

Role of Disorder in the Thermodynamics and Atomic Dynamics of Glasses

A. I. Chumakov,^{1,*} G. Monaco,^{2,1} A. Fontana,^{2,3} A. Bosak,¹ R. P. Hermann,^{4,5} D. Bessas,^{4,5,†} B. Wehinger,¹ W. A. Crichton,^{1,‡} M. Krisch,¹ R. Rüffer,¹ G. Baldi,⁶ G. Carini Jr.,⁷ G. Carini,⁸ G. D'Angelo,⁸ E. Gilioli,⁶ G. Tripodo,⁸ M. Zanatta,^{9,3} B. Winkler,¹⁰ V. Milman,¹¹ K. Refson,¹² M. T. Dove,¹³ N. Dubrovinskaia,¹⁴ L. Dubrovinsky,¹⁵ R. Keding,¹⁶ and Y. Z. Yue^{17,§}

¹European Synchrotron Radiation Facility, F-38043 Grenoble, France

²Dipartimento di Fisica, Università di Trento, I-38123 Povo, Trento, Italy

³IPCF-CNR, UOS di Roma, c/o Roma University La Sapienza, I-00185 Roma, Italy

⁴Jülich Centre for Neutron Science JCNS and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

⁵Faculté des Sciences, Université de Liège, B-4000 Liège, Belgium

⁶IMEM-CNR, Area delle Scienze, I-43124 Parma, Italy

⁷IPCF-CNR, UOS di Messina, Viale F. Stagno d'Alcontres 37, I-98158 Messina, Italy

⁸Dipartimento di Fisica e Scienze della Terra, Università di Messina, Viale F. Stagno d'Alcontres 31, I-98166 Messina, Italy

⁹Dipartimento di Fisica, Università di Perugia, I-60123 Perugia, Italy

¹⁰Geowissenschaften, Goethe-Universität, Altenhoferallee 1, D-60438, Frankfurt a.M., Germany

¹¹Accelrys, 334 Cambridge Science Park, Cambridge CB4 0WN, United Kingdom

¹²STFC Rutherford Appleton Laboratory, Chilton, Didcot Oxfordshire OX11 0QX, United Kingdom

¹³Materials Research Institute and School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

¹⁴Material Physics and Technology at Extreme Conditions, Laboratory of Crystallography, University of Bayreuth, D-95440 Bayreuth, Germany

¹⁵Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

¹⁶Max Planck Institut for the Science of Light, D-91058 Erlangen, Germany

¹⁷Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark

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We measured the density of vibrational states (DOS) and the specific heat of various glassy and crystalline polymorphs of SiO₂. The typical (ambient) glass shows a well-known excess of specific heat relative to the typical crystal (α -quartz). This, however, holds when comparing a lower-density glass to a higher-density crystal. For glassy and crystalline polymorphs *with matched densities*, the DOS of the glass appears as the smoothed counterpart of the DOS of the corresponding crystal; it reveals the same number of the excess states relative to the Debye model, the same number of all states in the low-energy region, and it provides the same specific heat. This shows that glasses have higher specific heat than crystals not due to disorder, but because the typical glass has lower density than the typical crystal.

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The low-temperature thermodynamic properties of glasses are accepted to be anomalously different from those of crystals due to the inherent disorder of the glass structure. At temperatures of ~ 10 K, the specific heat of glasses shows an excess relative to that of the corresponding crystals. The excess specific heat is related to a distinct feature in the spectrum of the atomic vibrations: At frequencies of ~ 1 THz, glasses exhibit an excess of states above the Debye level of the acoustic waves, the so-called “boson peak.” The excess of specific heat and the boson peak are universally observed for all glasses and by all relevant experimental techniques. However, the results still do not converge to a unified answer to how disorder causes these anomalies.

The majority of the models explain the boson peak by appealing to various glass-specific features. These include low-energy optical modes [1], onset of mechanical instability related to

saddle points in the energy landscape [2] or to jamming [3–5], local vibrational modes of clusters [6] or locally favoured structures [7], librations [8] or other coherent motions [9] of molecular fragments, crossover of local and acoustic modes [10], quasilocal vibrations of atoms in an anharmonic potential [11], broadening of vibrational states in the Ioffe-Regel crossover regime [12], spatial variation of the elastic moduli [13], breakdown of the continuum approximation [14,15], and topologically diverse defects [16], to cite the most important ones.

Alternatively, the boson peak is identified as the counterpart of the acoustic van Hove singularities of crystals, i.e., explained by the piling up of the vibrational states of the acousticlike branches near the boundary of the pseudo-Brillouin zone [17–20].

Diverging in explanations of the boson peak, all models agree that the excess states and the excess specific heat of

glasses are anomalies caused by *disorder*. The results presented below question this issue.

We studied the atomic dynamics of various glassy and crystalline polymorphs of SiO_2 . This is not only the archetypical system which established the problem of the boson peak. More important, SiO_2 exists in various glassy and crystalline polymorphs, which allows for an analysis of the atomic dynamics as a function of local structure and density. Different to many previous works, the densities of states were measured in absolute units. This allows for a quantitative comparison of the numbers of states for various polymorphs.

The density of states was measured by two techniques—nuclear resonant analysis of inelastic x-ray scattering (NRAIXS) [21] and inelastic x-ray scattering with crystal optics (IXS) [22]. The absolute scale of the DOS was verified by comparing the specific heat calculated from the derived DOS to the measured specific heat for each studied polymorph. For crystals, the reliability of the DOS was further confirmed by *ab initio* lattice dynamics calculations using density functional perturbation theory [23]. The details of the experimental methods and calculations are reported in the Supplemental Material [24].

Figure 1 shows the density of vibrational states for the ambient and the densified polymorphs of silica glass; Fig. 2 shows those for polycrystalline α -cristobalite, α -quartz, and coesite. The total (i.e., statistical and systematic) relative uncertainties of the presented DOS are 6% and 13% for NRAIXS and IXS data, respectively [24]. The agreement of the data obtained by the two IXS techniques [Figs. 1(a)–(d), Figs. 2(a)–(f)] and the consistency of the calculated specific heat with the experimental specific heat [Figs. 1(e)–(f), Figs. 2(g)–(i)] evidence the reliability of the obtained results.

Usually the comparison of thermodynamic and atomic dynamic properties of glasses and crystals is performed for the most common polymorphs, which for SiO_2 are ambient silica glass and α -quartz. Such a comparison is shown in Figs. 3(a)–(c). It illustrates the puzzle which established the problem of the boson peak: The DOS of the glass is significantly softer than that of the crystal [Fig. 3(a)], the reduced DOS shows the distinct peak at ~ 5 meV where the reduced DOS of the crystal is nearly flat [Fig. 3(b)], and at ~ 10 K the specific heat of the glass shows an excess over that of the crystal [Fig. 3(c)]. This trend is observed for nearly all glasses. According to the generally accepted point of view, it is attributed to disorder.

However, the other SiO_2 polymorphs studied here cast doubts on this conclusion. For instance, the comparison of densified silica glass and α -cristobalite [Figs. 3(d)–(f)] would lead to the *opposite* suggestion that disorder shifts the vibrational states to *higher* energy [Fig. 3(d)], makes the reduced DOS of the glass nearly *flat* at the position where the reduced DOS of the crystal has a distinct peak [Fig. 3(e)], and provides the *deficit* of specific heat at ~ 10 K [Fig. 3(f)]. Although this

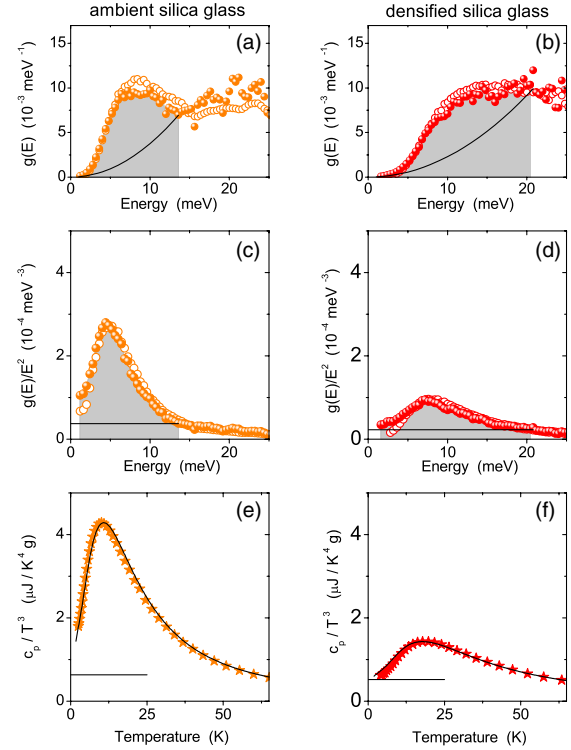


FIG. 1 (color online). The density of states (a)–(b) and the reduced density of states (c)–(d) of ambient and densified silica glass. The solid and the open circles refer to the NRAIXS and IXS data, respectively. The solid lines show the Debye levels for the DOS (a)–(b) and reduced DOS (c)–(d). The area of the filled region of the DOS above the Debye parabola in (a)–(b) gives the number of the excess states. The entire area of the filled region in (a)–(b) gives the number of all states within the same energy ranges. The filled areas in (c)–(d) show the same energy regions for the reduced DOS. (e)–(f) The measured specific heat (symbols) and the specific heat calculated from the corresponding DOS (solid lines). The horizontal lines in (e)–(f) show the Debye levels for the specific heat.

opposite trend is rare, it was observed, e.g., for amorphous and crystalline zeolite [27,28].

A check of the densities of the various SiO_2 polymorphs (Table 1) reveals that Figs. 3(a)–(c) compare a low-density glass with a high-density crystal, whereas Figs. 3(d)–(f) do the opposite—compare a high-density glass with a low-density crystal (as for amorphous and crystalline zeolite [27,28]). A different density is accompanied by different sound velocity [29], which determines different properties of the elastic medium of the glass and influences its atomic dynamics [20,30,31]. Therefore, in order to reveal the effect of disorder unambiguously, a proper comparison should be done for glassy and crystalline polymorphs with *matched densities*, i.e., for ambient silica and α -cristobalite (low-density polymorphs) and for densified silica and α -quartz (high-density polymorphs). Sound velocities, Debye energies, and diffraction patterns [24] show that these pairs indeed have close elastic properties and local structures.

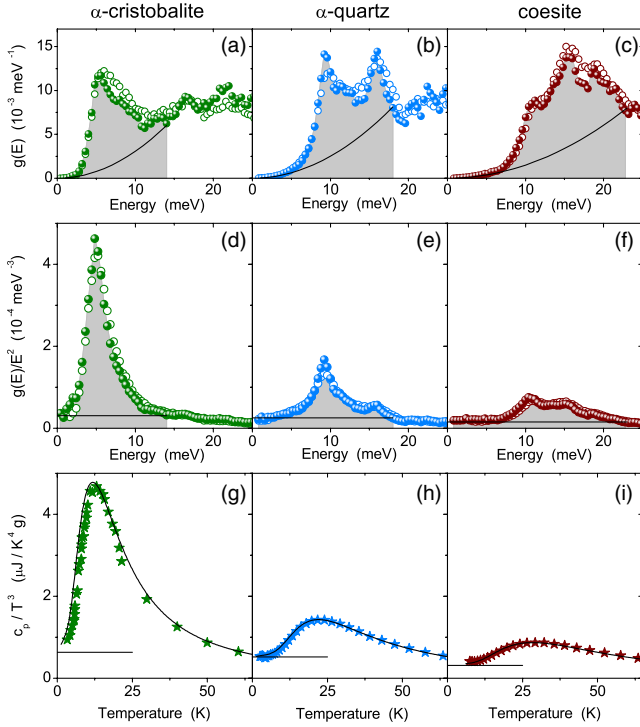


FIG. 2 (color online). The density of states (a)–(c) and the reduced density of states (d)–(f) of α -cristobalite, α -quartz, and coesite. (g)–(i) The measured specific heat (symbols) of α -cristobalite (from Refs. [25,26]), α -quartz, and coesite and the specific heat calculated from the corresponding DOS (solid lines). The symbols, solid lines, and the filled regions have the same meaning as in Fig. 1.

A comparison of SiO_2 glasses and crystals with *matched densities* (Fig. 4) reveals a simple but quite unexpected picture. The density of states of the glass does not differ much from that of the crystal except for some smearing out of the DOS features [Figs. 4(a),(d)], the peaks of the reduced DOS are located nearly *at the same energies* Figs. 4(b),(e)], and the specific heat is practically *the same* for the glassy and crystalline counterparts [Figs. 4(c),(f)].

In essence, Fig. 4 shows that the excess of specific heat of the typical (ambient) silica glass relative to the typical (α -quartz) crystal [(Fig. 3(c))] is related not to the structural *disorder* of the glass but to its lower *density*. Note that the lower density of glasses relative to crystals is not limited to the SiO_2 system but is a general trend well documented in the literature (often discussed as the excess volume of glasses).

The similarities of glasses and crystals with matched densities are further confirmed by a quantitative analysis of the *number of states*. The solid lines in Figs. 1(a)–(d) and Figs. 2(a)–(f) show the Debye levels calculated from density and sound velocities data [24]. The area of the filled region of the DOS above the Debye parabolas in Figs. 1(a)–(b) and Figs. 2(a)–(c) gives the number of the excess states N_{ex} . The entire area of the filled region gives the number of all states N_{all} within the same energy range.

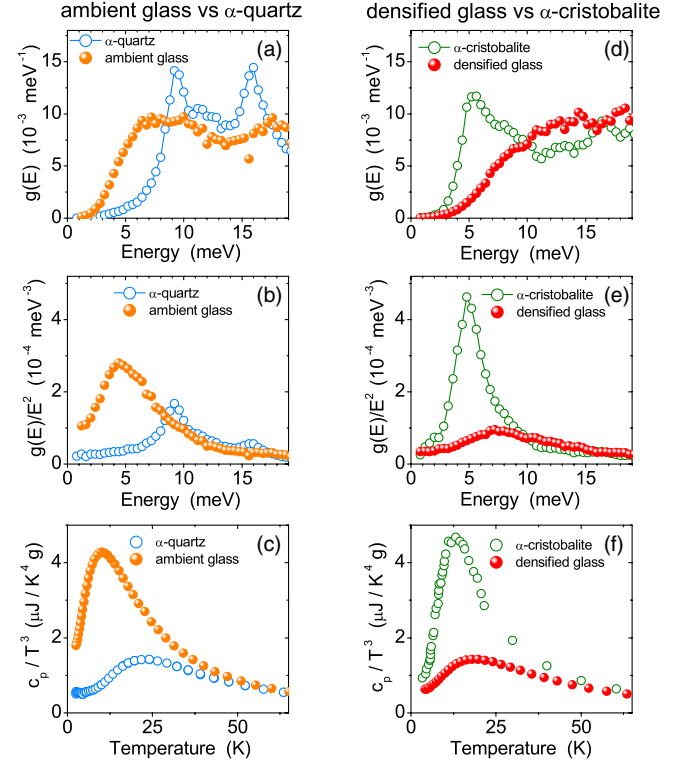


FIG. 3 (color online). Comparison of the density of states (a), (d) and the reduced density of states (b),(e) obtained with the NRAIXS technique, and of the specific heat (c),(f) for ambient silica glass and α -quartz (a)–(c), and for densified silica glass and α -cristobalite (d)–(f). The experimental data for the specific heat of α -cristobalite in (f) are those from Refs. [25,26].

Table 1 shows that the excess of states of silica glasses is not remarkable relative to their crystalline counterparts. It is about 5%–6% for both glassy polymorphs, which is nearly *the same* as the excess of states for α -cristobalite and α -quartz crystals (6%–7%) and even less than that for coesite (9%). These observations cannot be caused by an accidental underestimation of the excess states for the glasses: The analysis of the inelastic neutron scattering data for ambient

TABLE I. The number of the excess states N_{ex} in the DOS of glassy and crystalline polymorphs of SiO_2 , the number of all states N_{all} within the same energy regions derived from the NRAIXS data, and the fraction of the acoustic states N_{ac} for the three crystals given by $N_{ac} = N^{-1}$, where N is the number of atoms in a primitive unit cell of α -cristobalite ($N = 12$), α -quartz ($N = 9$), and coesite ($N = 24$). The numbers of states are given as a percentage of the unit area of the DOS.

Sample	Density (g/cm ³)	$N_{ex}(\%)$	$N_{all}(\%)$	$N_{ac}(\%)$
Ambient silica glass	2.20	5.3(3)	8.4(5)	...
α -cristobalite	2.29	5.6(3)	8.4(5)	8.333
Densified silica glass	2.67	5.9(4)	12.8(8)	...
α -quartz	2.65	6.6(4)	11.5(7)	11.111
Coesite	2.93	8.6(5)	14.6(9)	4.167

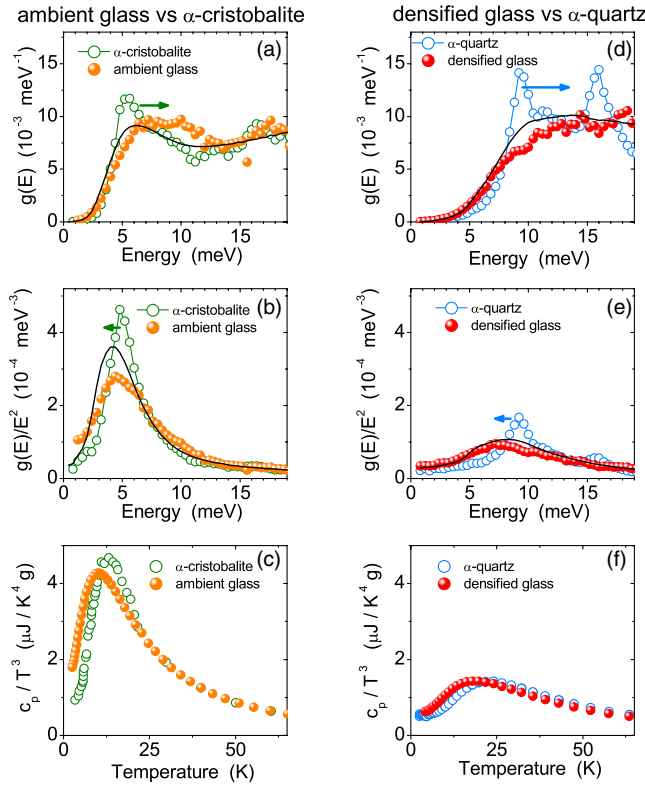


FIG. 4 (color online). Comparison of the density of states (a), (d) and the reduced density of states (b),(e) obtained with the NRAIXS, and of the specific heat (c),(f) for ambient silica glass and α -cristobalite (a)–(c), and for densified silica glass and α -quartz (d)–(f). The solid lines in (a)–(b), (d)–(e) show the modified DOS (a), (d) and reduced DOS (b),(e) of α -cristobalite (a)–(b) and α -quartz (d)–(e) calculated allowing for the finite size of the Brillouin zone (see text). The arrows in (a)–(b), (d)–(e) emphasize the shift of the peaks in the DOS and reduced DOS of glasses relative to those of crystals. The experimental data for the specific heat of α -cristobalite in (c) are those from Refs. [25,26].

silica glass [32] provides *the same* number of excess states [24]. Furthermore, an increase in the low-energy states of the studied crystals due to some kind of disorder is also excluded: The calculated DOS of *ideal* α -cristobalite, α -quartz, and coesite [24] contain nearly the same number of excess states.

Furthermore, Table 1 shows that the absolute number of all states N_{all} in the considered energy regions is nearly the same for the glassy and crystalline pairs with matched density. Moreover, it is close to the fraction of the *acoustic states* of the corresponding crystal [33]. For α -cristobalite the fraction of the acoustic states should be 8.333%. Consistently, the number of states N_{all} for both α -cristobalite and ambient silica glass in the considered energy region is 8.4%. For α -quartz, the fraction of the acoustic states should be 11.111%, and the number of states N_{all} for α -quartz and densified silica glass is 12.8% and 11.5%, respectively.

These observations revise the role of disorder in the thermodynamics and atomic dynamics of glasses. They

show that disorder does not influence much the energy spectrum of atomic vibrations. In the first approximation, the influence of disorder *in the DOS* is limited to the smearing out of the DOS features. Upon a closer view, disorder also separates in energy the peaks in the DOS and the reduced DOS. For crystals, they are located at the same energy. For glasses, the maximum of the DOS is shifted to higher energy, whereas the peak of the reduced DOS is shifted to lower energy [Figs. 4(a)–(b),(d)–(e)].

Before proceeding to discussion, we summarize the experimental observations and analyze what deserves an explanation. In terms of thermodynamics, the results show that the specific heat of the glasses and crystals with matched densities is essentially the same. This cancels the puzzle of the excessive specific heat of glasses for the studied system. In terms of atomic dynamics, the DOS of the glasses and corresponding crystals differ mainly by smoothening. In itself, this also looks natural and does not appeal for an explanation. However, the extensive studies of the boson peak define it as the puzzle and demand the explanation of the peak in the reduced DOS of the glasses.

In crystals, the peak in the reduced DOS is the acoustic van Hove singularity. It results from a piling up of the vibrational states near the boundary of the Brillouin zone. In our eyes, the striking qualitative and quantitative similarities in the DOS and reduced DOS for the glasses and corresponding crystals suggest that the boson peak is caused by the same mechanism. Indeed, similar to crystals, the dispersion relations in glasses reveal (see below for details) flattening near the boundary of the pseudo-Brillouin zone [34–36]. Furthermore, the studied glasses and corresponding crystals have nearly the same sound velocity and size of the Brillouin and pseudo-Brillouin zones [24]. Therefore, the dispersion curves for glasses and crystals should reveal the piling up effect at approximately the same energies. Consistently, the experimental results show that the boson peak and the van Hove singularity are located at 4.4 and 4.8 meV, respectively [low-density polymorphs, Fig. 4(b)], or at 7.4 and 9.2 meV, respectively [high-density polymorphs, Fig. 4(e)].

Near the boundary of the pseudo-Brillouin zone, the vibrational states in glasses (and liquids) are no longer the plane waves. The vibrational energy for a given wave vector is not a fixed value but reveals an energy spread [36–38]. This causes the difference in the dispersion curves related to the momentum-differential contributions to the DOS (current correlation function) and reduced DOS (dynamic structure factor). The dispersion curve related to the DOS is dominated by the upper edge of the energy spread. Therefore, while the dispersion curve related to the reduced DOS reveals the flattening near the border of the pseudo-Brillouin zone, the curve related to the DOS may continue to rise [39]. Accordingly, the DOS of the glasses does not show any special feature at the position of the boson peak, and reaches maximum at higher energy.

This explains the discussed separation of the peak in the DOS and reduced DOS [Figs. 4(a)–(b),(d)–(e)].

The smoother appearance of the DOS in glasses can be attributed to the variance of the local structures and described by the finite width of the pseudo-Brillouin zone boundary [37,38]. We modified the measured DOS of α -cristobalite and α -quartz, allowing for the finite width of the pseudo-Brillouin zone boundary determined by the width of the first sharp diffraction peak in the static structure factor of glasses [24]. The results [Figs. 4(a)–(b),(d)–(e)] show that the modified DOS and reduced DOS of the crystals become similar to those of the corresponding glasses. Moreover, the smearing out reproduces the discussed separation of the peaks in the DOS and reduced DOS.

The plausible dominance of the piling up effect does not exclude other contributions. The shape of the DOS and reduced DOS is certainly influenced by an additional broadening caused by the finite lifetime of vibrational states [12]. Furthermore, it can be affected by a possible proximity to mechanical instabilities related to saddle points in the energy landscape [2] and invoked in the description of systems close to jamming [3–5]. Usually, the boson peak in jamming systems is discussed in terms of mechanical instability. We suspect that it also relates to the pileup effect, because jamming systems reveal a well-defined pseudo-Brillouin zone and show an excess of states even far away from the unjamming transition [5]. In this view, the mechanical instability would be mainly responsible not for the *existence* of the boson peak but for its *shift* to lower energy when approaching the unjamming transition. Therefore, the effects of instability most possibly should appear in the low-energy region of the DOS [40].

Finally, we note that the obtained results disentangle the origin of the anomalous thermal conductivity and specific heat of glasses: while the former is clearly caused by disorder, the latter is related to the lower density of the glasses. Thus, the low-energy (meV) dynamics and the low-temperature (~ 10 K) specific heat of the covalently-bonded glasses studied here are not anomalous: They are similar to those of crystals, and as such are more reflecting the residual order present in glasses than their structural disorder.

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*Also at National Research Center “Kurchatov Institute,” 123182 Moscow, Russia.chumakov@esrf.fr

†Present address: European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble Cedex 9, France.

‡Also at Department of Earth Sciences, University College London, Gower St., London WC1E 6BT, UK.

§Also at State Key Laboratory of Silicate Materials for Architecture, Wuhan University of Technology, Wuhan 430070, China.

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