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To cite this version:

P. Panissod. STRUCTURAL INVESTIGATIONS OF AMORPHOUS METALS BY NMR. Journal de Physique Colloques, 1985, 46 (C8), pp.C8-241-C8-245. <10.1051/jphyscol:1985835>. <jpa-00225178>

HAL Id: jpa-00225178
https://hal.archives-ouvertes.fr/jpa-00225178
Submitted on 1 Jan 1985

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STRUCTURAL INVESTIGATIONS OF AMORPHOUS METALS BY NMR

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Abstract - In this paper, through the review of some relevant studies of amorphous metals, we show what information NMR measurements can give on the structure of such systems.

I - INTRODUCTION

NMR has now largely proved useful in identifying structural subunits in insulating materials: molecules or submolecular units in organochemistry and, closer to our topic, for example borate units in classical glasses. The aim of this paper is to present some of the few experiments done in that direction in amorphous metals.

In NMR measurements, nuclei probe their local electronic environment through hyperfine interactions (magnetic or electric shielding interaction). Most of the structural information is gained through the analysis of the anisotropic part of these interactions (quadrupolar interaction, anisotropic frequency shift) which reflects the symmetry of the local structure. The isotropic part (Knight or chemical shift) and their dynamic contributions (relaxation times) can also be useful as a signature of the chemical environment provided that NMR data in reference systems can be used as "fingerprints".

The next section (II) will be devoted to the investigation of the local symmetry and the structural coherence through the measure of the electric field gradient (EFG) and related properties. This is the most specific output of hyperfine interactions studies of the amorphous structure since conventional structural studies can hardly go beyond pair correlations measurements. The last section (III) will be a brief outline of measurements which are oriented towards the study of the electronic structure (Knight shift and hyperfine fields, relaxation time) but which can yield some information about the chemical short-range order by comparison with crystalline materials.

II - LOCAL SYMMETRY AND STRUCTURAL COHERENCE

As the related nuclear techniques (Mössbauer effect, perturbed angular correlations...) NMR provides the opportunity to measure the local EFG on selected sites and hence it can probe the site symmetries of the structure.

In the presence of an EFG the NMR spectrum is splitted in 21 lines (I is the nuclear spin) the separation of which depends on the EFG strength and symmetry and on the polar angles of the magnetic field in the EFG frame. The EFG is characterized by two independent parameters: its stronger principal component \( V_{zz} \) measured in NMR by the quadrupolar frequency \( \nu_q = 3e Q V_{zz} / 2I(2I-1)h \) (\( \nu_q = 0 \) for isotropic or cubic...
symmetry) and the asymmetry parameter \( \eta = \frac{|V_3 - V_4|}{V_2} \) \( (\eta = 0 \text{ for axial symmetry}) \). In a polycrystal or an amorphous system, the external field is randomly oriented in the EFG frame hence the NMR lines are distributed in position yielding characteristic "powder patterns". From the simple observation of the spectra it is rather easy to decide if the symmetry of the structure around the probe nuclei is isotropic (a single line is observed), axial \( (\eta = 0) \) or significantly non-axial. To go beyond this qualitative information it is useful for amorphous metals to perform computer simulations of the observed spectra so that quantitative values can be obtained for the average \( \nu \) and \( \eta \) and their distributions. It must be noted however that, contrary to Mössbauer effect, NMR cannot usually provide the sign of the EFG. Comparison with crystalline systems (experimental) or amorphous structure models (simulations) are then done.

Successful studies were carried out in metal-metalloid amorphous systems mainly on the metalloid element \( /2/ \) which show obvious similarities between the site symmetry in the glassy state and in the crystalline state for \( a\text{-Ni}_7B_{14}B_8 \), and \( c\text{-Ni}_3B \) \( (\text{non axial}, \eta = 0.6) \) and for \( a\text{-Mo}_3B_6 \) and \( c\text{-Mo}_3B \) \( (\text{axial}, \eta = 0) \). In \( a\text{-La}_{75}B_{25} \) a single line is observed as expected for an isotropic symmetry \( (c\text{-La}_7Ga \text{ is cubic}) \) but a computer analysis shows that the line shape is due to a broad EFG distribution consistent with computer simulations of random packing of spheres \( \text{(RPS)} /3/ \).

Combined measurements of the site EFG and spin-spin relaxation times allow a further investigation of the structural coherence as shown by the study described below of the amorphous nickel borides in a wide concentration range \( /4/ \).

The \( ^{11}\text{B} \) NMR spectra in \( a\text{-Ni}_{100-x}B \) \( (18 < x < 40) \) and crystalline nickel borides (Fig. 1) and their computer analysis indicate that the site symmetry around boron in the glassy state evolves gradually from that of \( c\text{-Ni}_3B \) \( (\eta = 0.6) \) to that of \( c\text{-Ni}_3B_3 \) \( (\eta = 0.4) \). The axial symmetry of \( c\text{-Ni}_3B \) is not observed in the amorphous modification \( (x = 0.33) \) nor is the broad distribution of high values of \( \eta \) which is characteristic of a RPS. On the contrary at both ends of the concentration range the EFG distribution is found quite narrow which shows that the boron environment

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Fig. 1 - Experimental NMR spectra in crystalline and amorphous nickel borides.
coordination and symmetry) is only weakly fluctuating from site to site. In the mid-range all the spectra can be exactly explained by a mixture of $C\text{-Ni}_B$ like and $C\text{-Ni}_B^4B_3$-like environment of boron.

A supplementary information is given by the transverse relaxation time $T_2$, which, in nickel borides, is only due to $^{11}\text{B}$ nuclear spins dipolar interaction. $T_2$, measured on the central line ($-1/2 \rightarrow +1/2$ transition) is nearly not-affected by the EFG; it is only related to the average B-B distance which is shown in the glasses to be equal to that in the crystalline borides of same composition. This implies B-B contacts for the highest B-concentrations. Contrarily to $T_2$, the relaxation time $T_2'$ measured on the wings of the spectra ($\pm 3/2 \rightarrow \pm 1/2$ transitions) is strongly dependent on the EFG distribution on neighbour B sites: if all B neighbours experience the same EFG (strength and orientation) then $T_2'$ is close to $T_2$ ($T_2'/T_2 \sim 1$); oppositely if there is a broad distribution of EFG on B-neighbours the dipolar relaxation is quenched ($T_2'$ decreases strongly).

Hence the ratio $T_2'/T_2$ is a measure of the structural coherence on a few interatomic distances. As shown on Fig. 2, $T_2'/T_2$ is close to 1 in $C\text{-Ni}_B$ in which all B sites are equivalent and identically oriented (in the same microcrystal), this ratio decreases in $C\text{-Ni}_B$ in which B sites are equivalent but with different orientations, and in $C\text{-Ni}_B^4B_3$ where three unequivalent B sites are present. In the amorphous samples $T_2'/T_2$ is generally lower than in the crystals as expected because of structural disorder but a clear trend to structural coherence is observed at both ends of the concentration range in agreement with the EFG distribution measured on the spectra.

It is then concluded that boron in the amorphous nickel boride is surrounded by nickel trigonal prisms which are the building units of $C\text{-Ni}_B$ and $C\text{-Ni}_B^4B_3$. The increase of the boron concentration from $x = 18$ to $x = 40$ is accomodated by prisms sharing more and more Ni atoms allowing B-B contacts when they share rectangular faces. This conclusion is consistent with the increased brittleness of the samples for high B-content and in agreement with neutron data /5/.

III - CHEMICAL SHORT-RANGE ORDER

Beside the determination of the site symmetries in amorphous materials, the sensitivity of NMR to the nature of the neighbours can be used to probe at least partially the chemical short range order (CSRO) in the samples. However for such purposes the NMR data have to be compared to those obtained in reference samples the structure of which is known; hence the information obtained is rather indirect. Two examples of such studies are given below for the non-magnetic compound $\alpha$-PdCuP (A) and the amorphous ferromagnet $\alpha$-CoB (B).

**A)** $^{31}\text{P}$ Knight shifts and relaxation times $T_1$ were measured in $\alpha$-(Pd$_{1-x}$Cu$_x$)$_2$P $/6/$. As can be seen on Fig. 4 both $K$ and $R = (T_1T)^{-1}$ vary much less with increasing Cu concentration in the glass than in the crystalline compound and their values remain close to those measured in pure Pd$_2$P. This shows that some kind of CSRO exists in the amorphous material such that P atoms are essentially surrounded by Pd atoms. Such CSRO can be compared to the well-established...
Fig. 3 - Knight-shift and relaxation rate on $^{31}P$ in the glass $\alpha$-$(Pd_{1-x}Cu_x)_{80}P_{20}$ ($\times$) and the crystal c-$(Pd_{1-x}Cu_x)_3P$ ($\circ$).

**Fig. 4** - $^{59}$Co hyperfine field in cobalt-metalloid compounds vs metalloid concentration ($\times$) and number of valence electrons ($Z_B = 3, Z_{Si} = 4$). Open circles represent the expected hyperfine field on Co for 1 to 5 boron atoms in its first coordination shell.

Metalloid-metalloid avoidance in metal-metalloid glasses and it suggests that Cu might play a role of "glass former" in the system.

**B.)** In ferromagnets the hyperfine field (HF) on the magnetic element is very sensitive to its environment; for example as shown on Fig. 4, the $^{59}$Co HF decreases linearly with increasing B content. With the crystalline borides for reference which for the numbers of B atoms around Co are known one can reasonably attribute a given hyperfine field to a given number (1 to 5) of B in the Co coordination shell. Then from the NMR spectrum which is essentially the hyperfine field distribution one can deduce the distribution of coordination numbers at a given concentration [7]. On the non-magnetic element the effect of local fluctuations in the number and nature of the neighbouring atoms are usually weaker and on the same basis one can only deduce an average coordination number which is more directly obtained by structural diffraction techniques.

**IV - CONCLUSION**

Through the few examples given above, we have attempted to show what insight on the atomic structure of amorphous metals one can have through NMR spectroscopy. Particularly we have emphasized its possibility to probe the site symmetries which are hardly attained by the usual diffraction techniques. Let us mention at last that NMR might be extremely useful for the study of dynamic structural properties (single and collective atomic movements) [8] but except in the domain of the Hydrogen diffusion [9] experiments in that field are nearly unexistent in amorphous metals.
REFERENCES