least-square fitting procedure, for distributed quadrupole splittings ($\Delta = e^2q_{zz}(1+q^2/3)^{1/2}$) and correlated isomershifts ($\delta_\text{IS}$):

$$\delta_\text{IS} = a + b\Delta + c\Delta^2$$

A linear correlation (c=0) fails when both signs of $\Delta$ are present with nearly equal probabilities, because the odd part of the correlation vanishes in the paramagnetic state where only $|\Delta|$ is detected. Addition of the quadratic term (c≠0) actually improves the quality of fittings (fig.2).

The in-field spectra were analyzed using the full Hamiltonian with a random orientation of the EFGT axes with respect to H and constraining the distribution $P(\Delta,\delta_{IS})$ from zero field spectra. The marginal $\eta$ distribution and the sign weighing of $q_{zz}$ are partly correlated. They were analyzed simultaneously by searching for a central value ($\bar{\eta}$) of a Gaussian distribution of the asymmetry parameter $\eta$, the width being deduced from the width of $P(\Delta)$ i.e. $\sigma_\eta = 0.6$.

In this procedure, care is given to discontinuities of the conventional definition of $q_{zz}$ and $\eta$ at $\eta=0$ and $\eta=1$.

III - RESULTS AND DISCUSSION

a) Chemical short range order and radial distribution functions:

Our EXAFS results at both K edges of Ni and Fe are mentioned briefly here. They are in excellent agreement with neutron data at high q-vector and with former EXAFS results for x = 33 at% /3/. Notice that except for the small difference in the central atom phaseshifts, EXAFS spectra at Fe (impurity) and Ni (matrix) are identical within statistical errors; this means that the mean Fe and Ni environments are similar, i.e. that the substitution of Fe by Ni is nearly random. This observation supports that the $^{57}$Fe nuclei probe the mean 3d "sublattice". This is surprising when considering the stronger interactions between Ni and B than between Fe and B /11-13/.

Indeed $^{57}$Fe substitution in crystalline nickel borides is not random; e.g. the relative occupation of the I/II sublattices in Ni₃B is 1.22 instead of 2 /14/.

The mean nearest neighbour distances between Ni-B and Ni-Ni are identical in all amorphous and crystalline phases of related composition. The distribution of distances is slightly asymmetric towards larger distances. The most significant feature of these radial distribution functions concerns the mean occupation numbers $N_{ij}$ in the nn shells. An attractive NiB chemical short range order (CSRO) is observed. Although a definition of CSRO parameter in discrete shells is oversimplified when the two element have different size ($r_B/r_{Ni} = 0.7$), it is worth estimating the c.s.r.o. parameters (y) as defined by Spaepen and Cargill /15/.
The values of $y$ in amorphous and crystalline phases are reported in fig.1 versus boron content.

Fig.1: Chemical short range order parameter ($y$), local symmetry (non-centrality /9/) order parameter at boron site ($\lambda^B$) and at $^{57}\text{Fe}$ substituting Ni ($\lambda^{3d}$) in amorphous Ni$_{1-x}$B$_x$ alloys versus x. The c.s.r.o. parameter $y$ in crystalline phases is also reported (open symbols).

The c.s.r.o. is similar in both states. More precisely, the orthorhombic structures (Ni$_3$B, Ni$_4$B$_3$ and NiB) which are based on trigonal prisms display higher c.s.r.o. parameters ($y = 0.18$) than Ni$_2$B (square antiprims based; $y = 0.06$).

b) Local symmetries around the 3d metal:

The distribution $P(|\Delta|)$ of the $^{57}\text{Fe}$ quadrupole splitting $|\Delta|$ is well represented by a Gaussian distribution centered at a non-zero value $|\overline{\Delta}|$ (fig.2).

These feature are the signature of a well-ordered local structure deriving from a weak disordering of a non-cubic underlying local symmetry. The order parameter $\overline{\Delta}/\sigma = \lambda^{3d}$ for the local symmetry at the 3d metal sites is shown in fig.1, together with the corresponding parameter $\lambda^B$ at the boron site /5/. The order in bondings is systematically stronger around boron than around the 3d element: $\lambda^B > \lambda^{3d}$. This is readily understood since the smaller metalloids are located a single trigonal prism whereas the 3d metals belong to the connecting sites between adjacent prisms.

These observations are consistent with the sign distribution of $\Delta$ and the Gaussian distribution of $\eta$ (fig.2). At all compositions between 18 and 40 at% boron, the more probable $\eta$ value at the 3d site is between 0.8 and 1, thus implying a
strong admixture of the two signs of $\Delta$. The estimated relative probability for the two signs $P(+\Delta)/P(-\Delta)$ actually amounts to 1.3 to 1 (fig.3). Notice that the slightly larger value of $P(+\Delta)$ is the fingerprint of the local symmetry at the regular sites of trigonal prisms in crystalline compounds /14/, the centroid of the $\eta$ distribution being consistent with the large value of this parameter in boron rich crystal structures ($\text{Ni}_4\text{B}_3$, $\text{NiB}$) based on trigonal prisms ($\eta = 0.65$ or $0.85$) (fig.3).

In line with the $^{11}\text{B}$ local symmetry for $x = 33$ at%, the symmetry at the 3d metal does not derive from a simple disordering of the tetragonal $\text{Ni}_2\text{B}$ structure ($\Delta < 0$, $\eta = 0.6$) (fig.3) built with square antiprism; a trigonal-prism-like order (fig.1,3) is rather suggested. At lower boron content, the distribution $P(\Delta,\eta)$ is centered at mean values which deviate from values corresponding to the $\text{Ni I}$ and $\text{Ni II}$ sites of $\text{Ni}_3\text{B}$ (fig.3).

This collapse of $|\Delta|$ as compared to $\text{Ni}_3\text{B}$ is assigned to an admixture of $\text{Ni I}$ and $\text{Ni II}$ character for connecting atoms /5,16,17/. In addition, it is likely that to accomodate the Ni content higher than in $\text{Ni}_3\text{B}$ there are zones depleted in metalloid where a nearly fcc (cubic-like) local structure might develop. Actually, the mean experimental values of $(\bar{\Delta},\bar{\eta})$ in $\text{Ni}_{62}\text{B}_{18}$ coincide with the weighted average over the two non cubic $\text{Ni}_3\text{B}$ sites and the cubic site of fcc Ni. One should notice that the experimental distribution is reasonably narrow ($\lambda \approx 2.1$) and single-peaked, implying that this averaging takes place on a local scale and is not associated to large scale heterogeneities. This result is fairly consistent with NMR data which concern B atoms located within the trigonal prismatic units.
Fig. 3: mean values of $(\Delta, \eta)$ in amorphous Ni$_{1-x}$B$_x$ at the $^{57}$Fe site substituting Ni. The polar coordinates representation /8/ is used with $r=\Delta$, $\eta = \sqrt{3} \tan(\pi/6 + \varepsilon \Phi)$ where $\varepsilon = +1$ or $-1$, depending on the + or − sign of the principal component $e^{\Delta}z^2Q$. The discrete values in crystalline phases are represented by open symbols.

IV - CONCLUSION

The local symmetry distribution at the 3d site in amorphous $^{57}$Fe:Ni$_{1-x}$B$_x$ (18 < x < 40 at%) is compared with the point symmetry in crystalline phases. The magnitude of the chemical short range order parameter, the local symmetry at the metalloid (11B) and at the transition metal compare with the corresponding parameters in crystal phases based on trigonal prisms centered around boron. The local symmetry at boron essentially proves the existence of these trigonal prisms, whereas the local symmetry at the 3d metal provides information on the way of connecting these units. This information on local symmetries, i.e. on many atoms correlation is anticipated to be particularly valuable for checking and developing structural models of amorphous alloys.

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