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## SNOEK AND GORSKY RELAXATIONS IN HYDROGENATED METALLIC GLASSES

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**Résumé** - Deux relaxations, l'une due à une réorientation atomique à courte distance, l'autre due à un effet Gorsky à longue distance, ont été observées dans du  $\text{Ni}_{64}\text{Zr}_{36}$  vitreux contenant jusqu'à 20 pour cent d'hydrogène (fraction atomique). Les caractéristiques complémentaires de ces deux relaxations dues à des réorientations montrent qu'elles sont du type Snoek. L'ampleur de la relaxation Gorsky est faible, et ne varie que légèrement en fonction de la température, ce qui indique une répulsion H-H.

**Abstract** - A short-range reorientation relaxation and a long-range Gorsky relaxation have been observed in glassy  $\text{Ni}_{64}\text{Zr}_{36}$  containing H up to 0.2 atom fraction. The relaxations exhibit mutually complementary characteristics that establish the reorientation relaxation to be of the Snoek-type. The Gorsky relaxation strength is small, and exhibits a weak temperature dependence indicative of a H-H repulsion.

## 1. INTRODUCTION

Hydrogen in solution in metallic glasses provides the first example of a point defect that can be studied both by a reorientation relaxation of the Snoek type, and by the Gorsky relaxation. One of the most important circumstances leading to this interesting situation is that the elastic dipole strength of the H-interstitial in a metallic glass is comparable to its size factor, in striking contrast to the situation thought to exist for hydrogen in crystalline niobium [1]. In Pd-Si glasses containing H at levels below 0.02 atom fraction, we have previously observed a direct proportionality between hydrogen concentration, volume dilatation, and the strength of the reorientation and Gorsky relaxations, as expected for a dilute solution of non-interacting defects [1]. The purpose of the present work was to compare these relaxations at substantially higher concentrations, where interaction effects may become evident. For this purpose, we found it convenient to use ribbons of the metallic glass  $\text{Ni}_{64}\text{Zr}_{36}$ , kindly supplied by Dr. F. H. M. Spit. This alloy is already known to be capable of substantial hydrogen absorption ( $H/M > 0.5$ ), and moreover is well-suited for Gorsky measurements because the surface oxide inhibits the desorption of hydrogen from the sample [2].

## 2. PROCEDURE AND RESULTS

Hydrogen was introduced into the  $\text{Ni}_{64}\text{Zr}_{36}$  ribbon by cathodic charging, using a 2:1 glycerol-phosphoric acid electrolyte and a current density of  $2 \times 10^{-5}$

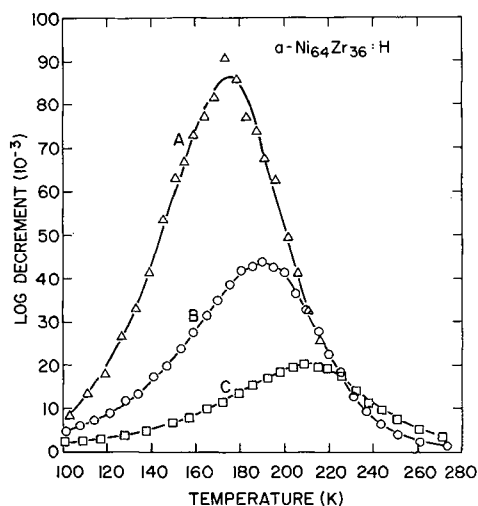


Fig. 1. Internal friction peaks shown by hydrogenated glassy  $\text{Ni}_{64}\text{Zr}_{36}$  at the approximate concentration levels  $H/M \approx 0.2$ , 0.09 and 0.04 (curves A, B and C, respectively). The vibration frequency was  $135 \pm 10$  Hz (Table 1).

amps/cm<sup>2</sup>. To monitor the progress of charging, the elongation of the ribbon was monitored via a simple dial gauge arrangement. After a minor initial transient, the elongation increased linearly with time. Charging was terminated when the volumetric strain  $\Delta V/V$  (calculated with the assumption of isotropic expansion) reached 3.4%, or ten times that produced in  $\text{Pd}_{82}\text{Si}_{18}$  by equilibration against 1 atm of  $\text{H}_2$  gas. Assuming the partial molar volume for hydrogen is approximately the same in both glasses, we estimate the hydrogen concentration in the  $\text{Ni}_{64}\text{Zr}_{36}$  sample to be  $H/M \approx 0.2$ . The charged ribbon was noticeably warped and twisted, but fortunately some pieces about 2cm in length were straight enough to be used for the anelastic measurements. Both the reorientation and Gorsky relaxations were observed on the same sample, using audio-frequency internal friction and dynamic modulus measurements for the reorientation relaxation, and flexural aftereffect measurements for the Gorsky relaxation [1].

The internal friction peaks shown in Fig. 1 were obtained from the electrocharged sample after a homogenization anneal at 423K in  $\text{H}_2$  gas at 700 torr (peak A), and after 1 hr desorption anneals in vacuum at 473K and 523K (peaks B and C, respectively). The large size of peak A is particularly noteworthy, and is evidence that a mutual proportionality between peak strength, volume dilatation and concentration is essentially valid over a substantially extended range. From the estimate  $H/M \approx 0.2$  for peak A, the concentrations corresponding to peaks B and C are thus judged to be  $H/M \approx 0.09$  and 0.04, respectively. Apart from their greater strength, the general characteristics of the peaks of Fig. 1 are similar to those observed at dilute levels ( $H/M < 0.02$ ) in the  $\text{Pd}_{82}\text{Si}_{18}$  alloy. The most probable relaxation time  $\bar{\tau}_R$  is concentration dependent, and on an inverse temperature scale the peaks exhibit a characteristic asymmetry in the form of an extended low-temperature tail (Fig. 2). Although the peaks are no broader than those observed in the dilute regime, there is a noticeable tendency for the  $1/T$  - shift between them to exhibit a curious narrowing at low temperatures (Fig. 2), in contradiction to the widening expected if the shape of the peak were due only to a distribution of activation energies. Values obtained for various relaxation parameters are listed in Table 1. The short-range nature of the relaxation is indicated by the magnitude of the prefactor  $\tau_{0R}$  shown in the last column.

Following each set of dynamical measurements, the sample was removed from the vibrating reed apparatus for complementary measurements of the Gorsky relaxation. Illustrative results for the three concentration levels A, B, C of Fig. 1 (and Table 1) are shown in Fig. 3. These results represent the flexural aftereffect (i.e. the recovery of the springback curvature  $1/R_s(t)$ , after winding the sample around a circular mandrel of radius  $R_w$  (0.48cm) for a period long enough to secure complete relaxation. In contrast to the considerable dispersion shown by the reorientation relaxation, the Gorsky aftereffect is well-fitted by a single relaxation time  $\tau_G$ . The solid curves of Fig. 3 are exponential decay curves calculated using the relaxation times indicated by the vertical arrows and the relaxation strengths  $\Delta^G$  obtained by extrapolation of each ordinate to zero time. As for the reorientation relaxation, it is evident from Fig. 3 that the relaxation time  $\tau_G$  is con-

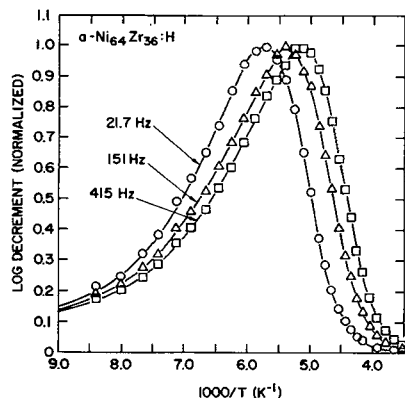


Fig. 2. The frequency dependence and asymmetry of the hydrogen peak in glassy  $\text{Ni}_{64}\text{Zr}_{36}$ , charged to a peak decrement of  $50 \times 10^{-3}$  ( $H/M \approx 0.12$ ).

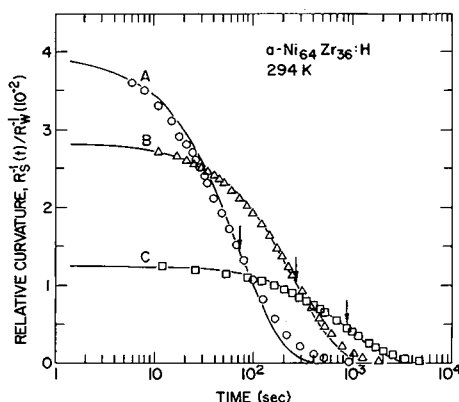


Fig. 3. The Gorsky aftereffect at 294K for the same sample and hydrogen concentrations used for Fig. 1.

Table 1. Parameters for the Hydrogen Reorientation Relaxation in Glassy  $\text{Ni}_{64}\text{Zr}_{36}$ .

Key	$H/M$ est.	$f_p$ (Hz) (a)	$T_p$ (K) (a)	$\delta_p$ (a)	$\Delta^R$ (b)	$r$ (c)	$\bar{Q}_R$ (eV) (d)	$\bar{\tau}_{0R}$ (s)
A	0.20	143	176	0.0842	0.194	3.62	0.364	$4 \times 10^{-14}$
B	0.09	131	191	0.0414	0.088	3.32	0.396	$5 \times 10^{-14}$
C	0.04	125	211	0.0183	0.042	3.61	0.438	$5 \times 10^{-14}$

(a)  $f_p$  and  $T_p$  are the frequency and temperature at the peak;  $\delta_p$  is the peak decrement above background. (b)  $\Delta^R$  is the reorientation relaxation strength measured from the transition in the dynamic modulus. (c)  $r$  is a broadening factor defined by  $\pi\Delta^R/2\delta_p$ . (d) Best estimates based on combined consideration of (i) frequency-shift results, (ii) the peak halfwidth and  $r$ -factor and (iii) a smooth variation with  $T_p$ .

centration dependent. The rate plots, diffusion activation energies  $Q_D$  and prefactors  $D_0$  obtained by measurements over a range of temperature are shown in Fig. 4, where the diffusion coefficient  $D$  has been calculated from  $\tau_G$  and the ribbon thickness  $d$  using the relationship  $D = d^2/\pi^2\tau_G$ . The complementary temperature dependence of the relaxation strength is given in Fig. 5, where the inverse relaxation strength  $1/\Delta^G$  is used as ordinate.

Two important comparisons between the reorientation and Gorsky relaxation are shown in Figs. 6 and 7. In Fig. 6, we have plotted the Gorsky relaxation strength  $\Delta^G$  against the reorientation relaxation strength  $\Delta^R$  using all the available results. Despite some scatter, a proportional relationship is indicated over most of the range. The close correspondence of both the magnitude and concentration dependence of the activation energies  $\bar{Q}_R$  and  $Q_D$  is shown in Fig. 7.

### 3. DISCUSSION

From the complementary nature of the reorientation and Gorsky relaxations, demonstrated with respect to both the concentration dependence of the relaxation strengths and the similarity of the activation energies, we conclude that (a) both relaxations arise from the general population of hydrogen atoms in solution, (b) hydrogen atoms are localized in interstitial sites of low symmetry and hence act as elastic dipoles as well as centers of dilatation, (c) the same jumps produce both reorientation and long-range diffusion. On this basis, the reorientation relaxation has the essential characteristics of the well-known Snoek relaxation produced by isolated solute interstitials in body-centered cubic metals, and may reasonably be described as being of the Snoek type.

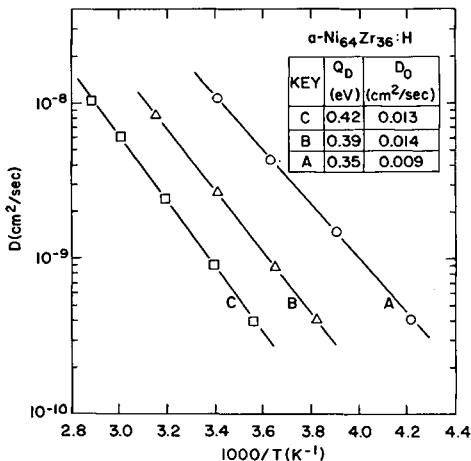


Fig. 4. Hydrogen diffusion in glassy  $\text{Ni}_{64}\text{Zr}_{36}$ , as obtained from the Gorsky effect.

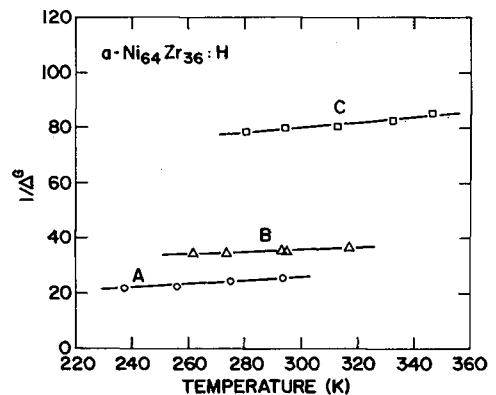


Fig. 5. Temperature dependence of the inverse Gorsky relaxation strength for glassy  $\text{Ni}_{64}\text{Zr}_{36}$  containing  $H/M \approx 0.2$ , 0.09 and 0.04 (plots A, B and C, respectively).

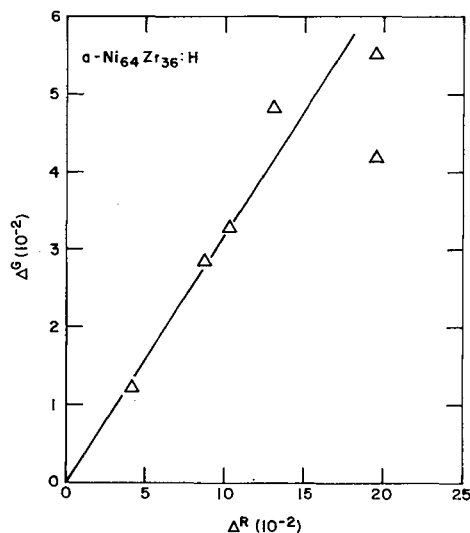


Fig. 6. Variation of the Gorsky relaxation strength  $\Delta^G$  with the reorientation relaxation strength  $\Delta^R$  for glassy  $\text{Ni}_{64}\text{Zr}_{36}$  containing various levels of hydrogen up to  $H/M \approx 0.2$ .

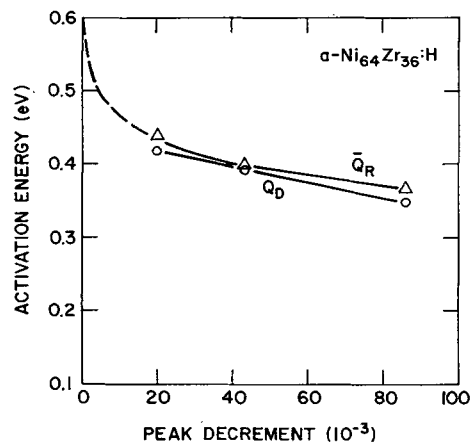


Fig. 7. Comparison of the activation energies  $\bar{Q}_R$  and  $Q_D$  for hydrogenated glassy  $\text{Ni}_{64}\text{Zr}_{36}$ . The estimated rapid turn-up in  $\bar{Q}_R$  at low concentrations, indicated by the broken line, is based on the location of the hydrogen peaks in other Ni-Zr glasses.

Although the conclusions listed above are identical to those given earlier [1] for glassy  $\text{Pd}_{82}\text{Si}_{18}$  containing  $H/M < 0.02$ , the present observations appear to represent the first time that complementary Snoek and Gorsky relaxations have been observed up to  $H/M \approx 0.2$ . Such behavior implies that an essentially disordered interstitial solid solution persists to relatively high concentrations. It seems possible that this situation may be linked to the existence of a repulsive H-H interaction. Such an interaction is indicated by the very weak temperature dependence of  $1/\Delta^G$  indicated in Fig. 5, which corresponds to the variation expected when the critical temperature for self-induced ordering assumes negative values. Interestingly, an opposite temperature dependence has been reported recently by Verbruggen et al. [3] for  $\text{Pd}_{80}\text{Si}_{20}$  containing about 1 a/o H. Although these measurements were made at higher temperatures in a difficult experimental regime, they are supported by our own unpublished results on a similar alloy at lower temperatures.

For  $\text{Ni}_{64}\text{Zr}_{36}$ , Fig. 6 yields  $\Delta^R/\Delta^G = 3$ , in contrast to the value 1.1 previously obtained for  $\text{Pd}_{82}\text{Si}_{18}$ . For an ideal solution of rotationally - symmetric defects characterized by a dipole shape factor ( $\lambda_1 - \lambda_2$ ) and a volumetric size factor ( $\lambda_1 + 2\lambda_2$ ),  $\Delta^R/\Delta^G$  is approximately given by  $(1 - e)^2/(1 + 2e)^2$ , where  $e$  denotes the dipole ellipticity ( $\lambda_2/\lambda_1$ ) [1]. In these terms, Fig. 6 implies that  $\lambda_2 = -0.16\lambda_1$ , i.e. that the principal expansion is accompanied by a small transverse contraction. While the difference between the ratio  $\Delta^R/\Delta^G$  for  $\text{Ni}_{64}\text{Zr}_{36}$  and  $\text{Pd}_{82}\text{Si}_{18}$  may be due in part to differences in the geometry of the interstitial sites, it must be pointed out that the absolute magnitude of  $\Delta^G$  for the  $\text{Ni}_{64}\text{Zr}_{36}$  sample is unexpectedly small and is in fact only about one-fifth the size expected for an ideal solution. Until this substantial reduction is better understood, the interpretation of the ratio  $\Delta^R/\Delta^G$  remains uncertain. Finally, it is now of interest to pursue similar measurements to even higher concentrations ( $H/M \approx 1$ ), in order to investigate the possibility that  $\Delta^R$  and  $\Delta^G$  may exhibit observable maxima as saturation of the interstitial sites is approached.

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