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STUDIES OF THE ELECTRONIC AND ATOMIC STRUCTURE OF AMORPHOUS METALS BY NMR

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The local character of the hyperfine interactions between nuclei and their electronic surroundings makes NMR a suitable tool to investigate the local electronic structure of metals and among them the newly introduced amorphous metallic alloys. Beside the electronic properties nuclei can also probe indirectly some structural characteristics of their environment such as symmetry properties which cannot be obtained by direct structural measurements in amorphous metals. In this paper we intend, while reviewing some relevant NMR measurements in amorphous metals, to point out what informations NMR can yield about the influence of the lack of long range order on electronic and magnetic properties of amorphous metals and about the atomic arrangements in these materials.

1. Introduction

Amorphous metallic alloys have been rather recently introduced in the world of solid state physics and have quickly excited a strong interest in the applied physics field because of interesting macroscopic properties (particularly magnetic) related to the disordered nature of their structure. It also appears that a controlled crystallization of these materials might offer a new approach to fabricate crystalline alloys with particular grains structures and properties. Hence as far as the basic research field is concerned these new materials are interesting from three points of view: i) they allow to study alloys with continuously variable compositions where crystalline intermetallics or compounds are often inexistent or have discrete formulae; ii) they allow to study the effect of structural disorder even at low temperatures; (iii) they
address the question of their structure and stability (thermodynamics of formation, structural relaxation, crystallization process...) these three points having obvious impacts on the applications of such materials.

On any of these points NMR as other related nuclear techniques (Mössbauer effect, perturbed angular correlations...) can yield informations which are very often specific since they use local probes weakly interacting with the system under investigation. The two first points are basically relevant of NMR investigations of the electronic structure of metals i.e. the measurement of say partial (site dependent) densities of electronic states and their dependences on chemical and topological environment. The third point specific to amorphous materials is more relevant of a use of NMR comparable to that in say organochemistry i.e. (crudely) identication and counting of structural units, observation of atom movements... However it should be noted that electronic and atomic structure studies through NMR are closely interrelated in amorphous metals because most of the data obtained by these measurements are essentially determined by conduction electrons - nuclei interactions. Therefore comparative measurements on crystalline materials of similar composition, the structure of which is known, are very desirable as they provide some reference for the relation between environment and local electronic properties.

This paper will be organized in two sections. In the first one we will present NMR measurements which have for primary aim to study the electronic structure and local magnetism of the alloys: magnetic susceptibilities or magnetic moments of the different components, occurrence of magnetism, magnetic structure, partial densities of states, superconductivity. Such studies are routine NMR works in metals and we will focus on similarities or differences between the results obtained in amorphous and crystalline materials so as to emphasize the effect (if any) of the structural disorder in amorphous systems. The second section will be devoted to the investigation of the atomic structure of amorphous metallic alloys, static properties (number, nature, distances of the neighbour atoms and particularly site symmetry) and dynamic properties (atom movements).
2. Electronic Structure and Magnetism of Amorphous Metals

The fundamentals of NMR in metals having been given in the introductory paper. Let us simply recall that most informations relative to the electronic structure are obtained through the measurement of the NMR frequency shift (Knight shift $K$) due to the field created by the conduction electrons spin and orbital magnetization (secular term of the shielding interaction) and of the relaxation time of the longitudinal nuclear magnetization ($T_1$ or $R = (T_1T)^{-1}$) due to the time dependent part of that field (non secular term of the shielding interaction). We shall discuss separately the case of paramagnetic and ferromagnetic materials.

2.1 Paramagnetic systems

Knight shift and relaxation rate: the Knight shift can be quite generally written as

$$K = \frac{1}{N_{\text{B}}} \left( \chi_s H_s + \chi_L H_{\text{cp}} + \chi_{\text{orb}} H_{\text{orb}} \right),$$

(1)

were $\chi$'s are the local susceptibilities of the conduction electrons on the observed sites ($s$ and non-$s$ spin susceptibilities and orbital susceptibility in sequence) and $H$'s are hyperfine coupling constants associated with the direct contact interaction, core polarization and orbital momentum. Similarly if electronic correlation and exchange effects can be neglected the relaxation rate $R$ reads:

$$R = (T_1T)^{-1} = \frac{1}{S(N_{\text{B}})^2} \left| \chi_s^2 H_s^2 + \chi_L^2 (F_1 H_{\text{cp}}^2 + F_2 H_{\text{orb}}^2) \right|$$

(2)

where $F_1$ and $F_2$ are reduction factors related to selection rules involving orbital symmetries of the non-$s$ electrons, $S$ is the Korringa constant. From equation (1) and (2) and the bulk susceptibility value $\chi_{\text{B}}$ one can deduce in a pure metal the various components of the susceptibility hence the partial densities of states at the Fermi level provided some estimations of the $H$'s.

In multicomponent systems the situation is more complicated and often one cannot observe the NMR on all elements, then equations (1) and (2) only yield a range of consistent values for the susceptibilities. This has been done for example in $\alpha$-NiPB metallic glasses [1] where it is shown that the non-$s$ susceptibility on P and B is at least 10 times larger than the $s$ term.
Korringa ratio: a more qualitative test of the s or non-s character of the electrons at the Fermi level is the value of the Korringa ratio \( k = K^2 / SR \) which is 1 for s electrons. Experimentally most of the measurements on metal-metalloid glasses yield values of \( k \) significantly larger than 1[2-4] for the metalloid (B, P...) which suggests strongly the existence of non-s electrons on those sites. This has some impact on our knowledge of this class of amorphous metals since it implies hybridization between the metalloid sp electrons and the d electrons of the metal, hence covalent (directional) bondings which in turn might have structural consequences.

Fig. 1. Bulk magnetic susceptibility and local susceptibility on boron sites in \( \alpha-Ni_{100-x}B_x \) (static: K; dynamic: R).
Comparison between amorphous and crystalline systems: even more
direct are the conclusions that one can draw from the simple comparison of the
measured K and R in amorphous metals and in the compositionally related crys-
talline compounds. As shown on Fig. 1 in nickel borides K and R are nearly
identical in the crystalline c-Ni$_3$B, c-Ni$_2$B and c-Ni$_4$B$_3$ and in the glasses of
same composition [5] which means that the structural disorder does not affect
the electronic structure at a local scale. This is a rather general result
which is also found by other techniques: the electronic structure is affected
by amorphisation only when the crystalline materials present strong singu-
larities in their band structure. However some differences in the local atomic
arrangements can lead to observable differences between crystalline and
amorphous compounds; this can be clearly seen on Fig. 2 for example in
(Pd$_{1-x}$Cu$_x$)$_3$P alloys [6]: K and R on the phosphorus site are much less dependent
on Cu concentration in the metallic glasses and take the value observed in
crystalline Pd$_3$P, this is an indication that in the amorphous structure P atoms
are surrounded mostly by Pd atoms even at relatively high Cu concentrations
while in the crystalline alloys they certainly have more Cu neighbours.

Effects of long range disorder: further than the atomic scale some
effects of the long range disorder were also expected in amorphous metals that
can be tested by NMR. A first example is the existence of a strong electron-
phonon coupling due to the softening of the phonon spectrum. Temperature
dependence of T$_1$ in superconducting materials can probe the opening of the BCS
gap and hence measure the electron-phonon coupling; actually NMR measurements
in α-MoRuP glasses [7] have shown that the strong electron-phonon coupling is
not a general rule in amorphous material since a gap equal to that predicted by
the BCS theory in the weak coupling limit was found. A second example of the
effect of disorder is the predicted extreme damping of RKKY oscillations around
magnetic impurities due to the reduced electronic mean free path. Again T$_1$
measurements, through indirect spin-spin interaction, can probe the existence
of long ranged RKKY interaction and some evidence of such effects has been
found in α-NiPB metallic glasses [2] close to the occurrence of magnetism where
Ni clusters act as magnetic impurities.
2.2 Ferromagnetic systems

In ferromagnetic materials NMR measurements are usually performed in the internal hyperfine field (HF) created at the nuclei by the spontaneous electronic magnetization. This hyperfine field is the relevant data in such experiments corresponding to the Knight shift in paramagnetic metals. $T_1$ measurements are much less used for electronic structure studies because nuclear relaxation if often driven by domains and domain walls dynamics (at least in zero external field).
Hyperfine fields in amorphous metals and related crystalline metals: in the amorphous ferromagnets it is also quite generally found that the HF is the same as in crystalline systems of identical composition; this is true for the magnetic element (eg Fe or Co in \(\alpha\)-FeB or \(\alpha\)-CoB) or for the non-magnetic ones (eg B). Moreover magnetic elements diluted in a ferromagnetic amorphous matrix (eg Co in \(\alpha\)-(Fe\(_{1-x}\)Co\(_x\))B) also experience the same HF as in the crystalline compounds. This confirms the weak influence of disorder on the local electronic properties. An extensive review of HF's in amorphous ferromagnets can be found in ref. [8].

Hyperfine fields and on-site magnetic moment: as the Knight shift the HF is directly related to the electronic magnetization that is in ferromagnets, to the electronic moments. Although the HF can be theoretically described as the sum of s electrons, core polarization and orbital contributions, the difficulty of computing and handling them has led the experimentalists to a more phenomenological description in terms of a local contribution due to the on-site moment (i.e. the moment on the site of the probe nucleus) and a non-local one due to polarization of the conduction electrons (CEP) by the surrounding moments. If the local contribution is dominant for the magnetic elements which is generally the case, except perhaps for nickel, the measurement of the HF can give reasonably the magnitude of the moment. As shown on Fig. 3, for example, there is a very good proportionality between the moment and the HF in many cobalt based amorphous and crystalline compounds (HF\(_{Co}\) \(\sim\) 115 KOe/\(\mu_B\)) a similar relationship can be found in interstitial Fe based compounds (HF\(_{Fe}\) \(\sim\) 125 KOe/\(\mu_B\)). On the basis of such numbers one can estimate the moments in amorphous alloys containing more than one magnetic specie which cannot be done as in crystalline materials by neutron diffraction [8]. Such analysis is however limited to the case of rather high moments so that non local contributions to the HF are not significant, also it cannot be used in alloys close to a magnetic transition where moments can strongly fluctuate from site to site due to environment effects.

Local environment effects on the hyperfine field: the effect of environment on the moment and on the HF is a field where NMR has always proved very useful. In amorphous ferromagnets the problem of the relation between the HF and the local coordination shell of the probe nucleus can be addressed from
both sides. First if one has some knowledge of the structure (through other measurements or within a structural model) as in crystalline materials one can probe the effect of, for instance, impurities in the neighbour shells through the occurrence of new NMR lines at different HF's. If reciprocally one can establish with confidence in reference compounds a relation between some structural characteristics and the HF then the HF distribution in amorphous ferromagnets can be used for structural investigations. An example of the first approach is given by the NMR study of $^{55}\text{Mn}$ diluted in the metallic glass $\alpha$-FePB: at low Mn concentrations only one spectrum is observed around HF = 260 K0e;
when Mn concentration increases a new spectrum builds up at much lower HF, knowing that in these metal-metalloid glasses the number of metallic atoms neighbours of a metal is around 10 the concentration dependence of the two spectra intensities shows that the low HF is due to the presence of at least 1 Mn atom among the nearest neighbours of Mn atoms [9]. The second approach will be treated in the next section of this paper.

**Magnetic structure:** at last let us mention that NMR can be of some help in determining magnetic structures when again neutron diffraction fails because of the absence of translational invariance. One makes use for such purpose of the NMR frequency dependence on external field which is an increase (decrease) if the HF is positive (negative): the external field is added to (subtracted from) the HF (the positive direction is that of the net magnetization in a ferromagnetic domain). For example the positive HF that was found on $^{59}$Co in concentrated GdCo amorphous alloys [10] suggests that Co moments are antiparallel to the Gd moments (ferrimagnetic structure): this is because the HF on Co is usually dominated by the negative core polarization contribution (i.e. HF is opposite to the Co moment). The decrease of the net moment per Gd atom with increasing Co content is consistent with this interpretation. Such measurements are often somewhat ambiguous since the non local contribution to the HF may play a significant role, the order of magnitude of this contribution can however be measured by NMR on a non magnetic element.

### 3. Structural Investigations of Amorphous Metals

The lack of translational invariance in amorphous material makes the determination of their structure a difficult task. Standard diffraction techniques can only give informations about pair correlations (i.e. distances, number and nature of the atoms in successive coordination shells) and none about angles and symmetries. On the other hand NMR has been used for years to identify molecular units in organochemistry and closer to our topic in insulating glasses [11]. The relevant data for such identification are the frequency shift and the spectrum shape (due to anisotropic shielding interaction and quadrupole interaction) this last one containing indirectly some information about the symmetry of the local structure. In amorphous metals it is rather difficult to extract structural information from the shielding interaction except in ferromagnets which for the dependence of the HF on the number
number and nature of the surrounding atoms is sufficiently strong with respect to the broadening due to distance fluctuations and long range disorder so that some information on the first neighbours can be obtained. But the major and specific yield of NMR (and Mössbauer effect) in that field is, through quadrupole interaction, the knowledge of the symmetry of the local atomic arrangement around the probe nuclei.

Apart from those static properties, NMR is also a suitable tool to investigate some dynamic structural properties (atom moments) through relaxation time measurements.

3.1 Static structure of amorphous metals

Local(site) symmetry: in the presence of electric field gradient (EFG) the NMR spectrum is splitted in 2I lines the separation of which depends on the EFG strength and symmetry and on the polar angles $\theta$ and $\phi$ of the magnetic field in the EFG frame. The EFG is characterized by two independent parameters only: its stronger principal component $V_{zz}$ measured in NMR by the quadrupole frequency $v_Q = 3e^2qQ/2I(2I-1)h$ ($v_Q = 0$ for isotropic or cubic symmetry) and the asymmetry parameter $\eta = |(V_{xx} - V_{yy})/V_{zz}|$ ($\eta = 0$ for axial symmetry: $V_{xx} = V_{yy}$). 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 the so-called "powder patterns" shown on Fig. 4. It is then rather easy from the simple observation of these spectra 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 these qualitative informations in amorphous metal it is useful to perform computer simulations of the observed spectra so that quantitative values can be obtained for the average $\bar{v}_Q$ and $\bar{\eta}$ and their fluctuations due to disorder. Then comparison with crystalline systems (experimental) or amorphous structure models (simulations) are needed because in metallic systems the EFG parameters cannot be quantitatively related to the atoms positions and charges because of the contribution of conduction electrons. Such studies have been undertaken mostly on the "glass former" element (i.e. the element added in quantity about 20% to a pure metal to amorphise it): B in $\alpha\text{Ni}_{78}P_{14}B_8$, $\alpha\text{Mo}_{70}B_{30}$, Ga in $\alpha\text{La}_{75}Ga_{25}$ [12]. These alloys had been chosen because their crystalline counterpart present three different site symmetries on the glass former site:
Fig. 4. Unbroadened "powder patterns" for a nuclear spin $I = \frac{3}{2}$ in a non-cubic site symmetry ($\nu \neq 0; 0 \leq \eta \leq 1$) (the central line, $1/2 \rightarrow -1/2$ transition is omitted).

Non axial, axial, cubic in sequence. In the amorphous alloys NMR spectra show that the site symmetry of the glass former is different in the three compounds ruling out the possibility of an unique amorphous structure suggested by models based on random packing of hard spheres that were used for liquid metals. On the contrary these measurements emphasize the role of directional bonding between metalloid atoms and the surrounding metallic atoms. Particularly the symmetry around boron was found identical in the glasses $\alpha$-NiPB and in the crystal $c$-Ni$_3$B (non axial: $\eta = 0.6$) on the one hand and in the glass $\alpha$-Mo$_{70}$B$_{30}$ and the crystal $c$-Mo$_2$B (axial: $\eta = 0$) on the other hand. In $\alpha$-La$_{75}$Ga$_{25}$ although an unique NMR line is observed which could suggest at first an isotropic symmetry as in $c$-La$_3$Ga the quantitative analysis of the spectra showed that the structure in the glass is highly disordered and can be
explained by a random packing of spheres.

Combined measurements of the EFG parameters and transversal relaxation time \( T_2 \) can help in getting a further insight on the amorphous structure as it has been shown in the \( \alpha-\text{Ni}_{100-x}B_x \) glasses [13]. Indeed in non magnetic metals \( T_2 \) is usually dominated by the nucleus spin-spin dipolar interaction. In the example above \( B \) has the only important nuclear spin hence \( T_2 \) measurements provide informations about boron-boron distances specifically. Furthermore this measurement can also give a measure of the coherence of the amorphous structure on a longer scale than the first coordination shell. Indeed the spin-spin relaxation is more efficient for "like" spins (i.e. nuclei of the same specie experiencing the same magnetic field and the same EFG) than for "semilike" or "unlike" spins (same or different nuclei in a different field and/or EFG); the reason is that only the zero frequency component of the dipolar field spectral density is effective for the two latter categories while the component at the resonance frequency is also effective for the former. Hence the more coherent will be the structure that is the more "like" will be a group of neighbour atoms the shortest will be \( T_{2w} \) measured on the quadrupolar wings and the closer will it be to \( T_{2c} \) measured on the central line (\(-1/2 \rightarrow 1/2\) transition) whose frequency is nearly not affected by the EFG.

Such study in the amorphous and crystalline nickel borides as shown that the glassy structure could be described as a packing of molecular like trigonal prisms of 6 Ni centered on B atoms. The concentration changes are accommodated by changes in the connections between the prisms which share more and more Ni atoms as the B content increases; they ultimately share rectangular faces allowing B-B contacts and giving a certain coherence to the structure of the high B content alloys (x \( \approx \) 40 % at B) which become more brittle.

Similar experiments on the metallic site have been undertaken which were less fruitful because of the strong broadening of the spectra due probably to a greater variety of environments of the metal atoms which is the majority element. It is also quite difficult to make EFG measurements in the amorphous ferromagnets for the fluctuations of the magnetic interactions dominate the spectra shape.

**Coordination number distribution:** oppositely coordination numbers (i.e. numbers of atoms of a given specie in the neighbour shell of the probe
nucleus) are more easily obtained through NMR on the metallic (magnetic) site in ferromagnetic materials. As introduced in section II the moment of the magnetic element and the hyperfine field on it are very sensitive to its environment. For example as shown on Fig. 5 in cobalt borides the $^{59}$Co hyperfine field linearly decreases with increasing boron content; with the crystalline c-Co$_3$B and c-Co$_2$B 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 [14]. On the non magnetic element the effect of local fluctuations in the number and nature of the neigh-

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

In these studies some problems may arise from a particular feature of NMR in ferromagnetic materials which is its sensitivity to magnetic anisotropy and domain walls stiffness. Indeed the NMR signal is not only proportional to the number of nuclei resonating at a given frequency but also to (crudely) the "technical" permittivity of the sample; then the spectrum may also reflect a possible distribution of magnetic anisotropy or domain wall mobility. Without going into details (see ref. [14]) the analysis of NMR spectra in terms of coordination number distribution must then be handled with great care but conversely one can get original informations on a relation between local structural properties and the macroscopic magnetic properties of these amorphous ferromagnets which are of particular industrial importance.

3.2 Dynamic structural properties

NMR and particularly relaxation times measurements are suitable tools to probe atom movements (individual or collective) and diffusion in a rather wide range of characteristic correlation times: $T_1$ probes fluctuations at the resonance frequency, $T_2$ fluctuations at vanishingly small frequencies as $T_{10}$. Since amorphous metals are basically very disordered systems at least in a range of a few interatomic distances and further it is expected on the one hand that the atomic diffusion processes and on the other hand the dynamical behaviour of "defects" (which are still to be characterized) will be quite different from that in crystalline materials.

Indeed NMR measurements of proton diffusion in several metallic glasses have proved the existence of non-Arrhenius thermally activated diffusion processes with activation broadly distributed, the hydrogen diffusion being generally strongly enhanced with respect to that in crystalline materials [15]. It is to be noted that this enhancement of hydrogen diffusion has been observed in glasses with high hydrogen content, some measurements in poorly hydrogenated glasses indicate a comparable or even slower diffusion with respect to crystalline material which could be due to a trapping of H atoms in "defects" or "voids" in the amorphous structure. However, the nature of defects in the amorphous structure is still an open question.
As far as collective motions of atoms are concerned let us mention the peak of relaxation observed at 55°K on P and B in α-NiPB glasses which could be related to internal friction peaks observed at lower temperature for lower frequencies in similar glasses [16]. Also relevant to this topic is the question of the existence of "two level systems" i.e. configuration of atoms with nearly equal energy separated by vanishingly small energy barriers; such TLS have been observed in insulating glasses but their observation in metallic glasses is somehow controversial. As for specific heat measurement, the NMR search for the TLS has to be done in the superconducting state (if any) of the material in order to quench the electronic contribution to the nuclear relaxation. Low temperature deviations to the thermally activated BCS relaxation process have been observed in α-MoRuP and α-MoRuB superconducting glasses that could be attributed to TLS induced relaxation but other mechanisms such as spin diffusion near the vortices or more trivially the existence of sample regions in the normal state can also explain the results [7].

4. Conclusion

In this paper, through some examples, we have attempted to show what informations NMR spectroscopy can yield about the atomic and electronic structure of amorphous metals: chemical short range order (coordination numbers and their distribution), topological short range order (site symmetry), medium and long range disorder effects on the electronic and magnetic properties. NMR investigations of these new kind of materials have been rather scarce to date; considering the variety of informations, often specific, that can be gained involving both basic solid state physics and applied physics, further work along these lines seems highly desirable.

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