

Local Symmetry around the Glass-Former Sites in Amorphous Metallic Alloys through Electric Quadrupole Effects

P. Panissod, D. Aliaga Guerra, A. Amamou, and J. Durand

Laboratoire de Structure Electronique des Solides, Université Louis Pasteur, F-67070 Strasbourg, France

and

W. L. Johnson

W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91109

and

W. L. Carter and S. J. Poon

Edward L. Ginzton Laboratory, W. W. Hansen Laboratories of Physics, Stanford University, Stanford, California 94305

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Through NMR investigation of quadrupolar effects in some amorphous alloys ($\text{La}_{75}\text{Ga}_{25}$, $\text{Mo}_{70}\text{B}_{30}$, $\text{Mo}_{48}\text{Ru}_{32}\text{B}_{20}$, $\text{Ni}_{78}\text{P}_{14}\text{B}_8$) the local symmetry is determined around the s - p element sites. A comparison with the corresponding crystalline compounds (La_3Ga , Mo_2B , Ni_3B) which have typically different crystal structures (cubic, tetragonal, orthorhombic, respectively) gives conclusive evidence that the amorphous structure retains to a significant extent the local symmetry of the crystalline counterpart.

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Alloys of transition metals (TM) with about 20 at. % of s - p elements such as B, C, P, Si, Ga, Ge... constitute perhaps the most widely studied branch of glassy metals. However, concerning the atomic-scale structure of these amorphous alloys, there still remain problems as to what extent the short-range order (SRO) of crystalline compounds is preserved in the related amorphous modifications. A complete determination of the SRO in these binary alloys would include for both atomic species j the knowledge of (i) the average coordination numbers \bar{Z}_j , (ii) the mean interatomic distances, \bar{r}_j , for the first surrounding shell, and (iii) the "topology" of the environment for a given reference atom.¹

The SRO around the *transition-metal* atoms, as far as \bar{Z}_j and \bar{r}_j are concerned, has been rather well established from x-ray and neutron scattering studies.² Some information about the topology of the SRO around the TM has been inferred from Mössbauer-spectroscopy experiments mainly in Fe-based amorphous alloys. On one hand, the SRO is thought to be reflected via the ^{57}Fe hyperfine field distribution as compared with that obtained in corresponding compounds.³ On the other hand, the Mössbauer absorption spectra in the paramagnetic regime exhibit well-resolved quadrupolar doublets⁴ ascertaining the existence of electric field gradients (EFG) at the Fe sites

whose magnitude is well defined and about the same as in crystals.⁵ However, because the Mössbauer quadrupolar splitting in the paramagnetic region depends upon the magnitude of the EFG, but not on its direction, these findings do not allow a proper comparison between the local symmetry in an amorphous alloy and that in the related crystal.⁵ Such a comparison would require the knowledge of the symmetry properties of the EFG as can be obtained through NMR measurements.

Concerning the SRO around the *glass-former* elements (GF), the experimental information is rather meager. X-ray and neutron scattering techniques encounter some severe limitations, due namely to the dominating contributions from the heavier elements, to the relatively low concentration of s - p elements and to the radius ratio of the constituents.⁶ These difficulties have been partially overcome with polarized neutron scattering. Nevertheless, the most reliable information about the local coordination around a GF atom was obtained from extended x-ray-absorption fine-structure measurements (EXAFS) on Ge in α -Pd₃Ge.⁷ In summary, while the average local symmetry around the TM sites is partially known, that around the GF atoms remains practically unknown to date. Such an experimental information seems to be highly desirable, since the ma-

for controversies concerning amorphous solid structure and its relation to crystal structure center on the topology of this SRO.¹ In this context, we undertook an NMR study of the electric quadrupole effects on *s-p* elements in some typical amorphous metallic alloys. It has to be noted that the NMR technique has been successfully used for years in investigating the local structure of nonmetallic glasses.⁸

We present the results of spin-echo spectra (i) of ⁷¹Ga in splat-cooled glassy La₇₅Ga₂₅, (ii) of ¹¹B in sputtered amorphous Mo₇₀B₃₀ and in splat-cooled glassy Mo₄₈Ru₃₂B₂₀, and (iii) of ¹¹B in glassy Ni₇₈P₁₄B₈ quenched from the melt. These alloys were chosen for the following reasons. First, the corresponding crystalline compounds (La₃Ga, Mo₂B, Ni₃B) represent three cases of crystal structures (cubic, tetragonal, orthorhombic, respectively), and thus three types of local symmetry (spherical, cylindrical, nonuniaxial, respectively), so that the effects of amorphousness could be detected in three significant situations. Secondly, these alloys allow one to determine whether the local symmetry depends on such factors as the techniques of fabrication (sputtering versus melt quenching) or the alloy composition (Mo₇₀B₃₀ versus Mo₄₈Ru₃₂B₂₀). We show that, irrespective of the preparation technique, the quadrupole spectra observed for the GF atoms in the different amorphous alloys reproduce to a large extent the symmetry properties of the EFG in the related crystalline compounds.

The glassy Ni₇₈P₁₄B₈, Mo₄₈Ru₃₂B₂₀, and La₇₅Ga₂₅ alloys were quenched from the melt by use of the "piston-and-anvil" technique. The amorphous Mo₇₀B₃₀ was obtained by sputtering on to an ambient temperature substrate. Samples of *a*-Ni₇₈P₁₄B₈ were the same as those used for bulk magnetic measurements and for previous studies of Knight shift and spin-lattice relaxation time.⁹ Samples of Mo₄₈Ru₃₂B₂₀ belong to the same batch of foils on which superconducting, mechanical, and structural properties were studied.¹⁰ Superconducting properties of amorphous La₇₅Ga₂₅ alloys have been reported.¹¹ The amorphous nature of our samples was checked by x-ray scanning. Concentrations are nominal. Measurements were performed on as-plated foils. A coherent spin-echo NMR technique was used at a fixed frequency of 9 MHz to observe the NMR spectra of ¹¹B and ⁷¹Ga (both having a spin $I = \frac{3}{2}$).

Let us summarize first the information which one can obtain from NMR¹² about the EFG together with the standard notation we will use in

processing the data.¹³ The EFG interacts with the quadrupole moment *Q* of the resonant nucleus (¹¹B, ⁷¹Ga) through the quadrupole coupling. The EFG traceless tensor is determined by the quadrupolar constant $\nu_Q = e^2qQ/2h$ for $I = \frac{3}{2}$ (proportional to the largest eigenvalue $V_{zz} \equiv eq$ of the EFG tensor $|V_{zz}| > |V_{yy}| > |V_{xx}|$) and by a dimensionless coefficient $\eta = (|V_{xx} - V_{yy}|)/|V_{zz}|$ ($0 \leq \eta \leq 1$). The asymmetry parameter η is a measure of the departure from a cylindrical symmetry ($\eta = 0$). The quadrupole frequency ν_Q is a measure of the deviation from the spherical symmetry ($V_{zz} = V_{yy} = V_{xx} = 0$). Since in amorphous materials the local EFG principal-axis system is randomly oriented with respect to external magnetic field, the observed NMR spectra will resemble the so-called "powder patterns", unbroadened examples of which are given in insets of Figs. 1–3 for various local symmetries. In these "theoretical" examples as well as in our experimental studies, the quadrupole interactions remain small as compared with the Zeeman interaction, which then mostly determines the resonant conditions. The shape of the observed spectra strongly depends on the values of ν_Q and η , making possible a characterization of the local symmetry which would be hardly or not obtainable by other techniques.

The spin-echo spectra presented in Figs. 1–3 are nearly self-conclusive. The symmetries of the EFG are quite different for *a*-La₇₅Ga₂₅ (Fig. 1), for *a*-Mo₇₀B₃₀ and *a*-Mo₄₈Ru₃₂B₂₀ (Fig. 2), and for *a*-Ni₇₈P₁₄B₈ (Fig. 3). The three types of local symmetries one can determine from the experimental data on these three groups of amorphous alloys exhibit obvious similarities with

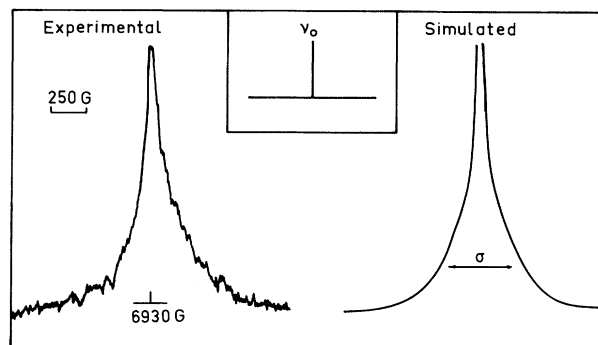


FIG. 1. Experimental ($T = 10^\circ\text{K}$) and simulated NMR spectra in *a*-La₇₅Ga₂₅. Inset: unbroadened spectrum for cubic local symmetry ($\nu_Q = 0$; $\eta = 0$). $\nu_0 = \gamma_n H$ (Larmor frequency). For definition of ν_Q , η , and σ , see text.

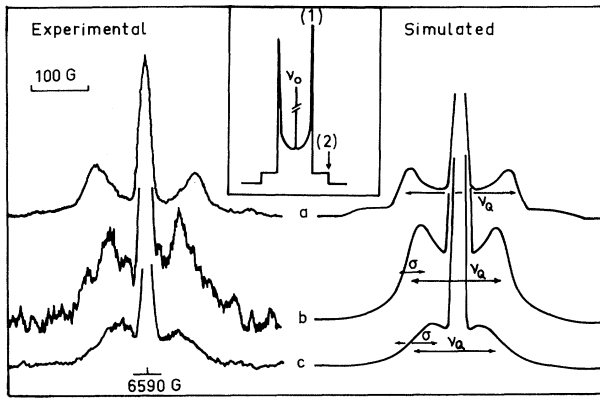


FIG. 2. Experimental ($T = 10^\circ\text{K}$) and simulated NMR spectra in (a) $c\text{-Mo}_2\text{B}$, (b) $a\text{-Mo}_{70}\text{B}_{30}$, and (c) $a\text{-Mo}_{48}\text{-Ru}_{32}\text{B}_{20}$. Inset: unbroadened "powder pattern" for cylindrical local symmetry ($\nu_Q \neq 0$; $\eta \neq 0$); (1) $\nu_0 + \frac{1}{2}\nu_Q$; (2) $\nu_0 + \nu_Q$.

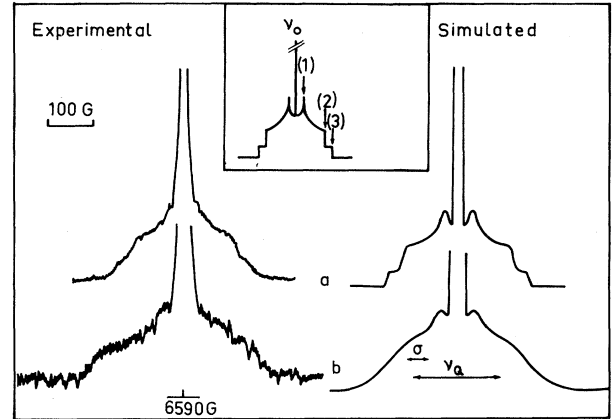


FIG. 3. Experimental ($T = 4.2^\circ\text{K}$) and simulated NMR spectra in (a) $c\text{-Ni}_3\text{B}$ and (b) $a\text{-Ni}_{78}\text{P}_{14}\text{B}_8$. Inset: unbroadened "powder pattern" for nonuniaxial local symmetry ($\nu_Q \neq 0$; $\eta = 0.6$); (1) $\nu_0 + \frac{1}{2}\nu_Q(1 - \eta)$; (2) $\nu_0 + \frac{1}{2}\nu_Q(1 + \eta)$; (3) $\nu_0 + \nu_Q$.

the symmetries of the related compounds, as shown by the ^{11}B spectra taken on crystalline uniaxial Mo_2B ($\eta = 0$) (Fig. 2) and nonuniaxial Ni_3B ($\eta \neq 0$) (Fig. 3). No spectrum was measured on ^{71}Ga in the metastable La_3Ga compound. Because of the absence of quadrupole effects in a cubic symmetry ($\eta = \nu_Q = 0$), this ^{71}Ga spectrum should look like a unique line with a slight broadening.

A more quantitative comparison can be obtained from computer simulations of the experimental spectra. For the crystalline compounds, a trial-and-error fit provides numerical values for ν_Q and η . For the amorphous alloys, the spectra were simulated by assuming a Gaussian distribution of ν_Q 's (with a rms half-width σ) around a central value $|\bar{\nu}_Q|$ and by using a single value for η . No *a priori* assumption was made on the values of $\bar{\nu}_Q$ and η in the amorphous cases. We did not try to introduce a distribution of η values due to the limited number of marked structures in the experimental spectra. The sensitivity of the fit on the various parameters was checked. The extreme values of $|\bar{\nu}_Q|$, η , and $\sigma/|\bar{\nu}_Q|$ compatible with our data are listed in Table I. It can be seen that the values we obtained for $\bar{\nu}_Q$ and η in our amorphous samples are rather close to that determined for the compositionally related compounds. For the simulations reproduced in Figs. 1–3, we used the values of ν_Q and $\bar{\nu}_Q$ given in Table I for the crystalline and amorphous alloys, respectively. The values of η in amorphous alloys were taken to be identical to those of the crystalline counterparts.

Several remarks have to be made concerning our fitting procedure. (i) For all simulated spectra, we had to introduce an additional broadening of the overall spectrum, in order to reproduce the central line broadening mostly due to experimental conditions and dipolar interactions. This parameter was found to have no significant influence on the shape of the remaining spectrum within reasonable limits. (ii) With use of a rectangular distribution of ν_Q 's instead of a Gaussian one with the same rms width introduces no meaningful difference within the limits of experimental accuracy. (iii) We could not rule out a non-zero value for $\bar{\nu}_Q$ in $a\text{-La}_{75}\text{Ga}_{25}$. But the shape of the spectrum is only compatible with strong values of the $\sigma/\bar{\nu}_Q$ ratio, which indicates a particular randomness of the quadrupole interactions in this metallic glass.

Our conclusions can be summarized as follows.

(i) There exist different types of local symme-

TABLE I. EFG parameters in amorphous (*a*) alloys and in related crystalline (*c*) compounds.

Compounds	$ \bar{\nu}_Q $ (kHz)	η	$\sigma/ \bar{\nu}_Q $
<i>c</i> - La_3Ga (cubic)	0	0	...
<i>a</i> - $\text{La}_{75}\text{Ga}_{25}$	<100	...	>2
<i>c</i> - Mo_2B (tetragonal)	240 ± 10	0	...
<i>a</i> - $\text{Mo}_{70}\text{B}_{30}$	210 ± 20	0–0.2	0.2–0.3
<i>a</i> - $\text{Mo}_{48}\text{Ru}_{32}\text{B}_{20}$	180 ± 20	0–0.3	0.4–0.6
<i>c</i> - Ni_3B (orthorhombic)	180 ± 10	0.6	...
<i>a</i> - $\text{Ni}_{78}\text{P}_{14}\text{B}_8$	220 ± 20	0.5–0.8	0.2–0.3

tries around the GF atoms in amorphous alloys of transition metals with sp elements. (ii) These local symmetries with rather well-characterized values of \bar{v}_Q and η and various degrees of randomness σ/\bar{v}_Q strongly reflect the local symmetries prevailing in the related crystalline compounds. (iii) For a given amorphous system, the local symmetry does not depend on the fabrication technique. The symmetry is defined with the same accuracy in sputtered a -Mo₇₀B₃₀ and in liquid-quenched Mo₄₈Ru₃₂B₂₀ and it is of uniaxial type in both amorphous alloys. (iv) The degree of randomness σ/\bar{v}_Q is sensitive to the supplementary chemical disorder introduced by substitution of Ru for Mo in a -Mo₄₈Ru₃₂B₂₀ as compared with a -Mo₇₀B₃₀.

Finally, let us make two concluding remarks. First, it does not seem compatible with our results to assume that—at least for the local structure of amorphous alloys of the type which we studied—geometrical considerations alone are important and that the glass-former atoms fit into holes whose shape and size would be determined only by the packing of the metallic atoms. For example, in a Bernal-Polk picture, the “canonical holes” have basically a spherical or cylindrical symmetry, so that they could not give rise without severe distortions to the large values for η found on B¹¹ in a -Ni₇₈P₁₄B₈ alloys. In a recent model,¹⁴ the amorphous structure is simulated by random packing of elementary motifs which are dominant in the transition-metal silicides, borides, and phosphides. Such an approach would seem more appropriate in view of our data. Second, it should be emphasized that our measurements concern only the glass-former atoms. Similar study has to be extended to the transition-

metal sites and to different families of amorphous alloys (of the metal-metal type, for instance).

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