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Time-differential perturbed-angular-correlation study of the electric field gradient in amorphous $Zr_{68}Hf_2Cu_{30}$

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The electric field gradient at Zr sites has been measured by time-differential perturbed angular correlations in amorphous and crystalline $Zr_{68}Hf_2Cu_{30}$ alloys. The results support a dense random packing of atoms and discard any kind of regular atomic arrangements in the amorphous alloy.

The relevance of electric-field-gradient (EFG)-sensitive techniques in the understanding of the local atomic order in amorphous alloys has been already emphasized in several papers.[1-4] The EFG at the probe sites depends on the symmetry of the charges surrounding them and therefore it provides direct experimental information about the angular distribution of local atomic arrays. Up to now, such techniques (Mössbauer spectroscopy, NMR, TDPAC) have been applied mainly to metal-metalloid amorphous alloys. The results demonstrated that in various systems the local symmetry at the metalloid site resembles that of crystalline compounds of close composition.[2] However, these techniques have been rarely applied to metal-metal amorphous alloys, particularly those containing an early transition metal and a late transition or noble one. Therefore scarce information is available on the angular distribution of local atomic arrangements in such systems. Recently, Eiffert, Elschner, and Buschow have reported on a NMR study, on Zr and Cu, in $Zr_{1-x}Cu_x$ alloys.[3] Their results have been interpreted as evidence for the occurrence of compositional short-range order in these alloys. In particular, for $x = 0.28$ they conclude that the local atomic arrangements are quite symmetrical and similar to that in crystalline Zr_2Cu. This contradicts recent studies on these alloys by x-ray diffraction and differential thermal analysis[5] and extended x-ray-absorption fine structure[6] which support a dense random packing (DRP) of atoms.

We then initiate a TDPAC investigation on such amorphous systems with the aim of contributing to the understanding of their local atomic structure. In this Communication we report on our first EFG measurements on the amorphous $Zr_{68}Hf_2Cu_{30}$ alloy with composition close to that of crystalline Zr_2Cu.

We included 2 at.% Hf in the alloy in order to have, after thermal neutron irradiation, the appropriate ^{181}Hf activity required for our measurements. The β decay of ^{181}Hf populates the 133–482-keV γ-γ cascade in ^{181}Ta well suited for TDPAC experiments. We do not expect that the presence of Hf will modify the structural properties of the alloy since Hf and Zr have practically the same metallic radius and almost identical chemical behavior. Indeed, diffraction studies on Ni-Zr-Hf alloys indicate that each atom—Zr or Hf—can freely substitute for the other without affecting their local environments.[7] Then, in the following, the alloy will be referred to as $Zr_{70}Cu_{30}$.

Alloys of adequate composition were prepared by arc melting in an argon atmosphere, broken up, and remelted several times. Finally, they were melt spun on a rotating copper wheel under argon.[8] The amorphous state of the resulting ribbons was verified by resistivity measurements. Both the temperature coefficient of resistivity TCR $\simeq 1.6 \times 10^{-4}$ K^{-1} and critical superconducting temperature $T_C \simeq 2.7$ K are in agreement with typical values in amorphous $Zr_{70}Cu_{30}$ alloys. Crystalline and amorphous samples were then irradiated with thermal neutrons in order to produce, through the reaction ^{180}Hf(n,γ)^{181}Hf, the desired ^{181}Hf activity.

The TDPAC measurements were performed using a conventional two-detector apparatus described elsewhere,[9] providing a time resolution full width at half maximum (FWHM) of 1.6 ns. After subtraction of chance coincidence background, time spectra corresponding to angles 90° and 180° between detectors were combined to form the ratio,

$$R(t) = 2\frac{N(180°,t) - N(90°,t)}{N(180°,t) + 2N(90°,t)} .$$

Theoretical functions of the form $A_2G_2(t)$, folded with the measured time resolution curve, were least-squares fitted to the experimental $R(t)$. For a given nuclear probe the factor A_2 just depends on the geometry of the experimental arrangement and the "perturbation factor" $G_2(t)$ contains the information about the EFG interacting with the probe's quadrupole moment. For the simplest case—a single static quadrupole interaction in a powder source—it takes the form

$$G_2(t) = s_0(\eta) + \sum_1^3 s_n(\eta)\cos[\omega_n(V_{zz},\eta)t] ,$$

where s_0, s_n, and ω_n are known functions of the EFG components V_{zz} and $\eta = (V_{xx} - V_{yy})/V_{zz}$.

Figure 1(a) shows the TDPAC spectrum of the amorphous sample obtained at room temperature, which has the shape characteristic of a broad distribution of quadrupole frequencies. First, the observed distribution was simulated by the distribution function,

$$P(V_{zz},\eta) = \left(\frac{2}{\pi}\right)^{1/2} \frac{\eta}{\Delta_{zz}} \exp\left(-\frac{(V_{zz} - V_{zz}^0)^2}{2\Delta_{zz}^2}\right) ,$$

based on a DRP of hard spheres.[1,4] Inserting this function in the perturbation factor, and integrating over V_{zz} and η,

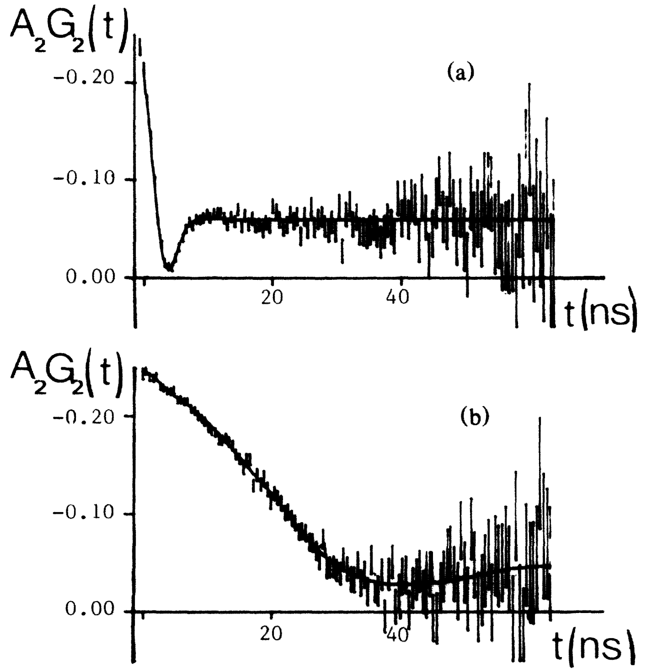

FIG. 1. TDPAC spectra obtained at room temperature on $Zr_{68}Hf_2Cu_{30}$ alloys: (a) amorphous (fast quenched) sample, (b) crystalline (annealed during 72 h at 900 °C) sample.

the fit yields the following parameters:

$$\omega_Q = eQV^0_{zz}/40\hbar = 80(1)\ \text{Mrad/s},\quad \delta = \Delta_{zz}/V^0_{zz} = 0.36(1)\ ,$$

and, obviously, $\eta(\text{average}) = \frac{2}{3}$. These values are weighted averages over five independent measurements.

Good fits were also obtained assuming simply a Gaussian distribution of V_{zz} (i.e., of ω_Q) and a unique value of η. In this case the fitted parameters were

$$\omega_Q = 86.4(3.1)\ \text{Mrad/s},\quad \eta = 0.56(6),\quad \delta = 0.37(1)\ .$$

Although both fits were of similar quality we think that the first approach is more realistic because it includes distributions in all the components of the EFG tensor.

We also measured the amorphous sample at 17 K and no variations were noticeable in the spectrum shape nor in the fitted parameters.

For further comparisons we measured a sample of the starting crystalline alloy after an homogenizing heat treatment.[10] The sample was capsulated in a quartz tube under Ar, treated for 72 h at 900 °C, and quenched in tap water. The spectrum obtained at room temperature is shown in Fig. 1(b); its overall shape corresponds to a small quadrupole interaction frequency. Since, from the equilibrium diagram we expect some α-Zr to be present, in addition to the Zr_2Cu compound, we attempted a fit with two quadrupole interactions. The resulting parameters were the following:

$$f_1 = 0.90(3),\quad \omega_{Q_1} = 6.6(2)\ \text{Mrad/s},\quad \eta_1 = 0.0(4),$$
$$\delta_1' = 0.03(3)\ ,$$
$$f_2 = 0.10(2),\quad \omega_{Q_2} = 49(4)\ \text{Mrad/s},\quad \eta_2 = 0.21(18),$$
$$\delta_2' = 0.12(9)\ ,$$

where f_1 (f_2) is the relative fraction of nuclei experiencing a given quadrupole perturbation (i.e., the relative concentration of each phase) and δ_1' (δ_2') the relative width (FWHM) of a Lorentzian frequency distribution around ω_{Q_1} (ω_{Q_2}). The second set of quadrupole parameters agree well with those previously reported for α-Zr (Ref. 11) and then, according to the equilibrium diagram, we ascribed the first one to crystalline Zr_2Cu. The low value of η obtained is consistent with the axial symmetry of its tcp structure.[10]

From the fitted parameters and the reported value for the quadrupole moment of $\frac{5}{2}^+$ level in ^{181}Ta, $Q = 2.51(15)$ b (Ref. 11), we determined the following EFG components:

$$V^0_{zz} = 8.4(5)\times 10^{17}\ \text{V/cm}^2,\quad \bar{\eta} = 0.67\ ,$$

and

$$V^0_{zz} = 0.69(5)\times 10^{17}\ \text{V/cm}^2,\quad \eta = 0.0(4)\ ,$$

at Zr sites in a-$Zr_{70}Cu_{30}$ and c-Z_2Cu, respectively. As can be seen the EFG strength in the amorphous alloy is 12 times larger than that in its crystalline counterpart. This disagrees with the result of Eiffert *et al.* who found similar V_{zz} values for both systems using ^{91}Zr probes. The discrepancy affects not only the amorphous to crystalline V_{zz} ratio but also their absolute magnitudes. A direct comparison is not possible because of the different antishielding factors of the probes used, but taking as a reference the quadrupole frequencies obtained with either probe in α-Zr (Ref. 11), we found

$$\frac{V^0_{zz}(^{181}\text{Ta in } Zr_{68}Hf_2Cu_{30})}{V^0_{zz}(^{91}\text{Zr in } Zr_{72}Cu_{28})} = 4.2(2)\ .$$

This is too large a difference to be accounted for by the experimental uncertainties or by the probe's dependent effects. Indeed, comparing the results obtained with either probe in pure transition metals[11] we found slight differences of both signs give no indication of a systematic trend. Nevertheless, the adequacy of ^{181}Ta for TDPAC experiments, in particular its quadrupole moment—well suited for the frequencies involved—and the quality and reproducibility of the obtained spectra are sufficient elements to rely on our measurements. Therefore we will discuss our results without guessing at the reasons of such discrepancies.

As we have already pointed out the V^0_{zz} at a-$Zr_{70}Cu_{30}$ is about an order of magnitude larger than that in tcp Zr_2Cu. We interpret this result as an indication for the lack of short-range order in the amorphous alloy. As Panissod[2] has discussed, in amorphous systems the net mean EFG at a probe site should be determined mostly by its closest neighbors (up to ≃4 Å), while due to the absence of long-range order, the distant ones would contribute just to the EFG fluctuations from site to site. The situation is quite different in crystalline structures where the distant neighbors are still important in that they considerably reduce the EFG due to the closer ones. This can justify the slightly higher V_{zz} found in some amorphous alloys,[2] with respect to the corresponding crystals, when a crystalline-like structure may be assumed. But this argument could not explain the factor of 12 encountered in our case. In other words, our results do not support a description of the a-$Zr_{70}Cu_{30}$ structure in terms of "cells" resembling the symmetry of c-Zr_2Cu. Considering the first coordination shell in Zr_2Cu—made up of four Cu atoms at 2.90 Å, four Zr at 3.09 Å, and four Zr at 3.22 Å—it is evident that a strong cancellation occurs between the contributions to the EFG from Zr atoms in the plane of the probe normal to the c axis and those from Zr and Cu atoms out of this plane. Certainly in the amorphous alloy there ought to occur pronounced alterations of this regular situation in order to account for the observed V_{zz} and η values. Indeed, extended x-ray-absorption fine-structure studies on this alloy[6] reveal an average first coordination shell composed by 3.5 Cu atoms at 2.71 Å, 4 Zr at 3.19 Å, and 3 Zr at 3.43 Å. As can be seen, Cu atoms have approached the central Zr atom at distances smaller than the sum of their Goldschmidt's radii (2.88 Å), so displacing the Zr first neighbors.

Heretofore, we have ignored the EFG arising from electronic charges. In metals, their contribution is normally assumed to be proportional to the ionic EFG, through a "universal" constant $K \simeq -3$. This simple picture has been seriously questioned by numerous new data on EFG's, particularly in transition metals where the predicted sign reversal was often not observed.[11,12] On the other hand, theoretical approaches to the problem indicate a linear dependence of the electronic EFG on the electronic density of states at the Fermi level. Susceptibility measurements of Altounian, Guo-Hau, and Strom-Olsen[13] indicate that the density of states at the Fermi level is 2.5 times larger in amorphous $Zr_{70}Cu_{30}$ than in c-Zr_2Cu. If the above prediction is correct we can expect a similar enhancement in the electronic contribution to the EFG, in passing from the crystalline to the amorphous structure. Nevertheless, this would not suffice to give account of the observed EFG differences.

In summary, the observed V_{zz}, η, and δ values in a-$Zr_{70}Cu_{30}$ confirm the hypothesis of a DRP of atoms for this alloy, discarding any kind of regular environment for Zr sites.

Further TDPAC studies on the crystallization of this alloy and the EFG dependence on the Cu content are in progress.

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