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H-induced anelasticity as a probe: Application to nanoscale quasicrystals

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Abstract

Anelastic relaxation peaks produced by hydrogen in icosahedral quasicrystals (at c_H = 0.001 to 0.2 H/M) have been studied with the vibrating-reed technique in several rapidly quenched Ti/Zr-based alloys. Although a full quantitative theory of the expected Snoek-type mechanism is still missing, the properties of the relaxation peaks are considered as a probe of local atomic order on a more empirical level. Examples are presented which show the distinction between different icosahedral structure types (like Bergman or Mackay clusters), and the development of quasicrystalline order from amorphous and nano-quasicrystalline structures.

Keywords: Quasicrystals; Nanostructures; Hydrogen as a probe; Anelasticity; Mechanical spectroscopy

1. Introduction

H-induced anelasticity of metallic materials, as a special case of mechanical property changes due to absorbed hydrogen, is fundamentally interesting from different viewpoints. Historically, it was the unexpected absence of the Snoek relaxation of hydrogen in pure bcc metals [1] (in contrast to the heavier interstitials C, N, O), which raised new questions and stimulated fundamental research on the non-classical behavior of hydrogen especially in bcc metals. But this vain search for the "pure" hydrogen Snoek effect also marked the beginning of a still continuing discovery of new kinds of H-induced anelastic relaxation ("Snoek-type" and others) in different crystalline, amorphous, and recently also quasicrystalline host structures (see, for instance, reviews [2–6] and recent original papers [7–14]).

Another important viewpoint is the use of "hydrogen as a probe" to study (micro) structural details around the interstitial hydrogen. This approach, generally based on the H concentration dependence of a suitable property which reflects the distribution of H site energies, has been fruitful for the study of H-trapping defects as well as of disordered (e.g. amorphous) structures [15]. Nanostructures were always included in such studies, like in the "classical" example of a grain-boundary thickness determination in nanocrystalline Pd by means of EMF measurements [16]. With respect to H-induced anelasticity, the Snoek-type reorientation mechanism (see below) is the most suitable "probe" in this context, because its macroscopically measured relaxation parameters are directly related to the local metal atom configurations around the moving H atoms. Even though these relationships have been solved theoretically only for simple cases (like a monatomic model glass [17]) but not for complex structures like quasicrystals, it is possible to use the method on a phenomenological level also in the latter case [12–14]. In the present paper, after a brief overview over the relevant relaxation mechanisms, a few examples of H-induced damping spectra are presented which show some characteristic features of local hydrogen mobility – and of the underlying short-range order – in nanoscale, icosahedral quasicrystals, situated between the limits of amorphous disorder and full quasicrystalline order.

2. Relaxation mechanisms in polytetrahedral structures

Polytetrahedral structures – metallic glasses, icosahedral quasicrystals, and specific crystal structures – are character-

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ized by a dense packing of tetrahedra, which are necessarily distorted because of the well-known impossibility of filling space with regular tetrahedra. Any H atom occupying such a distorted tetrahedral site then induces an anisotropic, local elastic strain field, a so-called “elastic dipole” [18]. If now the long-range structure is isotropic (as normally in amorphous and icosahedral [19,20] phases), or at least of higher symmetry than the individual elastic dipole, then different orientations of energetically equivalent elastic dipoles should exist, which can interact differently with an external stress field. This means that hydrogen dissolved in polytetrahedral metallic phases should generally give rise to a Snoek-type mechanism (reorientation of elastic dipoles formed by single foreign atoms) of anelastic relaxation when hopping from site to site.

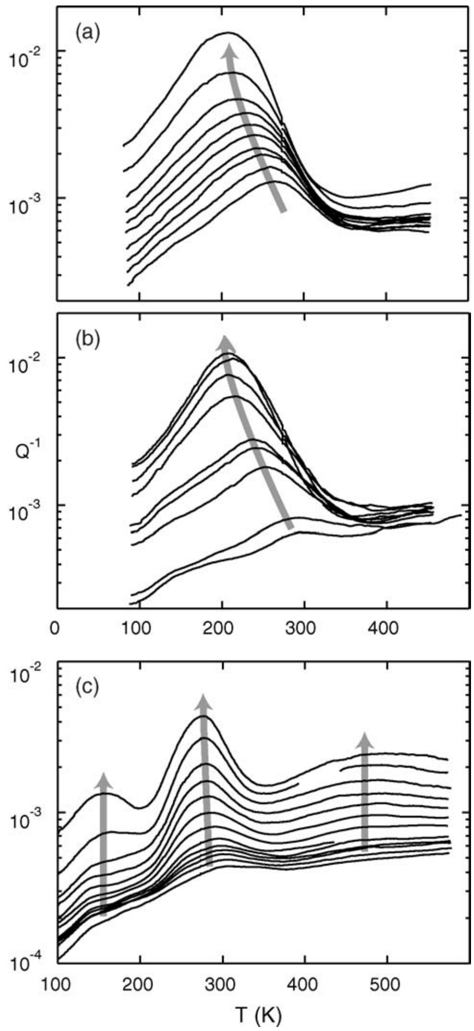

Fig. 1. Growth of the hydrogen damping spectra at 1 kHz (as produced by stepwise H charging from the gas phase, see Section 3 for experimental details and H concentration ranges) in different structural states of the glass-forming alloy $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ [13,21,22]: (a) Rapidly quenched glassy state; (b) metastable quasicrystalline state after annealing with 1 K/min to 688 K; (c) completely crystallized state.

Although, as mentioned above, the theoretical description of the Snoek-type relaxation in polytetrahedral structures is still unsatisfactory (for the amorphous case, see [4] for a review), it is clear that a close correlation must exist between the local atomic order in the host structure and the properties of a H-induced Snoek-type relaxation peak. Thus, the appearance of such a peak (height, position, shape, concentration dependence) may be taken as some empirical “signature” of the respective short-range order, especially for the purpose of comparing different phases to each other; this is illustrated in Fig. 1 using some previous results on the bulk glass-forming alloy $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$, which show very similar signatures in the amorphous and quasicrystalline states but a different one after complete crystallization [21,22]. In the first two cases, the shift of the growing peak to lower temperature (corresponding to a decrease of the average activation energy with respect to the low-concentration value of $\sim$0.5 eV [12]) partially reflects the successive filling of a broad site energy spectrum, in contrast to the crystalline case in Fig. 1c. Moreover, different mechanisms were identified in this latter case [8,23], like a Zener mechanism (reorientation of H-H pairs [24]) for the central peak and a long-range diffusion mechanism (intercrystalline Gorsky effect [9,25]) for the broad high-temperature peak. The latter mechanism requires an elastically anisotropic structure and should, consequently, not exist in amorphous or icosahedral phases.

3. Experimental procedure

In addition to the above-mentioned glass alloy $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ – well-known for the formation of a metastable icosahedral phase as the first devitrification product on heating above the glass transition [26] – the compositions $Ti_{53}Zr_{27}Ni_{20}$, $Ti_{41}Zr_{42}Ni_{17}$, and $Ti_{65}Zr_{10}Fe_{25}$ were chosen for the present study, because they have been classified as “Bergman-type” (Ti-Zr-Ni) and “Mackay-type” (Ti-Zr-Fe) icosahedral phases [27], i.e. they are different from the viewpoint of local atomic order. Samples were produced by melt-spinning at the National Institute of Materials Physics (Bucharest, Romania) with grain sizes $d \sim 100$ nm, except for $Ti_{53}Zr_{27}Ni_{20}$ which reaches a few micrometers [28]. Since, in this latter case, the substitution of only 2% Ti by Ag results in an extremely fine nano-quasicrystalline structure close to the amorphous limit [29,30], the composition $Ti_{51}Zr_{27}Ni_{20}Ag_2$ was also studied. The relevant structures and transformations were carefully characterized using X-ray and electron diffraction, transmission electron microscopy, differential scanning calorimetry, and mechanical spectroscopy, as published elsewhere [14,28–31].

Using a standard vibrating-reed vacuum equipment, the resonance frequency f and mechanical damping (internal friction) Q^{-1} of flexural vibrations were measured on clamped samples (thickness 0.02–0.06 mm) as a function of temperature during linear heating with 1 or 2 K/min (see [12] for details). Between these mechanical tests, the initial hydrogen content of the Ti/Zr-based alloys (between 0.001 and 0.005 H/M as determined by heat extraction analysis) was increased in a stepwise manner by in-situ gas-phase charging (usually at 473 K/0.1 MPa H_2) without touching the clamping geometry of the samples, resulting in series of H-induced damping peaks with successively increasing heights as in the case of Fig. 1 above. The hydrogen concentrations c_H (between 0.001 and 0.2 H/M in the present study, not specified in detail below) could be estimated from the heights Q_p^{-1} of the measured damping peaks (after background subtraction) with the help of previous calibrations on Zr-based metallic glasses [4,21], checked by a few vacuum extraction tests on actual samples.

4. Results and discussion

From a nanoscale viewpoint, the materials studied in Fig. 2 are all "coarse-grained" ($d \geq 100$ nm) in the sense that the measured damping peaks should be ascribed to hydrogen dissolved inside the quasicrystals, not in the grain boundaries. Assuming that small amounts of residual crystalline phases (which could not be avoided completely in all cases) are also not critical, the Mackay-type icosahedral phase in Fig. 2c shows indeed a clearly different signature of the H damping peak compared to the two Bergman-type phases in Fig. 2a and b: instead of a relatively sharp single peak, it seems to be composed of two partial peaks with different relative weight at different H concentrations. This might indicate a stronger splitting of hydrogen site and/or saddle point energies in the Mackay cluster; a closer atomistic analysis of this observation (as well as a detailed consideration of the related behavior of resonance frequency/Young's modulus) is, however, beyond the scope of this paper. Other differences even within the group of Bergman-type Ti-Zr-Ni quasicrystals (which neither fit into the "Bergman/Mackay" scheme nor follow a simple chemical rule) are apparently seen by another type of "signature" (plot of peak temperature versus peak height, representing the c_H dependence of activation energy) as pointed out elsewhere [12–14].

Following the known correspondence between amorphous and quasicrystalline structures (see above, Fig. 1), nano-quasicrystalline $Ti_{51}Zr_{27}Ni_{20}Ag_2$ and coarse-grained $Ti_{53}Zr_{27}Ni_{20}$ are compared in Fig. 3 by means of a more careful peak-shape analysis on a selected, intermediate level of H concentration. Although the initial, X-ray amorphous state of as-quenched $Ti_{51}Zr_{27}Ni_{20}Ag_2$ with $d < 5$ nm [30,31] is not included here, peak 1 in Fig. 3 – plotted as a function of reciprocal temperature after subtraction of a background Q_B^{-1} – may be considered as very close to this initial state. But also peak 2 is reduced in width only very slightly, even after a heat treatment which raised Young's modulus by more than 50% over the as-quenched state [31], and is also almost identical in shape with the respective H peak in amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ (cf. Fig. 7 in [12]). A substantial narrowing by annealing is only observed in the coarse-grained material (from peak 3 to 4), and in a similar way also for $Ti_{41}Zr_{42}Ni_{17}$ [14]. Since peak 3 is also not much narrower than peaks 1 and 2 (at least on the low-temperature side), one might conclude that the amount of local atomic disor-

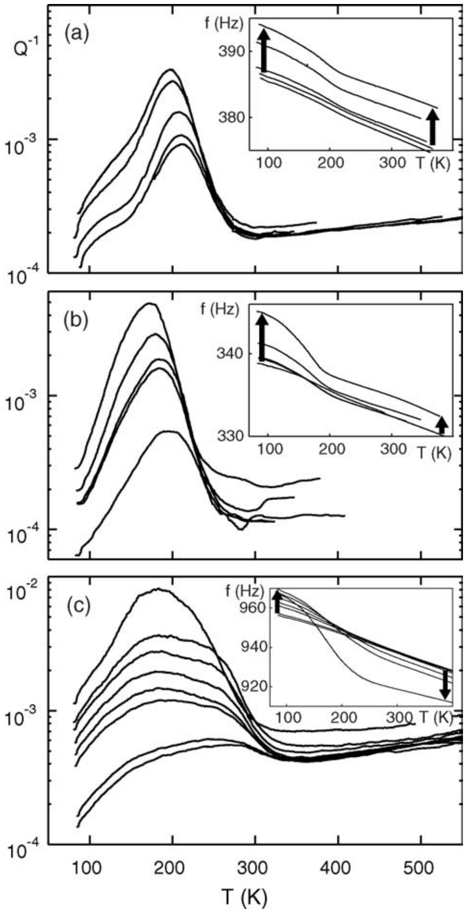

Fig. 2. Growth of the H damping peaks, after stepwise hydrogen charging, in different quasicrystalline alloys: (a) $Ti_{53}Zr_{27}Ni_{20}$; (b) $Ti_{41}Zr_{42}Ni_{17}$; (c) $Ti_{65}Zr_{10}Fe_{25}$. The insets show the corresponding changes of resonance frequency as a function of temperature.

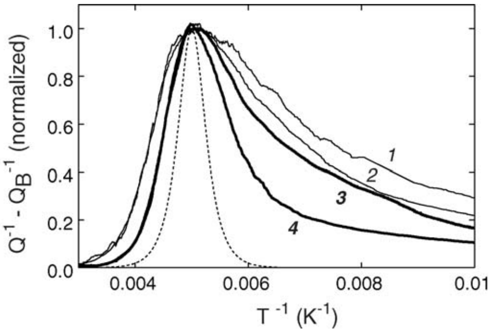

Fig. 3. Shape of H-induced damping peaks in $Ti_{53}Zr_{27}Ni_{20}$-type quasicrystals with peak heights Q_p^{-1} around 0.002 ($c_H \sim 0.02$–0.03 H/M; $f \sim 350$–550 Hz). Thin lines: nano-quasicrystalline $Ti_{51}Zr_{27}Ni_{20}Ag_2$, (1) heated with 2 K/min to 573 K, d = 5–10 nm; (2) annealed for 24 h at 733 K, d = 20–30 nm [31]; thick lines: "coarse-grained" $Ti_{53}Zr_{27}Ni_{20}$, (3) after 38 h at 473 K; (4) heated with 2 K/min to 878 K. For comparison, the dotted line shows a Debye peak with an assumed activation energy of 0.4 eV.

der after melt-spinning, as seen by this damping peak, is initially not very different between amorphous, nano- and poly-quasicrystalline states, but that afterwards the grain size is important for the sharpness of quasicrystalline order that can be achieved by subsequent annealing.

5. Conclusions

The properties of H-induced damping peaks can be used as a probe to distinguish between different types of local quasicrystalline order, like Bergman- or Mackay-type structures.

Nano-quasicrystalline structures are apparently characterized by a more amorphous-like short-range order which can be sharpened significantly by annealing, towards full quasicrystalline order, only if the grain size exceeds a certain value of about 100 nm.

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