Determination of Hydrogen Activation Energy Spectrum in Amorphous Solids from Internal Frictions*

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It is shown that the activation energy spectrum of hydrogen in amorphous materials can be determined from the temperature distribution of internal friction observed in anelastic relaxation measurements by using the deconvolution method of Fourier transform.

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Hydrogen absorption in amorphous metals and alloys have been extensively investigated in the last years.[1-3] Now it is well established that many behaviours of hydrogen in amorphous materials can be described with the use of a continuous distribution of site energy and saddle point energy.[4-6] Because a metallic glass always contains different kinds of elements whose affinities to hydrogen vary within a wide range (say, from that of an early transition metal to that of a late one), there may exist several kinds of interstitial sites coordinated by distinct combinations of host atoms. For example, in a typical glass Ni_xZr_{1-x}, there are in turn five kinds of tetrahedra with increasing site energies: Zr_4, Zr_3Ni, Zr_2Ni_2, $ZrNi_3$ and Ni_4.[7] Moreover, besides the chemical disorder there is also a structural disorder in amorphous solids. Both the volume and angular deformation of the tetrahedra may result in the broadening of the energy spectra.

It has been widely believed that hydrogen is responsible for a broad internal friction (IF) peak observed in anelastic relaxation experiments for a glassy material containing hydrogen.[8-10] There are mainly two relaxation processes concerned with hydrogen atoms, according to Berry and Pritchet (BP) in (Refs.1 and 3). One is the Snoek-type effect involving a short-range reorientation jump of a hydrogen atom,[11] the other is the Gorsky effect associated with the stress-induced long-range diffusion of hydrogen.[2] Since the hydrogen induced distortions of the host lattice associated with the elastic dipole of a hydrogen interestitial and the saddle point energies to prevent hydrogen from diffusion differ from site to site, a spectrum of the relaxation times or the activation energy spectrum (AES) is expected. On the other hand, the information embodied in the AES may be helpful to the understanding of hydrogen interactions with defects such as vacancies, dislocations and grain boundaries during the trapping of hydrogen.[5]

In general, the IF peak as a function of temperature for amorphous materials can be expressed by the following integral equation[8-10]

$$Q^{-1}(c,T) = \int_0^\infty \frac{\omega\tau}{1+(\omega\tau)^2} \Delta(c,T,E)P(E)dE , \tag{1}$$

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where $P(E)$ is the activation energy distribution due to the disordered nature of amorphous solids, $\Delta(c, T, E)$ is the total relaxation strength of the H interstitials, ω is the torsion frequency, τ is the relaxation time, which is supposed to follow the Arrhenius law

$$\tau = \tau_0 \exp(\frac{E}{kT}) \ . \tag{2}$$

As an approximation, the prefactor τ_0 can be taken as a constant for all the relaxation processes (following Ref.10). The relaxation strength is not only proportional to the concentration c and the inverse of temperature $1/T$ but also in principles dependent on E (Refs. 8,9 and 12)

$$\Delta(c, T, E) = \beta Y \Omega_0 (\lambda_1 - \lambda_2)_E^2 \frac{c}{kT} \ , \tag{3}$$

where Y is the Young modulus, β is a geometrical factor, $(\lambda_1 - \lambda_2)_E$ is the energy-dependent difference of the principal components of the λ tensor, Ω_0 is the mean molar volume of the material. In this work, we assume that the energy-dependent term can be separated from the relaxation strength as $\Delta(c, T, E) = \Delta_0(c, T)\delta(E)$ and $\Delta_0(c, T)$ follows the supposition of Ulfert and Kronmüller (UK) (Ref. 10)

$$\Delta_0(c, T) = \frac{\epsilon c}{kT} \ , \tag{4}$$

where ϵ is a constant. It has been found that the IF versus temperature is well described by a Gaussian function or a linear combination of series of Gaussian functions. For convenience, we employ a Gaussian function to mimic the measurement of UK

$$Q^{-1}(c, T) = B(c) \exp\{-[(T - T_0(c))/\beta(c)]^2\} \tag{5}$$

where $B(c)$, $\beta(c)$ and $T_0(c)$ are concentration-dependent parameters.

By inserting Eqs. (2) and (3) into Eq. (1) and denoting $P^*(E) = P(E)\delta(E)$ (which can be regarded as an effective distribution), we have

$$Q^{-1}(c, T) = \frac{\Delta_0(c, T)}{2} \int_0^\infty \frac{P^*(E)dE}{\cosh[\ln(\omega\tau_0) + E/kT]} \ . \tag{6}$$

Let $\lambda = \ln(\omega\tau_0)(\approx -29$, in Ref. 10), $e^x = E/k$, $e^y = T$, Eq. (6) can be re-expressed by

$$R(y) = \int_{-\infty}^{+\infty} \frac{S(x)dx}{\cosh[\exp(x - y) + \lambda]} \tag{7}$$

with $R(y) = [2/\Delta_0(c, e^y)]Q^{-1}(c, e^y)$ and $S(x) = ke^x P^*(ke^x)$. Equation (7) is namely a convolution equation

$$R(y) = \int_{-\infty}^{+\infty} \Phi(y - x)S(x)dx = \Phi(y) * S(y) \tag{8}$$

with the kernel

$$\Phi(u) = \frac{1}{\cosh[\exp(-u) + \lambda]} \ . \tag{9}$$

Note that $\lim_{u \to -\infty} \Phi(u) = 0$ and $\lim_{u \to \infty} \Phi(u) = 1/\cosh(\lambda) \approx 0$. Both the function $R(y)$ and the kernel $\Phi(u)$ sharply rise to finite peaks and fast fall to zero within short intervals on the

abscissas (Fig. 1). Therefore, it may be plausible to cut off them and as a good approximation, perform the forward and inverse fast Fourier transforms on them within certain intervals.
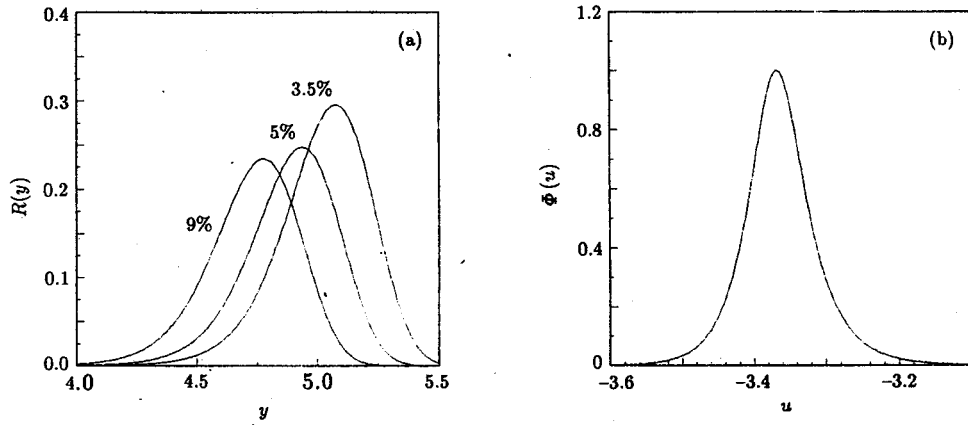

Fig. 1. Illustrations for the response function $R(y)$ and the kernel function $\Phi(u)$. (a) $R(y)$; (b) $\Phi(u)$.
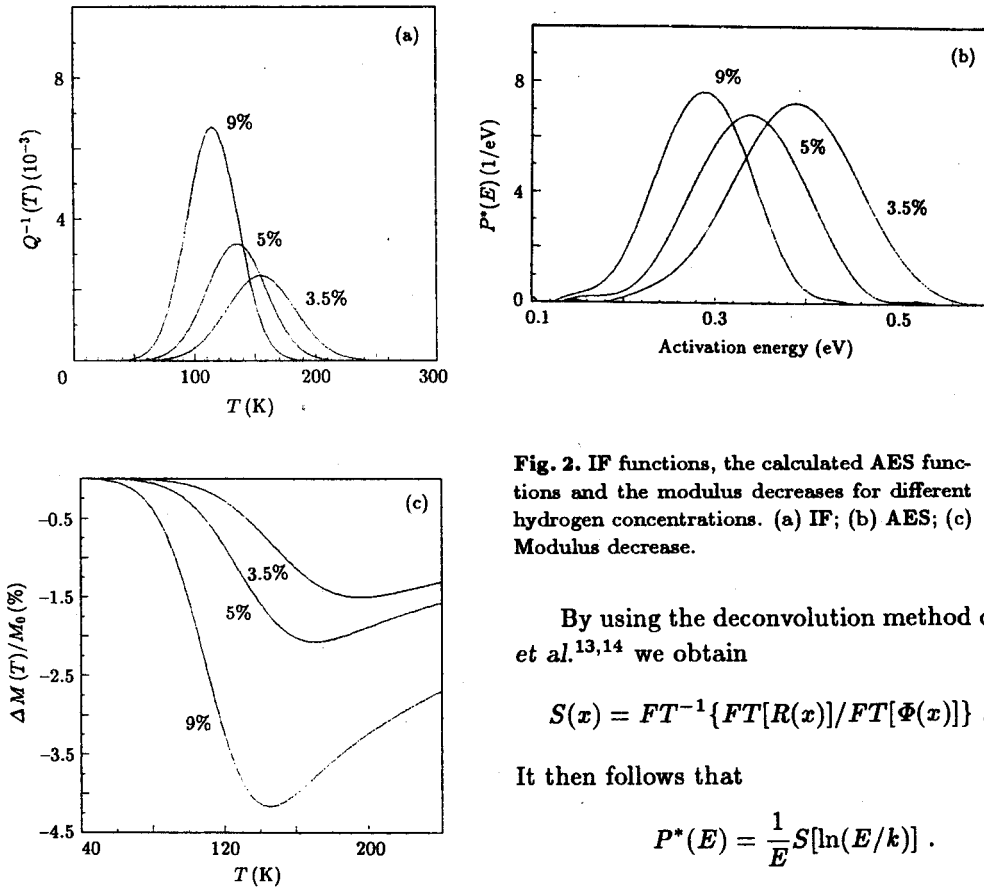

Fig. 2. IF functions, the calculated AES functions and the modulus decreases for different hydrogen concentrations. (a) IF; (b) AES; (c) Modulus decrease.

By using the deconvolution method of Chen et al.[13,14] we obtain

$$S(x) = FT^{-1}\{FT[R(x)]/FT[\Phi(x)]\} . \quad (10)$$

It then follows that

$$P^*(E) = \frac{1}{E}S[\ln(E/k)] . \quad (11)$$

The input IF functions measured for $(Pd_{40}Ni_{35}P_{25})_{1-c}H_c$ ($c = 9\%$, 5% and 3.5%) are taken from Ref. 10, with $\omega = 0.5\,Hz$, $\tau_0 = 5 \times 10^{-13}\,s$ and $\epsilon = 6.3\,meV$. The corresponding inverted AESs are shown in Fig. 2. We find that the inverted results are close to those of the approximate treatment of UK who integrated Eq. (6) around $T' = -E/k\ln(\omega\tau_0)$ and expanded the formula to the second-order derivative. The present predictions of concentration-dependence of the most probable activation energy are $0.288\,eV$ (9%), $0.338\,eV$ (5%) and $0.388\,eV$ (3.5%), in agreement with the results $0.26\,eV$ (9%), $0.31\,eV$ (5%) and $0.36\,eV$ (3.5%) presented in Ref. 10.

The calculated spectrum can be used to evaluate the modulus decrease

$$\frac{\Delta M(c,T)}{M_0} = -\Delta_0(c,T) \int_0^\infty \frac{P^*(E)dE}{1 + [\omega\tau_0 \exp(E/kT)]^2} \cdot \tag{12}$$

The predicted curves of modulus decreases exhibit maxima at some temperatures and gradually drop to zero when the temperature increases. This behaviour does not coincide with the experimental results of UK. In fact, the disagreement of this behaviour with experimental observation may lie in the $1/T$-dependence of relaxation strength Δ which may not be true according to the clarifications of BP.[3] BP measured the anelastic relaxations of $(Pd_{86}Si_{14})_{1-x}H_x$ and concluded that the relaxation strength may be independent on $1/T$. The predictions of the modulus decreases using the model of BP which considers site-pair correlation and H-H repulsion do not exhibit the behaviour like those of Stolz's model.[12] Based on the present calculations, we also surmise that the relaxation strength Δ may be weekly dependent on $1/T$.

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