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Anomalous Diffusion of Hydrogen in Amorphous Metals.

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Abstract. – Analysing the quasi-elastic neutron scattering from 8 at. % hydrogen in the metallic glass Ni₂₄Zr₇₆, we find that the hydrogen motion can be described in terms of anomalous diffusion. This process is analogous to that which leads to a strong frequency dependence of the conductivity in fast ionic conducting glasses. The data can be well described by an effective medium calculation based on a model with a broad distribution of activation energies. The same model can also successfully be applied to describe the anomalous temperature dependence of proton spin relaxation in amorphous metals.

Hydrogen diffusion in amorphous metals has attracted much attention in the last years because of its interesting features which differ appreciably from hydrogen diffusion in crystalline metals. From NMR [1,2], Gorsky relaxation [3] and electrochemical diffusion [4, 5] studies it emerged that the hydrogen motion can be discussed in terms of a broad distribution of activation energies which appear as saddle point energies between adjacent interstitial sites. Such a distribution has also been calculated theoretically [6].

Neutron quasi-elastic scattering can reveal much information on the details of the hydrogen motion because of its sensitivity to microscopic scales both in space and time. For a conventional diffusion process based on Fick's law one expects a Lorentzian spectrum the width of which is proportional to the diffusion coefficient D. A neutron quasi-elastic scattering investigation of amorphous Ni₂₄Zr₇₆, on the contrary, has shown a marked deviation from the Lorentzian shape [7] which on first sight looks like a superposition of two Lorentzians the widths of which differ appreciably (¹). Similar features have been found later also in amorphous $Pd_{85}Si_{15}$ [8]. It has been speculated that the hydrogen motion could be characterized by two separated processes, a «fast» and a «slow» one, correspondig to two

^{(&}lt;sup>1</sup>) It has been stressed in ref. [7] already that one cannot distinguish, by fitting the data with Lorentzians, whether the experimental $S(k, \omega)$ is composed of two or of a distribution of more than two Lorentzians.

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kinds of interstitial sites [8]. This hypothesis has been corroborated by a vibrational spectroscopy investigation [9]. Such a model, however, does not appear to have a reasonable physical justification, and it is in conflict with the current ideas of a continuous activation spectrum emerging essentially from all other investigations.

In what follows we report on a more thorough re-investigation of the Ni₂₄Zr₇₆ data, combined with new data measured by an instrument with a different resolution. We find evidence for anomalous diffusion of the protons in the frequency range of observation, *i.e.* $2 \cdot 10^9 \,\mathrm{s}^{-1} \leq \omega \leq 4 \cdot 10^{10} \,\mathrm{s}^{-1}$. Anomalous diffusion means that in the time scale of interest the mean square distance walked by the diffusing particle increases sublinearly instead of linearly with time. This implies that the generalized kinetic coefficient $\nu(\omega)$ (= complex frequency-dependent hopping rate) which describes the jump diffusion becomes strongly frequency dependent. Such a behaviour is well known from ionic conducting glasses in which $\nu(\omega)$ can be measured directly because it is proportional to the dynamic diffusivity $D(\omega)$ and hence to the dynamic electric conductivity $\sigma(\omega)$. The real part of the latter has been reported to vary as $\sigma'(\omega) \propto \omega^{1-\alpha}$ in a large number of cases [10, 11], where $0 < \alpha < 1$. Since $D'(\omega)$ is the Fourier transform of the velocity autocorrelation function [12] a $D'(\omega) \propto \omega^{1-\alpha}$ law corresponds to a time dependence of the mean square walk distance according to $\langle r^2(t) \rangle \propto t^{\alpha}$.

In terms of $v(\omega)$ the quasi-elastic incoherent scattering law $S(k, \omega)$ can be written as [13]

$$S(k,\omega) = \frac{1}{\pi} \operatorname{Re} \left\{ \frac{1}{i\omega + f(k) \nu(\omega)} \right\}.$$
 (1)

Here f(k) is a generalized Chudley-Elliott function [14] to be specified below. For small k we have the model-independent relation $f(k) v(\omega) = k^2 D(\omega)$ which follows from particle conservation [12]. In the regime where $|\omega| \gg |f(k) v(\omega)|$ (1) reduces to

$$S(k,\omega) \propto \nu'(\omega)/\omega^2$$
. (2)

If, for example, $\nu'(\omega) \propto \omega^{1-\alpha}$ we obtain $S(k, \omega) \propto \omega^{-(1+\alpha)}$.

As an example in fig. 1 we have plotted the combined spectra for $k = 15 \text{ nm}^{-1}$ obtained with two different spectrometers (IN10 and IN13 of the ILL Grenoble). The high-frequency tail of the data seems to follow a $\omega^{-(1+\alpha)}$ law with $\alpha \approx 0.43$. Data at other wavenumbers and temperatures show similar behaviour. We interpret this as evidence for the anomalous diffusion of the protons.

It has been shown in a number of theoretical investigations [13, 15, 16] that anomalous diffusion in disordered systems can be interpreted as the result of statistically distributed microscopic jump rates. In other systems, such as liquids near the glass transition [17], crystalline fast ionic conductors [18], or fractals [19], anomalous diffusion can also be caused by interactions or by fractal topology.

In the following we show by means of the effective medium approximation (EMA) developed by Movaghar *et al.* [20-22] that the $S(k, \omega)$ data of hydrogen in amorphous Ni₂₄Zr₇₆ can be described by a classical over-the-barrier hopping model with a broad distribution of activation energies [13]. By comparison with several numerical simulations of hopping transport the EMA has been shown to be an excellent approximation scheme for calculating $D(\omega)$ [21, 23, 24] (see also ref. [16], p. 210).

Details of the hopping theory based on the EMA have already been described elsewhere [13, 16, 20-22]. We start with a master equation of the form

$$\frac{\mathrm{d}n_i(t)}{\mathrm{d}t} = -\sum_j W_{ij} n_i(t) + \sum_j W_{ji} n_j(t) \,, \tag{3}$$



Fig. 1. – IN10 data (T = 440 K, crosses) and IN13 data (T = 450 K, circles) at $k = 15 \text{ nm}^{-1} \text{ compared}$ with the theoretical expression (eqs. (1) and (5) taking $\mu = 0.25 \text{ eV}$, $\nu_0 = 1.6 \cdot 10^{11} \text{ s}^{-1}$, $f(k = 15 \text{ nm}^{-1}) = 0.45$, $Z_s = 8$), convoluted with the corresponding resolution functions. The dashed line indicates an $\omega^{-1.43}$ law. Insert: f(k) obtained by treating the Chudley-Elliott function as fit parameter for T = 371 K (triangles), T = 403 K (diamonds), T = 429 K (squares), and T = 440 K(circles). The full line is f(k) as given by eq. (11) with R = 0.15 nm. The fluctuations in the results of the fits of f(k) are due to the rather different performances of the analyser-detector system (different statistical accuracy and resolution of the spectra).

where n_i denotes the occupation probability of site *i* and W_{ij} are (symmetrized) jump rates from *i* to *j* parametrized as

$$W_{ii} = W(r_{ii}, E_{ii}) = v_0(r_{ii}) \exp\left[-E_{ii}/k_{\rm B}T\right].$$
(4)

 E_{ij} is the energy barrier ⁽²⁾ leading from *i* to *j* and r_{ij} is the separation between the two sites. The attempt frequency v_0 is assumed to depend on *r* only through a cut-off *R*: $v_0(r) = v_0 \theta(R - r)$. Such a model has been shown to successfully describe diffusion and ionic conduction in nonmetallic glasses [13]. The functions $v(\omega)$ and f(k) are then obtained in the effective medium approximation as

$$\nu(\omega) = Z_{s} \int_{0}^{\infty} dE \frac{P(E)}{\frac{1}{i\omega + \nu(\omega) a_{p}} + \frac{\exp\left[E/k_{B}T\right]}{\nu_{0}}},$$
(5)

^{(&}lt;sup>2</sup>) The present version of the EMA is a simplification of a more general treatment [20] in which the W_{ij} are not symmetric but retain their detailed balance property. In this theory one does not average over a distribution of energy barriers but over a distribution of site energies, similar to the approach of Kirchheim[4]. While using this more sophisticated EMA is essential for describing thermoelectric effects [20] and energy relaxation [25], the simplified version is sufficient for describing particle transport. This has been checked explicitly for d.c. [20] and a.c. [26] variable-range hopping transport.

$$f(k) = \frac{\int_{0}^{R} \mathrm{d}r \, r^{2} p(r) \left(1 - \frac{\sin\left(kr\right)}{kr}\right)}{\int_{0}^{R} \mathrm{d}r \, r^{2} p(r)}.$$
(6)

Here $a_p = \exp[-1]$, Z_s is the site coordination number, P(E) is the distribution of energy barriers and p(r) is the radial distribution function of sites.

In particular in the limit $k \rightarrow 0$ one obtains the diffusivity $D(\omega)$ as

$$D(\omega) = \frac{1}{6} \langle r^2 \rangle v(\omega) \tag{7}$$

with

$$\langle r^2 \rangle = \frac{\int\limits_0^R \mathrm{d}r \, r^4 p(r)}{\int\limits_0^R \mathrm{d}r \, r^2 p(r)}.$$
(8)

The long-range diffusion coefficient D = D(0) is obtained by putting $\omega = 0$ in eqs. (5) and (7). It has been shown in ref. [13] that for models with $\nu_0(r) \propto \theta(R-r)$ the temperature dependence of D follows always an Arrhenius law $D \propto \exp[-\mu/k_{\rm B}T]$ in the regime $k_{\rm B}T \ll \mu$ irrespective of the details of P(E). In this regime μ and P(E) are related by (5) as

$$1 = a_p Z_s \int_0^{\varepsilon} P(E) \,\mathrm{d}E \,. \tag{9}$$

For describing the quasi-elastic neutron scattering data we have utilized a Gaussian energy barrier distribution

$$P(E) = P_0 \exp\left[-\frac{1}{2}\left(\frac{E-E_0}{\Delta}\right)^2\right].$$
(10)

The width parameter Δ has been chosen (³) to agree with the width of the activation distribution for hopping along a particular pair of sites i-j as calculated for amorphous Pd by Richards [6]. The position of the maximum E_0 was determined to yield the measured [5] activation energy of H diffusion in a-Ni₃₅Zr₆₅ ($\mu = 0.25 \,\mathrm{eV}$) via eq. (9) with $Z_s = 8$ (octaedral sites). Together with the normalization condition this gives $P_0 = 2.67 \,\mathrm{eV}^{-1}$, $E_0 = 0.307 \,\mathrm{eV}$, and $\Delta = 0.153 \,\mathrm{eV}$. For simplicity we have set $p(r) \equiv 1$. The Chudley-Elliott function f(k) is then a unique function of R:

$$f(k) = 1 + \frac{3}{(kR)^2} \left(\cos(kR) - \frac{\sin(kR)}{kR} \right).$$
(11)

^{(&}lt;sup>3</sup>) One can also obtain a fit to the data with a much broader activation spectrum. However, the parameters v_0 and R obtained by such a fit have values which are physically less reasonable than those obtained by using the present P(E).

The remaining parameters v_0 and R were used as adjustable parameters for the frequency and wavenumber scale.

In fig. 2 we have plotted the function $\nu'(\omega)$ (which is proportional to the velocity fluctuation spectrum $D'(\omega)$, see eq. (7)) as calculated from (5) corresponding to the present model for three temperatures.



Fig. 2.

Fig. 3.

Fig. 2. – Frequency dependence of $\nu'(\omega)$ for three temperatures; the parameters are the same as those in fig. 1.

Fig. 3. – Temperature dependence of T_1 measured in *a*-Zr₂PdH_{2.88} (ref. [2]) (\bigcirc) and calculated from eqs. (1), (5) and (12) with $v_0 = 3.7 \cdot 10^{12} \text{ s}^{-1}$, $E_0 = 0.422 \text{ eV}$ and $f(k_0) = 0.017$ (-----).

The feature of interest is the strong frequency dependence of $v'(\omega)$ in a certain frequency range. This frequency dependence is caused by the disorder, *i.e.* by the broad spectrum of activation energies. Note that in the present treatment this distribution does not enter via an incoherent superposition of exponentially decaying relaxation functions but via the selfconsistent EMA equation (5) which, for example, treats correctly the percolative aspects of hopping transport [13, 16]. The range where $v'(\omega)$ strongly depends on frequency is bounded from below by $\omega_0 \approx v(0)$ and from above by $\omega_1 \approx v_0$ as can be easily shown by eq. (5).

It can be seen from fig. 2 that for $\omega_0 < \omega < \omega_1 v'(\omega)$ only approximately follows a $v'(\omega) \propto \omega^{1-\alpha}$ law with $\alpha \approx 0.43$. This is because the present model does *not* involve any fractal structure. The frequency dependence of $v'(\omega)$ has to be calculated numerically from eq. (5) and is nonuniversal, *i.e.* depends on the particular form of P(E).

For $\omega < \omega_1$ a transition from anomalous to normal diffusion occurs. It is interesting to note that at the lowest temperature (T = 250 K) this transition takes place in the 10^6 s^{-1} region (⁴).

We would like to emphasize that the frequency dependence of $D'(\omega)$ predicted by the

^{(&}lt;sup>4</sup>) It should be noted that the «normal» frequency region contributes to the measured intensity albeit in an unresolved way.

present model is very similar to that observed via the electrical a.c. conductivity in ionically conducting glasses [10, 11, 13, 27].

The samples were made up of melt spun ribbons of which one was loaded with about 8 at. % hydrogen. An unloaded sample was measured under identical experimental conditions. This measurement was used to remove the scattering from the metallic glass so that the dynamic structure factor of the incoherently scattering hydrogen alone could be determined. However, for ω values larger than $10^{10} \,\mathrm{s}^{-1}$ (1N10), $4 \cdot 10^{10} \,\mathrm{s}^{-1}$ (IN13) the resulting data could be affected by the subtraction procedure. A V-spiral of the same dimension as the samples was used to determine the resolution function for each of the scattering angles. Both experiments were made using the backscattering spectrometers at the HFR of the ILL in Grenoble. The parameters for the experiment at IN10 (IN13) were: incident energy 2.08 (16.5) meV, range of energy transfers $\pm 15(-39 \text{ to } + 97) \,\mu\text{eV}$, resolution of the order of 0.8 to $1.5 \ (\sim 10) \,\mu\text{eV}$ depending on the performance (polished or unpolished) of the analyser crystals. All necessary corrections were applied in the determination of the dynamic structure factor.

The full lines in fig. 1 have been obtained by convoluting $S(k, \omega)$ as calculated from eqs. (1), (5), and (6) taking $v_0 = 1.6 \cdot 10^{11} \text{ s}^{-1}$ and R = 0.155 nm (corresponding to f(k) = 0.45 at $k = 15 \text{ nm}^{-1}$) with the resolution function measured at the same k-value. We have checked that this convolution procedure does not affect the anomalous frequency dependence. (The change of the apparent exponent α is only of a few percent.) With these parameters we obtain from (7) and (8) a (tracer) diffusion coefficient $D = 1.44 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1} (T = 445 \text{ K})$ which is of the same order of magnitude as the value $D = 3.45 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ determined from the electrochemical data in a-Ni₃₅Zr₆₅ reported in ref. [5].

We have fitted the IN10 data using various wavenumbers and temperatures with the same model keeping v_0 fixed and using the Chudley-Elliott parameter f(k) as fit parameter. The result is shown in the insert of fig. 1 together with the theoretical curve (eq. (11)) for R = 0.15 nm showing that the trend is represented correctly. In view of the scatter of the data it does not seem reasonable to try to use a more sophisticated model for f(k).

An important method for investigating diffusive motion in this frequency domain is nuclear spin relaxation. It is therefore interesting to consider the temperature dependence of the proton spin-lattice relaxation rate predicted by the present model. Experimental data in amorphous metals [1, 2] exhibit a strong deviation from the BPP [28] behaviour expected for normal diffusion. In order to estimate the temperature dependence of the nuclear spinlattice relaxation rate T_1^{-1} we use the rule-of-thumb formula [18, 29]

$$T_1^{-1} \propto \mathcal{S}(k_0, \omega), \qquad (12)$$

where ω is an integer multiple of the Larmor frequency and k_0 a typical wavenumber characterizing the spatial fluctuations of the hyperfine fields. In fig. 1 we compare the temperature dependence of T_1 measured in a-Zr₂PdH_{2.88} ($\omega = 2\omega_{\rho} = 3.9 \cdot 10^5 \,\mathrm{s}^{-1}$, see ref. [2]) with that predicted by the present model using eq. (12), where we have put $E_0 = 0.422 \,\mathrm{eV}$ to obtain agreement with the measured activation energy of D ($\mu = 0.36 \,\mathrm{eV}$), $\nu_0 = 3.7 \cdot 10^{12} \,\mathrm{s}^{-1}$, and $f(k_0) = 0.017$. Although the agreement is not perfect it is clearly seen that the present description accounts for the strong asymmetry of the data (BPP predict a symmetric minimum).

In conclusion we found evidence for the anomalous diffusion of hydrogen in amorphous metals both on the time scale of quasi-elastic neutron scattering as well as nuclear spin relaxation. These findings which cover a large frequency and temperature range can consistently be explained as the result of an activated jump diffusion process with a broad distribution of activation energies. This is in agreement with previous considerations [1-5]. * * *

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