PHYSICAL REVIEW B VOLUME 58, NUMBER 17 1 NOVEMBER 1998-I

Crossover temperature from tunneling to thermal activation in neutron-irradiated quartz

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(Received 17 March 1998)

The low-temperature internal friction data in neutron-irradiated quartz and amorphous SiO_2 are compared. The region of the tunneling plateau in irradiated quartz extends to much higher temperatures in comparison with amorphous SiO_2. It is interpreted within the soft-potential model that two-level systems in irradiated quartz have a higher crossover temperature T_c from tunneling to thermal activation than in the glassy state. The characteristic energies W of the particles in the double-well potentials are estimated. Their difference is ascribed to higher effective masses of the tunneling centers inside the amorphous network than in the distorted crystalline regions of irradiated quartz. [S0163-1829(98)01542-2]

During the last two decades it has been widely accepted that two-level systems (TLS's) are responsible for many of the low-temperature properties of glasses. The main idea which was put forward in Refs. 1, 2 is that in glasses there exist atoms or groups of atoms moving in a double-well potential. At low temperatures only the tunneling motion through the barrier is important. It leads to a universal glassy behavior which has been found in many experiments.[3] However, for some properties such as internal friction this universality is lost if we go to higher temperatures.[4] The main reason is that in this range the thermal activation processes over the barrier become dominant.

Indeed, as follows from the analysis of a particular model (see below) in the tunneling range many of the microscopic TLS parameters do not enter explicitly observable quantities (or enter under the logarithm sign).[5] As a result, such hidden parameters and peculiarities of their distribution function are hardly accessible for direct measurements. The only characteristics of TLS's in glasses available at low temperatures are the constant density of states $\overline{P}$ and the average value of the deformation potential γ. This is why glasses with different microscopic structure exhibit similar properties below a few K.

However, the situation is changed with increasing the temperature when we enter in the thermal activation range. For a particular double-well potential the crossover temperature from tunneling to thermal activation T_c can be defined as the temperature at which the thermal activation rate becomes equal to the tunneling rate.[6] Being defined in such a way, T_c depends obviously on the barrier height V. But in the internal friction experiment the barrier height is fixed by an additional condition $\omega\tau=1$, where ω is the frequency and τ is the relaxation time. As a result one can introduce T_c which is independent of V and is a characteristic of the particular glass. It can slightly depend on the frequency. As follows from this experiment for most of the glasses this temperature is rather low and is of the order of a few K.

Above this temperature the important microscopic parameters enter explicitly into the final formula (for the sound absorption and sound velocity for example). The temperature behavior of the observable quantities and in particular of the internal friction is also changed remarkably.[7,8] It is worth noting that at these temperatures the latter becomes much more sensitive to the details of the distribution function of the double-well potential parameters than in the tunneling range. This is, from our point of view, the main source of the nonuniversal behavior of glasses at higher temperatures. Therefore, measurements of the crossover temperature give important additional information concerning microscopic parameters of the tunneling centers.

From this point of view the study of defective crystals prepared by means of neutron or electron irradiation seems very promising. It was discovered that after irradiation tunneling defects appear in the crystalline matrix.[9–11] The important conclusion was drawn that in the neutron-irradiated quartz a considerable part of these TLS's has to be attributed to the distorted ''crystalline'' but not amorphous fractions of the samples. It was naturally supposed that the microscopic structure of these tunneling ''centers'' should be similar to those in amorphous SiO_2. Indeed the numerical value of the deformation potential γ was found to be close to its corresponding glassy value.

However, from this similarity one cannot exclude *a priori* the difference of the values of the other microscopic parameters. In the present paper we compare the internal friction data in neutron-irradiated quartz and amorphous SiO_2. This comparison shows clearly the different crossover temperatures T_c from tunneling to thermal activation in these two chemically identical disordered materials. On the other hand, within a microscopic theory T_c must be related to some characteristic energy W of the double-well potentials. However, the character of this relationship strongly depends on the particular microscopic model used for tunneling centers.

Our consideration in this paper will be based on the phenomenological soft potential model (SPM) proposed in Ref. 12 (for a recent review see Ref. 13), though it can be done within another microscopic approach[14] as well. The difference between these two approaches is that in the latter the form of the wells in the double-well potentials is supposed to

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be the same for all tunneling centers. In this case the vibrational frequency Ω of the particle in such a well plays the role of the crossover temperature, i.e., $kT_c=\hbar\Omega$.

The principal idea of the SPM is that the typical double-well potentials accessible for particle tunneling are *soft* (i.e., they are rather exceptional among the overwhelming majority of the atomic potentials in the glass). If one accepts this point then from the standard *catastrophe theory* it follows that in such a case it is sufficient to take into account only the first three terms in the Taylor expansion of the effective potential energy of the particle $V(x)$ as a function of some generalized coordinate x

$$V(x)=\mathcal{E}_0\left[\eta\left(\frac{x}{a}\right)^2+\xi\left(\frac{x}{a}\right)^3+\left(\frac{x}{a}\right)^4\right]. \tag{1}$$

Here a represents the typical atomic length ($\simeq 1$ Å) and $\mathcal{E}_0$ is the typical atomic energy in the glass ($\simeq 10$ eV). The values of the dimensionless parameters η and ξ are random due to short-range order fluctuations of the chemical bonds. The rare soft potentials are characterized by small values of these parameters $|\eta|, |\xi| \ll 1$.

The double well potentials correspond to negative values of η. The corresponding barrier height is $V=\mathcal{E}_0\eta^2/4$. It is worthwhile to mention that within this approach it is not necessary (though possible) to consider fluctuations of the forth order term. It is sufficient to take for corresponding coefficient some typical atomic value ($\approx \mathcal{E}_0/a^4$). This situation reminds us of the ansatz with the deformation potential γ in the standard tunneling model. There it is also supposed to be the same for all TLS's in the glass, though it is easy to take into account its fluctuations. The interaction of the soft potentials with deformation ϵ_{ik} (and the phonons) is described by the bilinear term[5,7]

$$\mathcal{H}_{\rm int}=\mathcal{E}_0\left(\frac{x}{a}\right)\acute{H}_{ik}\epsilon_{ik}, \tag{2}$$

where the dimensionless second rank tensor $|\acute{H}_{ik}|$ is of the order of unity and independent of parameters η and ξ.

There are two important quantities in the SPM: one is the characteristic energy W and the other is a small parameter of the model η_L,[15]

$$W=\mathcal{E}_0\eta_L^2, \quad \eta_L=(\hbar^2/2Ma^2\mathcal{E}_0)^{1/3}\approx 10^{-2}. \tag{3}$$

where M is the effective mass of the particle. The physical meaning of W is that it represents a characteristic energy for the particle motion in the pure quartic potential $\mathcal{E}_0(x/a)$.[4] The importance of this energy follows from the fact that it just determines the crossover temperature from tunneling to the thermal activation:[6]

$$kT_c=(3/8)^{4/3}W\ \ln^{1/3}(2/\omega\tau_0). \tag{4}$$

The formula for T_c follows from the comparison of two transition rates, the tunneling rate through the barrier $(1/\tau)_{\rm tun}$ and the thermal activation rate over the barrier $(1/\tau)_{\rm act}$. The tunneling rate is proportional to the tunneling splitting squared. In the SPM

$$\left(\frac{1}{\tau}\right)_{\rm tun}\propto\Delta_0^2\propto\exp\left[-\frac{8}{3}\left(\frac{V}{W}\right)^{3/4}\right]. \tag{5}$$

The thermal activation rate is defined as usual:

$$\left(\frac{1}{\tau}\right)_{\rm act}=\frac{1}{\tau_0}\exp\left(-\frac{V}{kT}\right). \tag{6}$$

Equating the two exponents we obtain the crossover temperature for a double-well potential with barrier height V

$$T_c(V)=\frac{3}{8}W\left(\frac{V}{W}\right)^{1/4}, \quad V\gg W. \tag{7}$$

Now taking into account that the maximum contribution to the internal friction at frequency ω is due to double-well potentials with $\omega\tau=1$ where $1/\tau=(1/\tau)_{\rm tun}+(1/\tau)_{\rm act}$ and that $\tau_{\rm tun}=\tau_{\rm act}$ at $T=T_c$ we arrive to Eq. (4).

The temperature dependence of the internal friction in the thermal activation range depends on the distribution function of the double-well potential parameters η and ξ. In the limit $|\eta|, |\xi|\to 0$ it is given by[16]

$$P(\eta,\xi)=\mathcal{P}_0|\eta|/2, \tag{8}$$

where $\mathcal{P}_0$ is a constant and the factor $|\eta|$ describes the so-called ''sea-gull'' singularity in the distribution of the parameter η. For this distribution function, the internal friction in the tunneling range ($T\ll T_c$) is temperature independent and given by its ''plateau'' value[5]

$$Q_{\rm tun}^{-1}=\frac{\pi}{2}C, \quad \text{where} \quad C=\frac{\mathcal{P}_0\acute{H}^2W}{\rho v^2\sqrt{\eta_L}}. \tag{9}$$

Here ρ is the density and v is the sound velocity. For $T\gg T_c$ we are in the thermal activation range where the internal friction increases with temperature[7] $\propto T^{3/4}$

$$Q_{\rm act}^{-1}=\pi C\left(\frac{kT}{W}\right)^{3/4}\ln^{-1/4}\frac{1}{\omega\tau_0}. \tag{10}$$

For comparison with experiment it is useful to introduce a characteristic temperature T_a, where the classical relaxation (10) reaches the tunneling plateau level (9):[17]

$$T_a=\left(\frac{1}{2}\right)^{4/3}W\ \ln^{1/3}\frac{1}{\omega\tau_0}\approx 1.5T_c. \tag{11}$$

This temperature is directly related to the crossover temperature T_c. It gives the onset of the rise of the internal friction with temperature in the thermal activation range. For $\tau_0=10^{-13}$ sec and ω in the kHz region, $T_a\approx 1.1W$. Therefore, comparison of theory with experiment gives us a possibility to determine the important third parameter of the tunneling centers, the characteristic energy W.

Figure 1 shows the result of this comparison. It presents the low-temperature internal friction data in the sample of amorphous SiO_2 (at two frequencies) and in two samples (K14 and K15) of crystalline quartz irradiated by neutrons with doses 10^{19} n/cm^2 and 2.1×10^{19} n/cm^2, respectively, and nearly the same frequencies. All the data are scaled to the corresponding low-temperature plateau level. The two

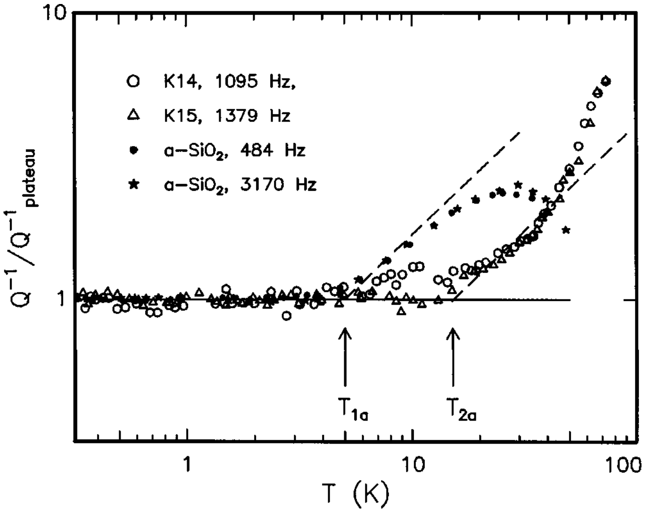

FIG. 1. Internal friction data from vibrating reed experiment in two samples of neutron irradiated quartz (Ref. 18) and amorphous silica (Ref. 19) scaled to their plateau values. They are equal to 3×10^{-5} (K14), 5×10^{-5} (K15), 3.6×10^{-4} (a-SiO$_2$, 484 Hz), and 4.2×10^{-4} (a-SiO$_2$, 3170 Hz).

dashed lines present $T^{3/4}$ dependences but with different strengths (i.e., with different values of W).

From the presented data one cannot say that in the thermal activation range the observed temperature dependence of the internal friction for both materials perfectly follows the theoretical prediction, Eq. (10) (see below). However, it is clearly seen that for irradiated quartz the tunneling plateau region extends to much higher temperatures than in the case of amorphous SiO$_2$. From the figure we can deduce that $T_{1a}\approx5$ K and $T_{2a}\approx15$ K. It corresponds to $W_{a\text{-SiO}_2}/k\approx4.5$ K and $W_{\text{irr quartz}}/k\approx13.5$ K. The first value is close to what is known from literature for W in amorphous SiO$_2$ (within the accuracy of our comparison procedure which we estimate as $\approx10\%$).[17] The second value one should consider as a left boundary for W in neutron irradiated quartz if there is a distribution of this parameter as it takes place, for example, in amorphous silica.[8] As a result the characteristic energy W in irradiated quartz is at least about three times higher than in the corresponding glassy state.

What is the main reason for such a large difference? If the geometry characteristics a and the typical energy scale of tunneling centers $\mathcal{E}_0$ are similar in amorphous SiO$_2$ and in the distorted crystalline regions of irradiated quartz, then the difference in W values can only result from the difference of the effective masses of tunneling particles. As follows from Eq. (3)

$$W=\frac{\hbar^{4/3}\mathcal{E}_0^{1/3}}{2^{2/3}a^{4/3}M^{2/3}}\propto M^{-2/3}, \tag{12}$$

i.e., a factor of 3 difference in W implies a difference of a factor of 5 in effective mass M. This is a rather acceptable value. The different surrounding of the tunneling centers in these two materials can lead (because of *dressing effect*) to a rather big difference in effective mass M. Since particle motion in the soft potential is relatively slow the surrounding atoms adiabatically follow the tunneling atom, thereby increasing its effective mass. When the coherent displacements of the surrounding atoms are included the effective mass M is given by[20]

$$M=M_0+\sum_i m_i\left(\frac{dq_i}{dx}\right)^2. \tag{13}$$

Here M_0 is a bare mass and m_i and q_i are the mass and displacement of the ith atom in the soft potential environment, correspondingly. Using numerical simulation it was shown that this effect can indeed increase the effective mass by one order of magnitude or even more.[21] Molecular dynamic simulations of model glasses also do not contradict this idea. It was found that soft vibrational modes consist of twenty to one hundred atoms.[22] We think that soft amorphous media in a-SiO$_2$ can much more easily respond to the particle motion than in the case of the rigid crystalline environment in irradiated quartz. As a result, the larger dressing effect in glasses leads in its turn to higher values of the effective mass of the tunneling particles.

The high value of W in neutron irradiated quartz explains also why the onset of the tunneling plateau can still be seen in the ultrasound data at high frequencies where one does not expect to see the tunneling states anymore (see Refs. 10 and 11, for instance; for recent new data see Ref. 23). The similar analysis of these data for sample n5, for instance[24] (for frequency 340 MHz, irradiated with dose 2.6×10^{19} n/cm^2), leads to $T_a\approx12$ K. It corresponds to the value of $W/k\approx15$ K which is close to W derived from the internal friction data. In addition it can be seen from these data that T_a increases with decreasing dose.

It is interesting to note that soft potentials with a high value of W were found from the analysis of heat release data in amorphous SiO$_2$ as well.[8] The distribution of W derived from the experiment shows two peaks. One corresponds to the usual small value of $W/k\approx4$ K and another corresponds to $W/k\approx20$ K. It was concluded that different microscopic configurations of double-well soft potentials can account for this difference. From this point of view there exists another explanation of the phenomena under discussion. Due to some unknown reasons neutrons ''prefer'' to create in crystalline quartz double-well potentials with big values of the characteristic energy W. However, this point needs some justification which we do not have at the moment.

Finally a few words about the observed nonuniversal behavior of the internal friction in the thermal activation range. From our point of view, the deviation of the temperature dependence, plotted in the figure, from the theoretical prediction given by Eq. (10) is a consequence of the deviation of the distribution function $P(\eta,\xi)$ from Eq. (8) which is valid only in the limit $|\eta|$, $|\xi|\to0$.

In the thermal activation range the main contribution to the absorption comes from the systems with $\omega\tau_{\text{act}}=1$, i.e., with

$$|\eta|\approx\eta_T\equiv2\,\eta_L\sqrt{\frac{kT}{W}\ln(1/\omega\tau_0)}. \tag{14}$$

Therefore, for example, if the dependence (8) saturates at some value of $|\eta|=\eta_c$ [so that $P(\eta,\xi)=\text{const}$ at $|\eta|>\eta_c$] it leads to a leveling off of the temperature dependence of the internal friction

$$Q_{\mathrm{act}}^{-1} \propto T^{1/4} \tag{15}$$

in the corresponding temperature range.[25] On the contrary, if the dependence $P(\eta,\xi)$ becomes steeper as a function of η then each additional factor of $|\eta|$ in the distribution function leads to an additional factor of $\sqrt{T}$ in $Q^{-1}(T)$.

In other words, changing the distribution function $P(\eta,\xi)$ one can always account for deviations in the temperature dependence of the internal friction from the simplest prediction described by Eq. (10). Of course, it needs additional fitting parameters. From our point of view this is the main source of the abovementioned nonuniversal behavior of some properties in the thermal activation range of many glasses[4] and in neutron-irradiated quartz as well.

In conclusion we analyzed experimental data on internal friction in amorphous and neutron irradiated quartz in the framework of the soft potential model. From the analysis we conclude that the crossover temperature T_c from tunneling to thermal activation in neutron-irradiated quartz is at least three times higher than in the glassy state. We hypothesized that this is related to the fact that the effective masses of the tunneling particles are larger when surrounded by the amorphous network than when they are imbedded in the crystalline matrix.

One of the authors (D.A.P.) gratefully acknowledges pleasant hospitality and financial support of the Catholic University of Leuven where part of this work was done. One of the authors (C.L.) thanks the Belgian FWO for financial support.

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