Effect of Densification on the Density of Vibrational States of Glasses

A. Monaco,[1] A. I. Chumakov,[1,*] G. Monaco,[1] W. A. Crichton,[1] A. Meyer,[2] L. Comez,[3,4] D. Fioretto,[3,4]
J. Korecki,[5] and R. Rüffer[1]

[1]*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France*
[2]*Physik Department E13, Technische Universität München, D-85747 Garching, Germany*
[3]*INFM CRS-SOFT, c/o Universitá di Roma "la Sapienza," I-00185 Roma, Italy*
[4]*Dipartimento di Fisica, Universitá di Perugia, I-06123 Perugia, Italy*
[5]*Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Kraków, Poland*

(Received 18 July 2006; published 25 September 2006)

We studied the effect of densification on the vibrational dynamics of a $Na_2FeSi_3O_8$ glass. The density of vibrational states (DOS) has been measured using nuclear inelastic scattering. The corresponding changes in the microscopic, intermediate-range, and macroscopic properties have also been investigated. The results reveal that, in the absence of local structure transformations, the Debye level and the glass-specific excess of vibrational states above it have the same dependence on density, and the evolution of the DOS is fully described by the transformation of the elastic medium.

DOI: 10.1103/PhysRevLett.97.135501 PACS numbers: 63.20.−e, 07.85.−m, 76.80.+y

It is well accepted that the anomalous thermodynamic properties of glasses are related to a particular feature in their density of vibrational states: an excess of states above the Debye contribution known as the "boson peak." Its origin, however, remains strongly debated [1].

Several studies focused on the dependence of the boson peak on pressure or density [2–13]. In contrast to temperature—which affects the density of vibrational states (DOS) mainly in the vicinity the liquid-glass transition—densification causes significant changes of the DOS. Furthermore, several theoretical studies emphasize the role of density to discriminate among different models of the boson peak [14,15]. The dependence of the DOS on pressure or on densification has been investigated by measurements of specific heat [2,3], Raman [4–8], and inelastic neutron scattering [9–13]. The various techniques reveal the same trend: an increase in density results in a decrease of the boson peak height and in its shift toward higher energies. Despite the consistency of the experimental results, there is still no general agreement on their interpretation. In particular, (i) Raman data have been used to support the idea that the boson peak is an effect of phonon localization in a characteristic intermediate-range-order length [4–6]; (ii) neutron scattering data have been analyzed in terms of glass-specific excitations called soft modes [11–13]; (iii) specific heat data show that the effect of pressure on the boson peak can be described by the corresponding changes in the Debye contribution, i.e., in the sound waves [2,3].

One should note that most of the studies based on Raman and neutron scattering refer to the boson peak as to the total intensity of the peak in the reduced density of states $g(E)/E^2$ rather than to the *excess* of states above the Debye level $3/E_D^3$, where E_D is the Debye energy. Meanwhile, the explicit reference to the Debye level in the latter appropriate definition clearly suggests to consider densification effects on the Debye level and on the excess of states separately. Following this idea, we report in this Letter on the effect of densification on the density of vibrational states of glasses and on the Debye level. Our results show that, as far as densification does not induce changes in the local structure, the evolution of the DOS with densification is entirely described by the corresponding changes of the Debye level, i.e., by the modification of the elastic medium.

We studied a $Na_2FeSi_3O_8$ glass with 95% enrichment of iron in the ^{57}Fe isotope. The ambient-pressure glass transition temperature $T_g = 744$ K (determined by calorimetric measurements) is close to that of binary sodium silicate glass. The permanently densified samples were prepared by compressing the initial glass at 1, 2, and 3 GPa at a temperature of 673 K ($\sim 0.9T_g$) using a large-volume Paris-Edinburgh press [16]. The samples of $\sim$5 mm^3 size have been kept at high-pressure high-temperature conditions for $\sim$10 min before being cooled down and then released to ambient pressure. Compression to higher pressures did not provide further permanent densification of the glass. In what follows, we denote the samples according to the pressure at which they have been compressed, with 0 GPa standing for the initial glass.

The density of vibrational states of the iron atoms was measured using nuclear inelastic scattering at the Nuclear Resonance beam line [17] ID18 of the European Synchrotron Radiation Facility (ESRF). This technique allows for the measurement of the density of vibrational states of atoms with low-energy nuclear transition—in this case, of ^{57}Fe. The distinguished features of nuclear inelastic scattering are ideal momentum integration and exact scaling of the DOS in absolute units [18]. In this study, the deviation of the DOS area from unity does not exceed 1%. In the studied glass, iron substitutes for silicon in the network structure [19]. Therefore, the measured partial

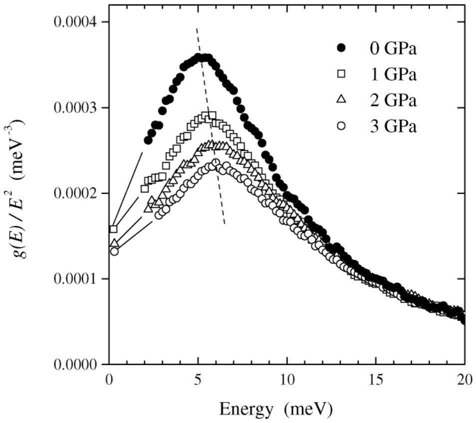

FIG. 1. Reduced density of vibrational states of the initial and densified $Na_2FeSi_3O_8$ glasses. The dashed line emphasizes the shift of the peak position on densification. The thin lines show the consistency of the data with the calculated Debye levels indicated by symbols at $E = 0$.

density of states of the iron atoms directly reflects the vibrational properties of the glass.

The obtained reduced densities of states $g(E)/E^2$ have a peak at ~5 meV (Fig. 1). The pronounced maximum in the reduced DOS and the high energy of the peak are typical for strong [20] sodium silicate glasses. Densification causes a clear transformation of the low-energy part of the DOS. In agreement with previously reported observations [2–13], the peak decreases in height and shifts toward higher energies. This transformation is significant mainly for the low-energy part of the reduced DOS: at 20 meV all curves superimpose. The strongest modification of the reduced DOS occurs at the first step of compression from the initial glass to the 1 GPa sample.

The effect of pressure on the density of vibrational states of glasses is often attributed to structural changes at short- and intermediate-range-order scales [4–6]. Therefore, we analyzed in detail the influence of densification on the glass structure using Mössbauer spectroscopy and x-ray scattering (Fig. 2).

Mössbauer data give information on the local environment of the ^{57}Fe atoms, i.e., those atoms whose partial DOS has been measured. Conversion electrons Mössbauer spectra [Fig. 2(a)] measured with the ^{57}Co/Rh source reveal only the Fe^{3+} ions doublet. The isomer shift suggests that iron is surrounded by oxygen in tetrahedral coordination, confirming that iron substitutes for silicon in the network structure. The first step of densification causes a pronounced change of the quadrupole splitting, which reveals an ~12% increase of the electric field gradient on the ^{57}Fe nucleus site. This implies that on the initial step of densification a significant modification of the local environment around the iron atoms takes place. On the further densification steps the local structure is not significantly modified.

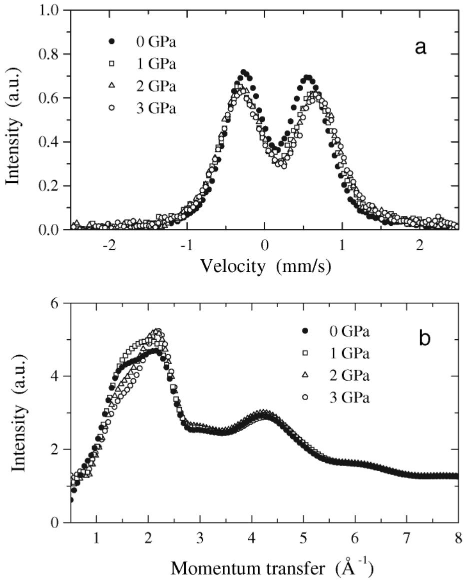

FIG. 2. Characterization of the microscopic and intermediate-range structure of the initial and densified glass using (a) conversion electron Mössbauer spectroscopy (the spectra are normalized to an equal area) and (b) x-ray scattering.

X-ray scattering gives additional information on the glass structure in the microscopic to intermediate-range scale. The measured signal consists of almost equal contributions of the Fe, Si, and O atoms while the Na contribution is lower. The measurements were performed at ID27 beam line [21] of the ESRF. Figure 2(b) shows pronounced changes in the first sharp diffraction peak at ~2 Å^{-1}. This peak appears to consist of two components whose relative weight changes on densification. It is commonly accepted that the transformation of the first sharp diffraction peak is related to changes at the intermediate-range-order scale [22]. The details of this interpretation, however, are still debated [4–6,23–25]. Here, we merely emphasize a continuous change of the intermediate-range structure with densification.

The evolution of the macroscopic properties of the glass was investigated with density and sound velocity measurements. The density was determined by weighting the samples in air and ethanol. The sound velocities, both longitudinal and transverse, were measured by Brillouin light scattering using a tandem Fabry-Perot interferometer with an energy resolution of 0.45 GHz in back- and 90°-scattering geometries [26,27]. The measurements were performed with an argon laser of 514.5 nm wavelength. Figure 3 shows that the initial step of compression does not influence much the properties of elastic medium: density and sound velocity reveal only a slight increase. The main transformation of the elastic medium occurs starting from the second step of compression. The increase of density of the last sample is not evident [Fig. 3(a)], possibly because of the moderate accuracy of the measurement due to the

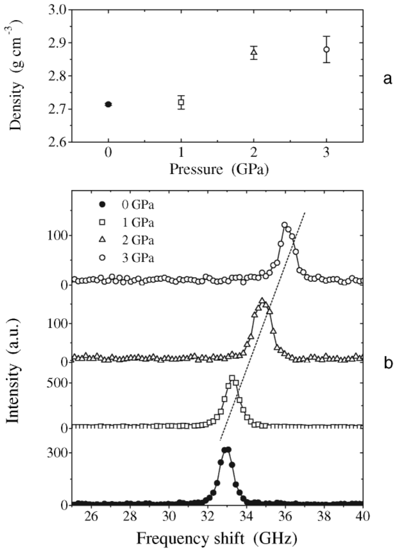

FIG. 3. Dependence on densification of (a) density and (b) longitudinal acoustic frequency measured by Brillouin light scattering in backscattering geometry. The dashed line emphasizes the shift of the longitudinal mode with pressure.

small size of that sample, while the effect on the sound velocities is well pronounced [Fig. 3(b)].

The Debye energies E_D were calculated according to the Debye approximation for the density of states $g(E)$:

$$\lim_{E\to 0}\frac{g(E)}{E^2}=\frac{m_r}{\langle m\rangle}\frac{1}{2\pi^2\hbar^3 n\langle v\rangle^3}\equiv\frac{3}{E_D^3},\tag{1}$$

where $m_r/\langle m\rangle$ is the ratio of the resonant ^{57}Fe and the mean atomic masses [28,29], n is the number of atoms per unit volume, and $\langle v\rangle$ is the mean sound velocity defined as

$$\frac{1}{\langle v\rangle^3}=\frac{1}{3}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right).\tag{2}$$

The obtained Debye energies are shown in Table I. The calculated Debye levels $3/E_D^3$ are in good agreement with the extrapolation of the reduced DOS to $E \longrightarrow 0$ (Fig. 1).

The comparison of Figs. 2 and 3 shows that the short-range and macroscopic properties of the studied samples evolve with densification differently. The first step of compression causes significant modification of the local structure [Fig. 2(a)], but almost does not change the density and the sound velocity (Fig. 3). The main changes in density and sound velocity occur on the further compression steps where, conversely, the short-range order appears not to change.

TABLE I. The density (ρ), the longitudinal (v_L) and transverse (v_T) sound velocity, and the Debye energy (E_D) for the initial and the densified glasses.

Sample	ρ (g cm^{-3})	v_L (km s^{-1})	v_T (km s^{-1})	E_D (meV)
0 GPa	2.714(3)	5.28(2)	3.07(3)	26.7(5)
1 GPa	2.72(2)	5.32(2)	3.06(3)	26.7(5)
2 GPa	2.87(2)	5.41(2)	3.12(5)	27.7(7)
3 GPa	2.88(4)	5.58(3)	3.18(5)	28.3(8)

In order to figure out the role of the macroscopic properties in the transformation of the DOS, we rescaled the energy axes of the density of states in Debye energy units and renormalized the DOS to a unit area. This removes the influence of the Debye energy and allows for comparing the reduced DOS under conditions of identical elastic medium. Figure 4 shows that the rescaling removes the differences among the reduced DOS for the 1, 2, and 3 GPa samples. Thus, the transformation of the DOS with density is entirely described by the transformation of the elastic medium. In particular, the increase of density does not change the boson peak: the decrease of the vibrational states is compensated by the corresponding decrease of the Debye level. On the contrary, the change of the DOS on the initial step of compression cannot be accounted for by the modification of the elastic medium and has to be related to the local structure transformation revealed by the Mössbauer data.

These observations can be compared to the expectations of various models of the boson peak. Our results show that in the absence of structural changes the position of the peak in the reduced DOS increases with density as $n^{1/3}\langle v\rangle$ and its height decreases as $1/(n\langle v\rangle^3)$. This is consistent with a sound-wave model [30,31], where the evolution with density of the DOS is described by the only parameter of the Debye energy.

In the phonon localization model, the boson peak is attributed to modes localized over a characteristic intermediate-range-order length, which has been connected to either the width [5,24] or the position [6,23] of the first sharp diffraction peak. The dependence of the boson peak on density is consequently related to the corresponding modification of the first sharp diffraction peak.

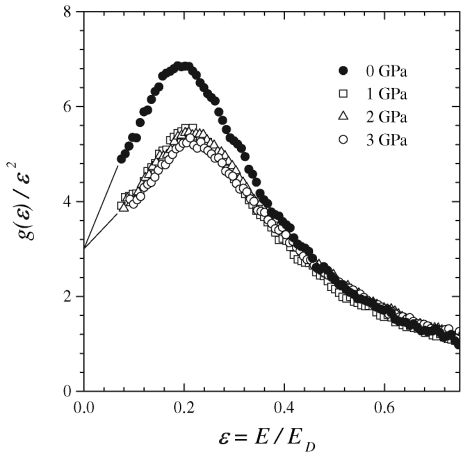

FIG. 4. Reduced density of states after rescaling the energy axes in Debye energy units and the corresponding renormalization of the DOS area. The thin lines emphasize the consistency of the data with the Debye level $g(\varepsilon)/\varepsilon^2 = 3$.

In contrast, our results show that the transformation of the DOS with density is sufficiently described by the changes of the macroscopic properties. The continuous changes in the intermediate-range order revealed by the x-ray scattering data [Fig. 2(b)] seem to be not necessarily required to describe the transformation of the boson peak with density.

The soft-mode model predicts a linear shift of the boson peak and a faster-than-exponential suppression of its height with density [14,15]. It remains to be checked whether these two predictions are compatibles with the density dependence of the single parameter of the Debye energy.

In summary, we investigated the effect of densification on the density of vibrational states of a $Na_2FeSi_3O_8$ glass. We also analyzed the corresponding changes in microscopic, intermediate range, and macroscopic properties. Our results show that—in the absence of structural modifications in the short-range order—the transformation of the DOS with density is accounted for by a single parameter of the Debye energy. This property is lost if a local structural transformation takes place. Similar to the recent investigation of hyperquenched glasses [32], our results suggest that the transformation of the density of vibrational states of a glass with a given structure can be entirely described by the corresponding modification of the elastic medium.

We are grateful to M. Arai for the advice on the densification procedure, F. Kargl for the preparation of the glass, M. Zajac for fitting the Mössbauer spectra, and F. Scarponi for support during the Brillouin light scattering measurements.

---

*Corresponding author.
Electronic address: chumakov@esrf.fr
Also at Russian Research Center "Kurchatov Institute," 123182 Moscow, Russia.

[1] See, e.g., B. Frick and D. Richter, Science **267**, 1939 (1995), and references therein.
[2] J.D. Boyer, J.C. Lasjaunias, R.A. Fisher, and N.E. Phillips, J. Non-Cryst. Solids **55**, 413 (1983).
[3] R. Geilenkeuser, Th. Porschberg, M. Jäckel, and A. Gladun, Physica (Amsterdam) **263B–264B**, 276 (1999).
[4] T. Arai, H. Kataura, H. Yasouka, and S. Onari, J. Non-Cryst. Solids **77–78**, 1149 (1985).
[5] S. Sugai and A. Onodera, Phys. Rev. Lett. **77**, 4210 (1996).
[6] R.J. Hemley, C. Meade, and H.K. Mao, Phys. Rev. Lett. **79**, 1420 (1997).
[7] Y. Inamura, M. Arai, N. Kitamura, S.M. Bennington, and A.C. Hannon, Physica (Amsterdam) **241B–243B**, 903 (1998).
[8] M. Yamaguchi, T. Nakayama, and T. Yagi, Physica (Amsterdam) **263B–264B**, 258 (1999).
[9] B. Frick, C. Alba-Simionesco, J. Herndicks, and L. Willner, Prog. Theor. Phys. Suppl. **126**, 213 (1997).
[10] B. Frick and C. Alba-Simionesco, Appl. Phys. A **74**, S549 (2002).
[11] Y. Inamura, M. Arai, O. Yamamuro, A. Inaba, N. Kitamura, T. Otomo, T. Matsuo, S.M. Bennington, and A.C. Hannon, Physica (Amsterdam) **263B–264B**, 299 (1999).
[12] Y. Inamura, M. Arai, T. Otomo, N. Kitamura, and U. Buchenau, Physica (Amsterdam) **284B–288B**, 1157 (2000).
[13] Y. Inamura, M. Arai, M. Nakamura, T. Otomo, N. Kitamura, S.M. Bennington, A.C. Hannon, and U. Buchenau, J. Non-Cryst. Solids **293–295**, 389 (2001).
[14] M.I. Klinger, J. Non-Cryst. Solids **293–295**, 345 (2001).
[15] V.L. Gurevich, D.A. Parshin, and H.R. Schober, Phys. Rev. B **71**, 014209 (2005).
[16] M. Mezouar, T. Le Bihan, H. Libotte, Y. Le Godec, and D. Häusermann, J. Synchrotron Radiat. **6**, 1115 (1999).
[17] R. Rüffer and A.I. Chumakov, Hyperfine Interact. **97–98**, 589 (1996).
[18] See, e.g., A.I. Chumakov and W. Sturhahn, Hyperfine Interact. **123–124**, 781 (1999), and references therein.
[19] L.A. Johnson, C.E. Jonson, D. Holland, A. Mekki, P. Appleyard, and M.F. Thomas, J. Non-Cryst. Solids **246**, 104 (1999).
[20] R. Böhmer, K.L. Ngai, C.A. Angell, and D.J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
[21] M. Mezouar *et al.*, J. Synchrotron Radiat. **12**, 659 (2005).
[22] P.S. Salmon, R.A. Martin, P.E. Mason, and G.J. Guello, Nature (London) **435**, 75 (2005).
[23] V.N. Novikov and A.P. Sokolov, Solid State Commun. **77**, 243 (1991).
[24] A.P. Sokolov, A. Kisliuk, M. Soltwisch, and D. Quitmann, Phys. Rev. Lett. **69**, 1540 (1992).
[25] L. Börjesson, A.K. Hassan, J. Swenson, L.M. Torell, and A. Fontana, Phys. Rev. Lett. **70**, 1275 (1993).
[26] L. Comez, D. Fioretto, F. Scarponi, and G. Monaco, J. Chem. Phys. **119**, 6032 (2003).
[27] The refraction index has been directly measured for the 0 GPa sample, while its density dependence has been estimated using the Clausius-Mossotti relation.
[28] M.Y. Hu *et al.*, Phys. Rev. B **67**, 094304 (2003).
[29] A. Bosak and M. Krisch, Phys. Rev. B **72**, 224305 (2005).
[30] E. Maurer and W. Schirmacher, J. Low Temp. Phys. **137**, 453 (2004).
[31] W. Schirmacher, Europhys. Lett. **73**, 892 (2006).
[32] A. Monaco, A.I. Chumakov, Y.-Z. Yue, G. Monaco, L. Comez, D. Fioretto, W.A. Crichton, and R. Rüffer, Phys. Rev. Lett. **96**, 205502 (2006).