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Low-Energy Vibration Excess in Silica Xerogels

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Specific heat (1.5–25 K) and Raman scattering (below 100 cm^{-1}) in silica xerogels permit one to assess the frequency dependence of the coupling coefficient $C(\omega)$ and the low-energy density of states $g(\omega)$. Different network connectivity does not change the shape of the quasielastic scattering, but alters the spectral shape of $C(\omega)$. The results permit one to ascribe the frequency shifts of the boson peak to the contribution of $C(\omega)$ and to the Debye density of states $g_D(\omega)$. Furthermore, the different magnitudes of $g(\omega)$ appear to be a manifestation of changes in the Debye-like phonon contributions arising from connectivity changes. [S0031-9007(96)02257-0]

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The distortion of the structures due to the topological disorder in glasses has the main effect of introducing additional vibrations besides the acoustic phonons in the density of vibration states (DVS) $g(\omega)$. The existence of these low-energy vibrations must be included in order to explain the excess of specific heat in the region between 1 and 20 K and the boson peak in the low-frequency region (below 100 cm^{-1}) of the Raman spectrum. The main problem in determining the DVS from the Raman scattering is the evaluation of the light-vibration coefficient $C(\omega)$. The reduced Raman intensity I_R can be written as [1]

$$I_R(\omega) = I_{\exp}\,\omega/[n(\omega,T) + 1] = C(\omega)g(\omega)\,, \qquad (1)$$

where $n(\omega,T) + 1$ is the Bose-Einstein population factor and $1/\omega$ the harmonic propagator.

The complexity of the vibration characteristics of disordered systems can affect both the functions $C(\omega)$ and $g(\omega)$ [2,3]. In particular, it has been shown that, in the low-frequency region, the DVS exhibits a broad maximum in a number of glasses [4], while $C(\omega)$ shows a ω^{α} frequency dependence where α is usually lower than one [5]. The present concern is to show that, by using low-frequency Raman spectroscopy and low-temperature heat capacity in glasses of silica-xerogel, it is possible to assess the frequency dependence of $C(\omega)$ and the intensity, together with the shape of the low-energy region of the DVS. Furthermore, it has been found that the revealed differences among the DVS's of glasses of annealed silica xerogels and of vitreous silica (Spectrosil, named in the following as a-SiO_2) arise from variations in the connectivity of the system which change the Debye-like phonon contributions. As will be seen, the excess density of vibrations is independent on the degree of three-dimensional network connectivity.

The silica-xerogel samples were obtained by annealing for 24 hours silica gels with nominal stoichiometric formulas $Si_8O_{15}H_2$ at 500 °C (named in the following as D gel) and $Si_2O_3H_2$ at 800 °C (named in the following as A gel). The silica gels were prepared by hydrolysis of mixtures of triethoxysilane and tetraethoxysilane dissolved in ethanol. Details concerning the preparation of xerogels will given elsewhere [6].

The random network of quenched SiO_2 is essentially built up on SiO_4 tetrahedra, which are covalently linked at four corners. In the as-prepared gels, one oxygen atom in some SiO_4 groups is replaced by one hydrogen atom, the substitution of one oxygen for each tetrahedron being obtained in $Si_2O_3H_2$ gel. These hydrogens are nonbridging and cause a reduction of the cross-links Si-O-Si between pairs of tetrahedra. In consequence of this structural modification a smaller connectivity paralleled by a relevant softening of the network is expected. As a matter of fact, the measured density was $\rho = 1280\ \mathrm{kg\,m^{-3}}$ in the A sample and $\rho = 1800\ \mathrm{kg\,m^{-3}}$ in the D sample. The effect of the thermal annealing is to cause the densification of the as-prepared gels by favoring the removal of hydrogens and by restoring the cross-links between the tetrahedra. A higher annealing temperature gives rise to an increase of the density of the samples, which ranges from $\rho = 1940\ \mathrm{kg\,m^{-3}}$ in D gel, through $\rho = 2140\ \mathrm{kg\,m^{-3}}$ in A gel, to $\rho = 2200\ \mathrm{kg\,m^{-3}}$ in a-SiO_2.

The experimental results of specific heat, obtained between 1.5 and 30 K for A gel and D gel and plotted as $C_p(T)/T^3$, are compared to those reported [7] for spectrosil glass in Fig. 1(a). These data show the

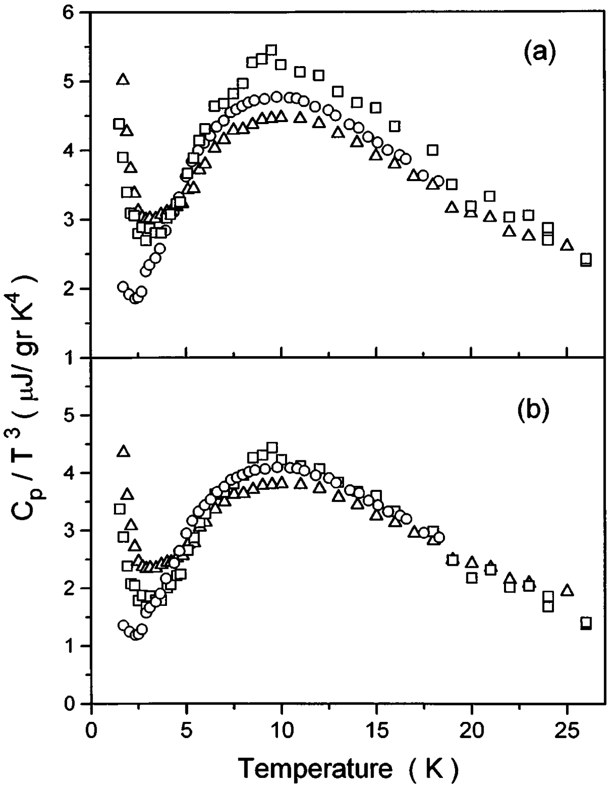

FIG. 1. (a) The temperature dependence of $C_p(T)/T^3$ for *A* gel (squares), *D* gel (circles), and *a*-SiO$_2$ (triangles), (b) The temperature dependence of $[C_p(T) - C_{\mathrm{Debye}}]/T^3$ for the same samples.

characteristic broad peak for a glass with a maximum which is located at about 10 K for all the glasses. When plotted as $[C_p(T) - C_{\mathrm{Debye}}]/T^3$ [see Fig. 1(b)], the excess specific heats over those predicted by the Debye theory appear to be almost the same within the experimental error between 3 and 25 K. It is well established in glasses [8] that the peak in $C_p(T)/T^3$ arises from a peak in the DVS [reported as $g(\omega)/\omega^2$ in the energy range 1–10 meV]. So it is expected that the strictly overlapping excess specific heats are strong evidence for the same behavior in the excess DVS's.

Marked differences between the specific heats are observed below 3 K and arise from the contribution of the "two level systems" [9]. In the present data, which extend down only to 1.5 K, the relevant differences between the upturns of silica-xerogels and *a*-SiO$_2$ could be associated to corresponding variations in the two level systems density, but the limited temperature range does not makes significant any evaluation of the magnitude of this term. The Debye contributions have been evaluated using the Debye temperatures Θ_D, as determined by the sound velocities obtained by shifts of the Brillouin lines [6]: for *A* gel $v_l = 6380$ ms^{-1}, $v_t = 3997$ ms^{-1}, and $\Theta_D = 526$ K; for *D* gel $v_l = 5534$ ms^{-1}, $v_t = 3613$ ms^{-1}, and $\Theta_D = 458$ K; for Spectrosil glass $v_l = 6130$ ms^{-1}, $v_t = 3962$ ms^{-1}, and $\Theta_D = 524$ K.

The HV normalized Raman intensities, $I_N = I_{\mathrm{exp}}/[n(\omega,T) + 1]\omega$, for *D* gel at 10 and 290 K are compared to those for *a*-SiO$_2$ in Fig. 2. The Raman intensity below 25 cm^{-1}, due to the light scattering excess or quasielastic scattering (QS), increases with increasing temperature much faster than the Bose population factor. By using a procedure described elsewhere [10], the contribution of QS has been separated from that of the boson peak. The frequency behaviors of QS for *D* gel and *a*-SiO$_2$ are compared in the inset of Fig. 2. The very close behavior revealed in *A* gel has been not inserted for clarity. The QS intensity decreases with increasing frequency and becomes negligible above 25 cm^{-1}. An important result is that, within the experimental error, in the studied frequency range, the spectral shape of the QS is the same in all the samples studied. Moreover, QS shape does not depend on the temperature, confirming the evidence already observed in glasses prepared by quenching [10]. These observations show that, in *A* and *D* gels, the relaxation of intrinsic defects, which in the existing models [11–13] are believed to cause the QS, are the same as those characterizing *a*-SiO$_2$ despite the different connectivity of these systems.

To analyze the vibration contribution of the boson peak, the lowest temperature Raman spectra have been considered, because a temperature of 10 K is low enough to completely depress the QS. The result is that the boson peak is centered at about 35 cm^{-1} in *D* gel and at about 46 cm^{-1} in *a*-SiO$_2$. It is straightforward to note that the spectral region over 30 cm^{-1} is temperature independent showing a harmonic behavior. Now the behavior of the specific heat results leads one to explain the differences revealed in the boson peak of *D* gel and *a*-SiO$_2$, as arising from the frequency behavior of $C(\omega)$

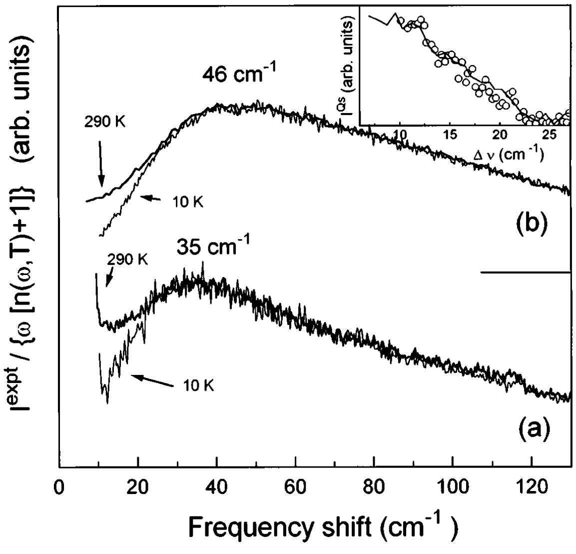

FIG. 2. The high voltage normalized Raman intensities, $I_N = I_{\mathrm{exp}}/\{\omega[n(\omega,T) + 1]\}$ for *D* gel (a) and *a*-SiO$_2$ (b) at 10 and 290 K. Inset: normalized QS excess in *D* gel and *a*-SiO$_2$ at 300 K.

and from the contribution of different Debye density of states $g_D(\omega)$. In order to confirm this prediction we have to find the spectral shape of $C(\omega)$. This datum can be obtained by fitting the low-temperature heat capacity with the low-frequency Raman scattering [10,14]. By assuming $C(\omega) \propto \omega^{\alpha}$ in the low-temperature reduced Raman intensity [see Eq. (1)], it has been possible to fit C_p as expressed by the following equation:

$$C_p \approx C_v = 3Nk_B \int_0^{\omega_0} g(\omega)\left(\frac{\hbar\omega}{k_B T}\right)^2 \times \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2}\, d\omega\,, \tag{2}$$

where N is the number density and ω_0 the highest vibration frequency. In addition to the exponent α, the magnitude of $g(\omega)$ also represents a fitting parameter. In Fig. 3 the experimental results of $C_p(T)/T^3$ are compared to theoretical fits obtained by using different values of α. The resulting exponents for the frequency dependence of $C(\omega)$ are $\alpha = 0.80$ in a-SiO$_2$, $\alpha = 0.68$ in A gel, and $\alpha = 0.29$ in D gel. The function obtained with $C(\omega) = \text{const}$ is also reported in order to show the very narrow range of variation allowed for the parameter α in this approach. The value of α in D gel is quite different from those usually found in glasses [10,14]. A possible explanation could be given in terms of a correlation between the frequency dependence of $C(\omega)$ and the connectivity of the system, which introduces different degrees of electrical and mechanical disorder in the network. It is expected, in fact, that elasto-optical and elastic local inhomogeneities are the origin of the two kinds of disorder which regulate the $C(\omega)$ behavior [9]. Now the connectivity (defined as the number of bridging bonds per network forming cation) of 4 characterizing a-SiO$_2$ is reduced to 3.75 and 3 in as-prepared D and A gels, respectively [6]. Such a decreasing connectivity leads to a strong softening of the glassy network as clearly indicated by the dramatic decrease of the longitudinal modulus $c_1 (= \rho v_1^2)$ from 82.67 GPa (a-SiO$_2$), through 17.3 GPa (as-prepared D gel), to 2.18 GPa (as-prepared A gel) [6]. As discussed before, the thermal annealing of the as-prepared gels tends to restore the missing cross-links between the SiO$_4$ units and to enhance both the density and the rigidity of the network. After annealing, in fact, the values of the shear (c_t) and longitudinal (c_1) modula become $c_t = 34.18$ GPa, $c_1 = 87.1$ GPa, in A gel; $c_t = 25.32$ GPa, $c_1 = 59.41$ GPa, in D gel. The values of A gel are close to those of a-SiO$_2$ ($c_t = 34.53$ GPa, $c_1 = 82.67$ GPa) and are consistent with a strongly connected three-dimensional topology, where the restored cross-links will generate strong covalent bonds to resist the tensile forces. Instead, the sample annealed at the lowest temperature (D gel) shows smaller values of the elastic constants, a feature which can be considered as a rough indication of the fact that the connectivity of this network is lower than 4. This finding must be associated with a substantial proportion of unrestored bridging bonds, which are the origin of local microscopic inhomogeneities and can cause the anomalous frequency dependence of $C(\omega)$ in this sample. The existence of nonbridging bonds in D gel is confirmed by the presence in the Raman spectrum above 500 cm^{-1} of a line at about 960 cm^{-1}, not present in that of a-SiO$_2$ and assigned to Si-H and Si-OH asymmetric stretching vibrations [6].

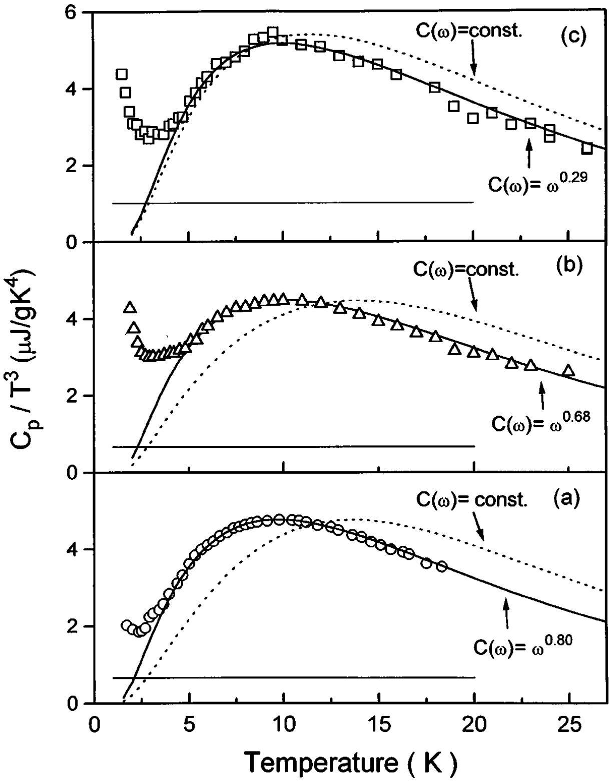

FIG. 3. C_v data of a-SiO$_2$ (a), D gel (b), and A gel (c). Horizontal lines show the Debye values [6]. The curves represent the fit by Eq. (1) to the data using $g(\omega)$ from the lowest temperature Raman spectra and different values for α in the expression $C(\omega) \propto \omega^{\alpha}$.

The numerical coefficient for $g(\omega) = I_R(\omega)/C(\omega)$, obtained from the fit of C_P data, allows the determination of the $g(\omega)$ in *absolute* units. Figures 4(a) and 4(b) (bold line) show the density of states obtained with the above procedure in D gel and a-SiO$_2$; a very close behavior to that of a-SiO$_2$ is also obtained in A gel. Assuming that the excess modes are different from phonons and coexist with them, $g_D(\omega)$ (obtained by the sound velocities and normalized to C_P with the above procedure) can be subtracted from $g(\omega)$ (thin line). The resulting absolute excess density of states for D gel compared to that obtained for a-SiO$_2$ shows that no difference exists in the density of additional vibrations for the two systems, in the boson peak range. This last datum is put better in evidence if plotted as divided by ω^2 [Fig. 4(c)]. The corresponding curve for A gel overlaps strictly to the others, and has not been reported for the sake of clarity. These observations show that small variations in the

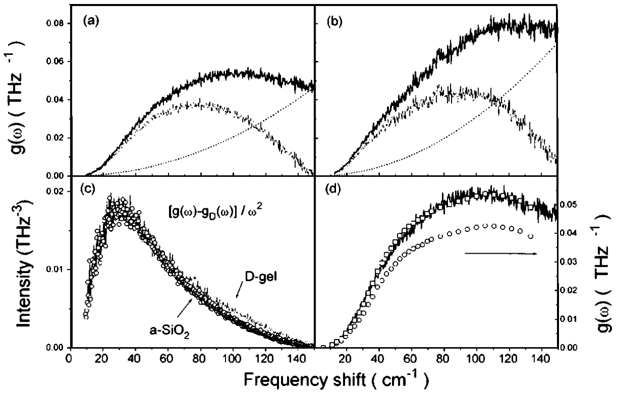

FIG. 4. Density of vibration modes as deduced from the fits of Fig. 3: a-SiO$_2$ (a) and D gel (b). Bold lines represent the densities of states, thin lines correspond to the density of excess modes, and dotted lines the Debye density of states. (c) Comparison between the densities of excess modes divided by ω^2, in D gel and a-SiO$_2$. (d) Comparison between the density of states obtained by Raman scattering in a-SiO$_2$ (bold line) and neutron scattering in heralux (circles) [16]. Squares indicate the neutron data normalized for the specific heat (see text).

connectivity in glassy networks with very close chemical compositions do not affect the excess vibrations, the differences in the magnitude of the peak in $C_p(T)/T^3$, and of the boson peak being ascribed to the contribution of Debye phonons. More importantly, the change in the frequency of the maximum of the boson peak (larger than 10 cm^{-1} in our systems), with sample density, *in our approach,* does not correspond to a parallel variation of the frequency of the maximum in the excess density of states as predicted by the Elliott model [15]: *the revealed frequency shift in the boson peak being introduced by the frequency dependence of $C(\omega)$ and by different Debye contributions.*

The DVS in a-SiO$_2$ obtained from the previously described procedure in spectrosil silica (solid line) is compared with that obtained by inelastic neutron scattering (reported in Ref. [16]) in heralux silica (circles) in Fig. 4(d). Because the neutron data are referred to heralux silica, the agreement is to be considered reasonable either for the spectral shape or for the intensity. We emphasize that this result has been obtained by independent measurements. Moreover, taking into account that the measured specific heat in spectrosil silica is greater that of heralux silica [$\sim$(15–20)%], we have normalized the neutron data for this value, obtaining a DVS reported as open squares in Fig. 4(d): the agreement is *quite* satisfactory in showing the correctness of our procedure.

In conclusion, by specific heat and Raman measurements, we were able to obtain the $g(\omega)$ in absolute units of the same kind of glasses with different connectivity. From the analysis of our data we have found (1) The differences in the C_p data are ascribed to the different contributions of Debye density of states due to the less rigid structure of xerogels. (2) The observed experimental shift of boson peak frequency maximum is ascribed to the different behavior of $C(\omega)$ and $g_D(\omega)$ due to the different connectivity in these systems. (3) The density of states of excess (with respect to Debye) vibrations in xerogels and a-SiO$_2$, as deduced from Raman and C_p data, show the same shape and intensity in the boson peak frequency range and is in agreement to that obtained, in a completely different way, by inelastic neutron scattering.

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