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# Nuclear quadrupole interaction in glassy $Hf_{1-x}Cu_x$ alloys and their local structures

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The electric field gradient (EFG) at Hf sites in amorphous $Hf_{1-x}Cu_x$ alloys was measured for $x=0.33$, 0.44, 0.50, and 0.59 with use of the time-differential perturbed angular correlation technique. The results show no evidence of crystallinelike local order in these alloys, supporting a description of their local structure in terms of a dense random packing of atoms. The local and lattice contributions to the EFG, as well as their dependence on composition, are discussed.

## I. INTRODUCTION

The structure of amorphous metals is characterized by the absence of long-range atomic order but the actual atomic arrangement around an atom, the short-range structure, is still an open question. Dense random packing (DRP) of ions and a random network (RN) of structural units have alternatively been proposed to explain the short-range order (SRO) observed in various systems, mainly through diffraction experiments.

The electric field gradient (EFG) at a given atomic site is sensitive to local atomic coordinations, especially with respect to the angular distribution of near neighbors.[1] Thus the observation of nuclear quadrupole interactions through "hyperfine" techniques, such as time-differential perturbed angular correlations (TDPAC), could be helpful in understanding the local structure of amorphous alloys.

Early transition metals and late transition or noble ones form amorphous alloys through a wide composition range with distinctive electronic properties. Among them, $Zr_{1-x}Cu_x$ is by far the most studied system and much work has been published about its structural and electronic properties.[2] Even in this case scarce information is available on the angular distribution of local atomic arrangements. We have thus initiated a systematic TDPAC investigation on such amorphous systems with the aim of contributing to the understanding of their local atomic structure.

In a previous work we substituted some Hf atoms for Zr, $^{181}$Hf being an excellent probe for TDPAC measurements, in order to study the EFG in *a* (amorphous) -$Zr_{70}Cu_{30}$ and its crystalline counterpart $Zr_2Cu$.[3] The conclusion arrived at in that paper was that the observed quadrupole interaction could be attributed to an EFG originating in a dense random packing of atoms around the probes.

We turned our attention to the system *a*-$Hf_{1-x}Cu_x$ and made TDPAC experiments in order to analyze the compositional dependence of the EFG at Hf sites. Few papers have been published on this amorphous system. Particularly, the thermal stability of *a*-$Hf_{71}Cu_{29}$ and *a*-$Hf_{44}Cu_{56}$ was investigated by Buschow and Beekmans[4] and that of *a*-$Hf_{67}Cu_{33}$ and $Hf_{50}Cu_{50}$ by Schulz *et al.*[5] Recently, Sakurai *et al.*[6] reported on TDPAC experiments in an alloy of composition $Hf_{43}Cu_{57}$ but, as we will see later, the amorphicity of that sample is open to doubt.

We present here results on the EFG components: $V_{zz}$ and $\eta$, at Hf sites in *a*-$Hf_{1-x}Cu_x$ alloys with $x=0.33$, 0.44, 0.50, and 0.59. The compositions of two of them, *a*-$Hf_{67}Cu_{33}$ and *a*-$Hf_{41}Cu_{59}$, were selected to coincide with those of the only two known intermetallics: $Hf_2Cu$ (Ref. 7) and $Hf_7Cu_{10}$ (Ref. 8) within the expected range of amorphization: $0.3 \le x \le 0.7$. We measure also the EFG in these crystalline compounds to contrast with the results in the amorphous samples.

## EXPERIMENT

Alloys of adequate compositions were prepared by arc melting in an argon atmosphere, broken up and remelted several times. Finally they were melt spun on a rotating (water cooled) copper wheel under argon.[9] All alloys were found to have x-ray diagrams characteristic of the amorphous state. Sharp diffraction lines indicating the presence of crystalline material were absent.

Crystalline and amorphous samples were then irradiated with thermal neutrons in order to produce the desired activity of $^{181}$Hf. The $\beta$ decay of $^{181}$Hf populates the 133–482-keV $\gamma$-$\gamma$ cascade in $^{181}$Ta well suited for TDPAC experiments. They were performed in a conventional two-detector apparatus described elsewhere[10] providing a time resolution [full width at half maximum (FWHM)] of 1.6 ns.

The amorphous samples were measured as irradiated and after a relaxing heat treatment at 250 °C for 2 h. The crystalline ones were measured after homogenizing heat treatments of 2 h at 600 °C for $Hf_2Cu$ (Ref. 7) and 2 h at 750 °C for $Hf_7Cu_{10}$.[8] All measurements were performed at room temperature.

## RESULTS

Figure 1 shows the TDPAC spectra of the unrelaxed amorphous samples, all of them displaying the shape characteristic of a broad distribution of quadrupole frequencies. Also shown is the result of least-squares fittings to the data of the perturbation factor:

$$G_2(t)=\int_0^1 d\eta \int_{-\infty}^{\infty} dV_{zz}\, P(V_{zz},\eta) G_2^0(t;V_{zz},\eta)\ , \quad (1)$$

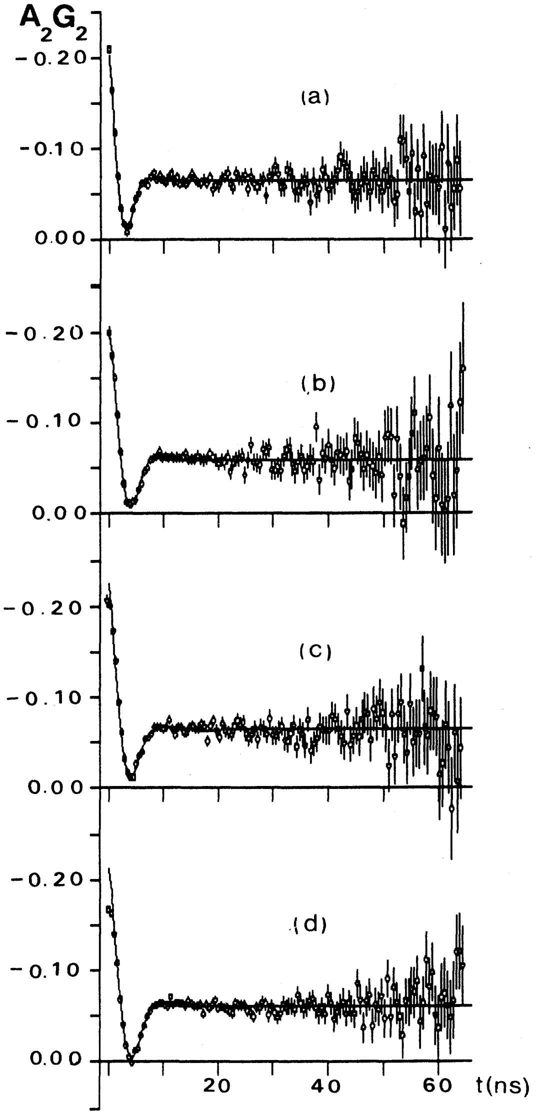

FIG. 1. TDPAC spectra and theoretical fits of amorphous samples: (a) $Hf_{67}Cu_{33}$, (b) $Hf_{56}Cu_{44}$, (c) $Hf_{50}Cu_{50}$, and (d) $Hf_{41}Cu_{59}$.

where $G_2^0(t;V_{zz},\eta)$ is the usual quadrupole perturbation factor for polycrystalline samples. The quadrupole frequency is determined by $\omega_Q = eQV_{zz}/40\hbar$ and $Q = 2.51_{15}b$[17]. The distribution function[11]

$$P(V_{zz},\eta) = \sqrt{2/\pi}\,\eta/\Delta_{zz}\exp[-(V_{zz}-V_{zz}^0)^2/2\Delta_{zz}^2] \qquad (2)$$

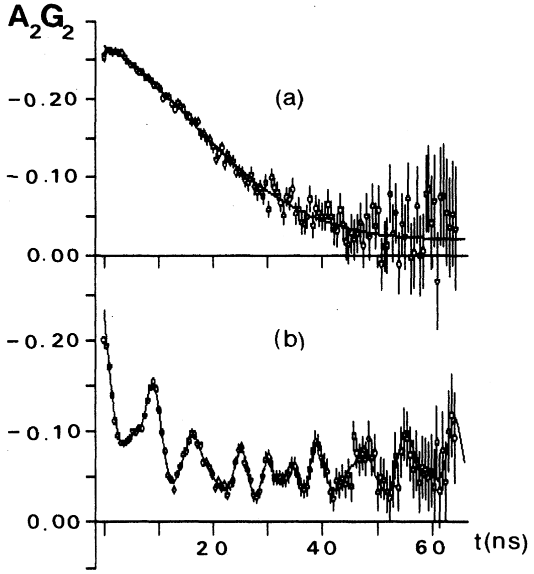

FIG. 2. TDPAC spectra and theoretical fits of crystalline samples: (a) $Hf_2Cu$ and (b) $Hf_7Cu_{10}$.

approximately accounts for the EFG distribution in a DRP of ions[1] (see Appendix). Similar results were obtained for the relaxed samples. Other attempts to fit these data will be discussed in the next section.

Figure 2 shows the results for the homogenized crystalline samples and fits with the perturbation factor:

$$G_2(t) = \sum_i f_i G_2^i(t;V_{zz},\eta,\delta) \;, \qquad (3)$$

where $G_2^i(t;V_{zz},\eta,\delta)$ describes a Lorentzian-distributed quadrupole interaction at sites with relative population $f_i$. As expected from its crystalline structure, $Hf_2Cu$ can be fitted with a single symmetric quadrupole interaction of relatively low strength. At this low-frequency limit it is difficult to obtain the true values of $\omega_Q$ and $\delta$ from the spectrum. The reported values are the result of an unconstrained fit which yields a rather broad distribution. Instead, at least four interactions are needed to fit the $Hf_7Cu_{10}$ spectrum. Again this is consistent with crystallographic data which yield a very complicated unit cell for this compound, with five different Hf sites of relative populations: $\frac{1}{7}$, $\frac{1}{7}$, $\frac{1}{7}$, $\frac{2}{7}$, and $\frac{2}{7}$.[12] The fitted populations agree with these if we admit similar EFG's at two minority sites. A closer inspection of the crystalline structure suggests that this could be the case for sites 1a and 1b in Ref. 12.

TABLE I. Fitted parameters and principal components of EFG tensor for amorphous samples.

| | Unrelaxed | | | Relaxed | | |
|---|---|---|---|---|---|---|
| (at. % Cu) | $\omega_Q^0$ ($10^6$ rad/s) | $\delta$ | $V_{zz}^0$ ($10^{17}$ V/cm$^2$) | $\omega_Q^0$ ($10^6$ rad/s) | $\delta$ | $V_{zz}^0$ ($10^{17}$ V/cm$^2$) |
| 0.33 | $95.4_{1.1}$ | $0.33_2$ | $10.0_6$ | $87.6_{1.0}$ | $0.35_1$ | $9.2_6$ |
| 0.44 | $84.3_{1.0}$ | $0.32_3$ | $8.8_6$ | $81.8_{2.0}$ | $0.35_2$ | $8.6_6$ |
| 0.50 | $79.7_{2.0}$ | $0.36_2$ | $8.4_6$ | $72.7_{1.9}$ | $0.37_2$ | $7.6_5$ |
| 0.59 | $75.4_{1.0}$ | $0.31_1$ | $7.9_5$ | $68.7_{1.2}$ | $0.33_1$ | $7.2_5$ |

TABLE II. Quadrupole parameters of crystalline Hf-Cu alloys.

| Sample | $f_i$ | $\omega_Q(10^6$ rad/s) | $\eta_i$ | $\delta_i$ |
|---|---|---|---|---|
| $c$-$Hf_2Cu$ | $1.0_0$ | $5.1_2$ | $0.00_0$ | $0.29_3$ |
| $c$-$Hf_7Cu_{10}$ | $0.28_1$ | $10.2_2$ | $0.30_8$ | $0.06_4$ |
|  | $0.30_4$ | $107.3_8$ | $0.26_2$ | $0.01_1$ |
|  | $0.14_3$ | $111.4_{1.4}$ | $0.48_2$ | $0.00_1$ |
|  | $0.28_3$ | $123.8_4$ | $0.22_1$ | $0.00_1$ |

The results of the fits described below are displayed in Tables I and II. From these results a few conclusions may readily be extracted.

(1) The TDPAC spectra, concurrently with x-ray diffraction (XRD) observations, confirm the amorphous nature of all the studied samples, two of them, $Hf_{56}Cu_{44}$ and $Hf_{41}Cu_{59}$, not reported previously. Furthermore, based on the present results, we may conclude that the "crystallinelike atomic arrangements" reported by Sakurai *et al.*[6] in their TDPAC study of $Hf_{43}Cu_{57}$ are not characteristic of the amorphous "state" but simply indicate a deficient amorphization of the alloy. They could be produced by partial crystallization of their sample (too low quenching rate) or correspond to atomic clustering in the melt (too low starting temperature).

(2) The average EFG strength $V_{zz}^0$ (i) is systematically reduced (8% on the average) by the relaxing treatment; (ii) it decreases monotonically with copper concentration in both relaxed and unrelaxed samples [the dependence on $x$ is roughly linear with a relative slope: $(dV_{zz}^0/dx)/V_{zz}^0(0)\approx\frac{2}{3}$]; (iii) it differs markedly from those observed in the crystalline phases.

(3) The relative width of the EFG distribution $\delta=\Delta_{zz}/V_{zz}$ appears to be independent of the alloy composition and approaches the DRP value, $\delta\approx0.35$ (see Appendix).

(4) In the crystalline phases all the observed perturbations have $\eta$ values lower than 0.5.

## DISCUSSION

The above remarks and even the plain shape of our spectra, denoting a broad distribution of the EFG components through the sample, allow us to discard the existence of well-defined structural units. This gives no support to a RN model for these alloys and favors a DRP description of their local structure.

In order to gain further insight into the EFG distribution in these alloys we followed a procedure suggested by Maurer *et al.*,[13] to analyze the marginal $\eta$ distribution. A perturbation factor similar to that of Eq. (3) was used to fit the data with a sum of four quadrupole interactions Gaussian distributed and of fixed asymmetry: $\eta=\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, and $\frac{7}{8}$ representing four equal intervals covering the full range of $\eta$ values. Then, from the fitted population factors $f_i$ a histogram of $P(\eta)$ was determined as shown in Fig. 3 for unrelaxed samples (the analysis of relaxed samples yields similar results). Also shown is the predicted distribution for a DRP model.[1]

In all the studied samples we found approximately a $\frac{2}{3}$ probability for $\eta\geq0.5$ as predicted by Czjzek *et al.*[1] for a DRP structure. The histograms for $x=0.33$, 0.44, and 0.50 are very similar, showing a maximum probability for $\eta$ values in the interval 0.50–0.75. Within the experi-

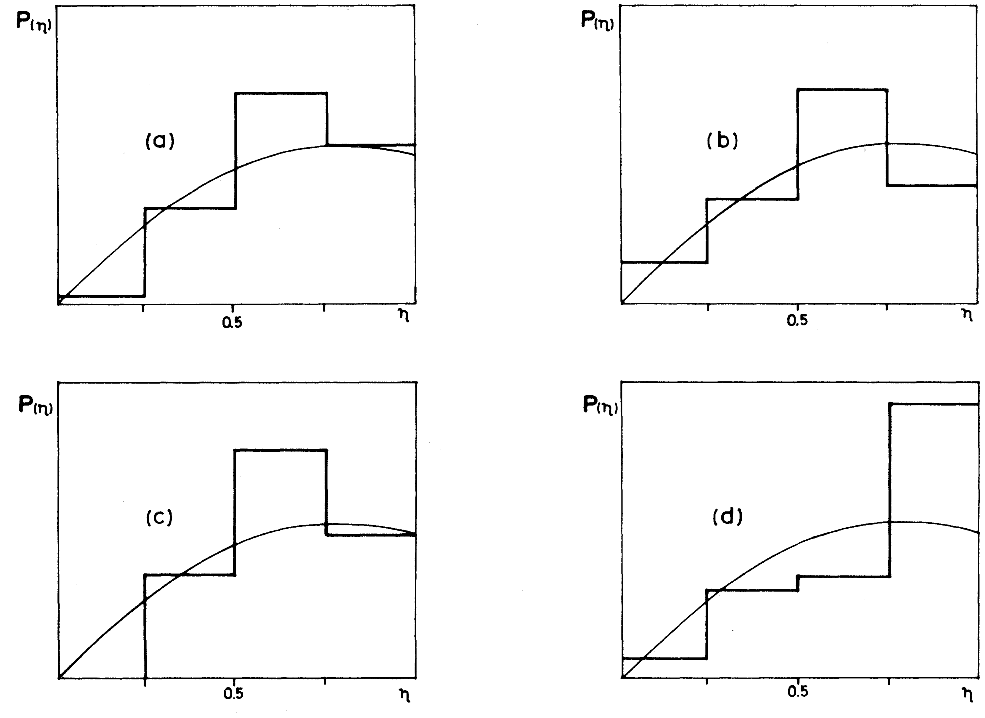

FIG. 3. Histograms of $\eta$ distribution (arbitary units) in (a) $Hf_{67}Cu_{33}$, (b) $Hf_{56}Cu_{44}$, (c) $Hf_{50}Cu_{50}$, and (d) $Hf_{41}Cu_{59}$.

mental errors and the uncertainties involved in the present analysis, they seem to reproduce the expected distribution for a DRP model. In the case of $x=0.59$ we found a marked preference for higher $\eta$ values which would indicate a variation in the local atomic environments at this composition which merits further investigations. Experiments with improved statistics to confirm the above findings are in progress.

The observed reduction of $V_{zz}^0$ upon annealing clearly evidences the effect of structural relaxation on the EFG. The removal of voids, tunneling states, etc., increase the topological SRO and lead to more "symmetric" configurations in the ideal amorphous structure, thus reducing $V_{zz}^0$.

Up to now we have not speculated about the origin of the observed EFG, usually divided into a lattice contribution (enhanced by the Sternheimer antishielding factor) and a local or electronic one. The studied alloys having a high $d$ density of states we must take into account a local contribution to the EFG coming mainly from the $d$ electrons around the probe, distorted from the spherical configuration by the presence of neighboring ions. On the other hand, a long distance screening of ions by $d$ electrons will occur, reducing the lattice EFG to the nearest-neighbors contribution (with adequate effective charges). Hence, the observed EFG would be of a very local nature, thus reflecting the local (electronic- and ionic-) charge distribution.

However, in amorphous systems the situation is further complicated by the fact that the orientation of both contributions would not necessarily coincide and we must, in principle, write $V_{ij}=(1-\gamma_\infty)V_{ij}^{\text{latt}}+V_{ij}^{\text{loc}}$. Since the perturbing potential for electrons and the gradient operator each contributes a $P_2(\cos\theta)$ factor, it has been argued that some "coherence" must then exist between both terms. Nevertheless, we think that for a thorough analysis of our results a detailed evaluation of the EFG tensor components for each contribution is needed.

To our knowledge there is one such calculation due to Levy Yeyati *et al.*[14] for the system $a$-$\mathrm{Zr}_{70}\mathrm{Cu}_{30}$. They obtained distributions for lattice, local, and total EFG at Zr sites, with mean values of $V_{zz}$ at 9.4, 11.3, and $18.2\times10^{17}$ $\mathrm{V/cm^2}$ (these values have been corrected to take into account the substitution of Ta for Zr as probe atom) and relative widths $\Delta_{zz}/V_{zz}$ of 0.27, 0.37, and 0.29, respectively. They also found that the $\eta$ distribution is practically the same for both contributions giving, for the total EFG, $\langle\eta\rangle=0.64$ and $\Delta\eta/\langle\eta\rangle=0.42$.

We may then conclude that both contributions are important in determining the strength of the observed EFG but also that the shape of the distribution is still representative of the local atomic arrangements. Furthermore, in this scheme we may interpret the observed dependence of $V_{zz}$ on $x$ as being mainly produced by the reduction in the $d$ charge localized at the probe, predicted by electronic structure calculations in $a$-$\mathrm{Zr}_{1-x}\mathrm{Cu}_x$.[15]

Finally, we must point out that the above-mentioned dependence of $V_{zz}^0$ has a suggestive similarity to that of the $d$ density of states at the Fermi level $N_d(0)$ in this kind of amorphous system.[15,16] Taking into account that several authors[17] have proposed an overall dependence of the local EFG on $N_d(0)$ we think that further theoretical work will be helpful for the understanding of this behavior.

## CONCLUSIONS

The observed EFG in $a$-$\mathrm{Hf}_{1-x}\mathrm{Cu}_x$ reveals the random nature of the atomic local environments in these alloys. Some deviations in the asymmetry distribution are observed for $\mathrm{Hf}_{41}\mathrm{Cu}_{59}$. Although there is an important electronic contribution to the EFG, the shape of $P(V_{zz},\eta)$ seems to be representative of the local atomic structure. Further theoretical work is needed to adequately understand the measured dependence of $V_{zz}^0$ on $x$.

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## APPENDIX

Czjzek *et al.*[1] derived an expression to describe the EFG distribution produced by a DRP of ions. Retaining only even terms in $V_{zz}$—since the perturbation factor for TDPAC just depends on $|V_{zz}|$—it reads

$$P(V_{zz},\eta)=\frac{(1-\eta^2/9)V_{zz}^4}{\sqrt{2\pi}\sigma^5}\exp[-(1+\eta^2/3)V_{zz}^2/2\sigma^2]\ ,$$

where $\sigma$ determines both the average and width of the distribution of $|V_{zz}|$. For a given value of $\eta$ this function has a maximum $P^0$ at $V_{zz}^0=2\sigma/(1+\eta^2/3)^{1/2}$ and a full width at $P^0/\sqrt{e}$, $2\Delta_{zz}=1.404\sigma/(1+\eta^2/3)^{1/2}\approx0.7V_{zz}^0$. Hence the predicted relative width $\delta=\Delta_{zz}/V_{zz}\approx0.35$ is independent of $\eta$.

The $V_{zz}$ dependence may then be approximated by a Gaussian distribution, i.e.,

$$P(V_{zz},\eta)\approx\frac{3\eta(1-\eta^2/9)}{[(1+\eta^2/3)^5]^{1/2}}\frac{1}{\sqrt{2\pi}\Delta_{zz}}\times\exp[-(V_{zz}-V_{zz}^0)^2/2\Delta_{zz}^2]$$

with $\Delta_{zz}=0.35V_{zz}$. Obviously this function yields the same marginal distribution of $\eta$ as the original one.

In this work, for the evaluation of the perturbation factor (3) we further simplify the distribution by assuming a linear dependence on $\eta$, but leave $\Delta_{zz}$ as a free parameter.

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