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Equivalence of the Boson Peak in Glasses to the Transverse Acoustic van Hove Singularity in Crystals

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We compare the atomic dynamics of the glass to that of the relevant crystal. In the spectra of inelastic scattering, the boson peak of the glass appears higher than the transverse acoustic (TA) singularity of the crystal. However, the density of states shows that they have the same number of states. Increasing pressure causes the transformation of the boson peak of the glass towards the TA singularity of the crystal. Once corrected for the difference in the elastic medium, the boson peak matches the TA singularity in energy and height. This suggests the identical nature of the two features.

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The thermodynamic and transport properties of glasses are remarkably different from those of crystals. At low temperature, glasses reveal an excess of specific heat and a plateau in the thermal conductivity. It is generally accepted that these anomalies originate from the corresponding anomaly in the frequency spectra of atomic vibrations: At low energy, glasses exhibit an excess of vibrational states over the level determined by the acoustic waves, the so-called 'boson peak'. The boson peak is universally observed for all glasses in measurements of specific heat, light, x-ray, and neutron scattering. The nature of this feature, however, remains unclear.

Driven by the distinction from crystalline properties, the majority of theoretical models explain the boson peak appealing to features beyond acoustic dynamics. These include a phonon-saddle transition in the energy landscape [1]; local vibrational modes of clusters [2] or locally favored structures [3]; librations of molecular fragments [4]; crossover of local and acoustic modes [5]; and vibrations in an anharmonic potential [6].

However, there are indications that the anomalies can originate still from acoustic waves: In analytical and computer models of harmonic crystals, the boson peak appears as the counterpart of the acoustic van Hove singularity shifted to lower energy by force-constants disorder [7, 8]. In simulations of disordered systems, the boson peak is assigned to flattening [9] or Ioffe-Regel crossover [10] in the transverse acoustic (TA) branch near the pseudo-Brillouin zone boundary of the glass.

A still different scenario comes from *continuum* models, where the anomalies arise from force-constant disorder

without involving the pseudo-Brillouin zone [11] and from molecular dynamics simulations [12, 13], where the boson peak is related to the vibrational states of the TA branch well within the pseudo-Brillouin zone.

Identifying the true origin of the boson peak in real glasses out of many theoretical models remains difficult: Most of the experimental results fit many models. Therefore, an undoubted verification of the nature of the boson peak is still missing. In this Letter, we report on the experimental results which, without invoking any model, evidence a *gradual transformation* of the boson peak of a sodium silicate glass $\text{Na}_2\text{FeSi}_3\text{O}_{8.5}$ into the TA van Hove singularity of the corresponding crystal. *Ab initio* calculations show that the vibrational states of the TA singularity of the crystal and, possibly, of the boson peak of the glass include librations of SiO_4 tetrahedra.

The iron-partial density of vibrational states (DOS) was measured using nuclear inelastic scattering. Details of the method [14], preparation and characterization of the samples are described in Supplementary Material. Fig. 1 shows the evolution of the DOS and reduced DOS as a function of pressure. In the studied glass, iron substitutes for silicon as a tetrahedrally coordinated specie. Therefore, the iron-partial DOS directly reflects the vibrational properties of the Si-O-Si network of the glass.

Fig. 1 also shows the data for the polycrystalline counterpart of the studied glass, aegirine $\text{NaFeSi}_2\text{O}_6$, the dominant product obtained by crystallization of this particular glass (Supplementary Material). At 11 meV, the DOS of aegirine reveals a shoulder (Fig.1a). In the reduced DOS, it is seen as a peak (Fig.1d). *Ab initio* cal-

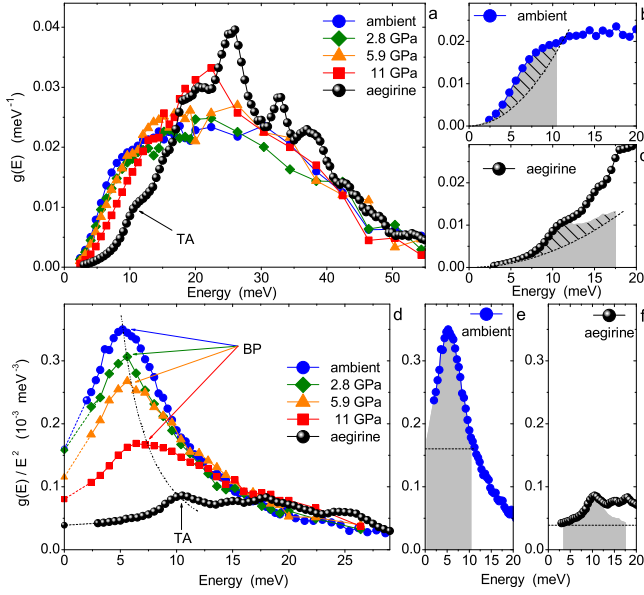


FIG. 1: DOS (a-c) and reduced DOS (d-f) of the sodium silicate glass at various pressures and of the crystalline counterpart of the glass, the aegirine crystal. The arrows show the transverse acoustic (TA) van Hove singularity of the crystal and the boson peak (BP) of the glass. The symbols at $E=0$ in (d) show the Debye levels calculated from the measured density and sound velocity. The dashed lines in (d) emphasize the consistency of the reduced DOS with the Debye levels. The dashed-dotted line in (d) indicates the transformation of the boson peak towards the TA singularity. The filled areas of the DOS of the ambient glass (b) and the aegirine crystal (c) correspond to the filled areas of the reduced DOS within the FWHM of the boson peak (e) and of the TA singularity peak (f), respectively. The dashed lines in (b, c, e, f) show the Debye levels. The hatched part of the filled area in (b, c) marks the excess of states over the Debye level.

culations (Supplementary Material) identify this feature with the most visible transverse acoustic van Hove singularity: It is reproduced both in the iron-partial and the total calculated DOS (Fig.2b). The dispersion relations (Fig.2a) reveal that the shoulder originates mostly from the saddle point of two close TA branches at the $(0,0,1/2)$ boundary (A-point) of the Brillouin zone.

Fig. 1d illustrates the discussed anomaly of the boson peak: At 5 meV, the reduced DOS of the glass reveals a big excess of states relative to the Debye level. At this energy, the reduced DOS of the crystal is consistent with the Debye model and does not show any special feature.

The filled region in Fig. 1e marks the reduced DOS of the glass within the full width at half maximum (FWHM) of the boson peak. In Fig. 1f, the filled region shows the part of the reduced DOS around the TA singularity. For a proper comparison to the symmetric boson peak, here the marked region above 12 meV is defined as the mirror image of the left side of the peak. In Figs. 1b,c, the same regions are shown in the density of states. The filled areas give nearly the same number of vibrational states for the boson peak and TA singularity, namely 0.098(8) and

0.102(7), respectively. Furthermore, the excess of states above the Debye level (the hatched region in Figs.1b,c) is also nearly the same, 0.034(8) and 0.032(7) for the boson peak and TA singularity, respectively. Thus, in the *reduced* DOS the boson peak is higher than the TA singularity not because of the larger excess of states, but because these states are located at lower energy.

The equivalence of the boson peak and the TA singularity in the *absolute number of states* suggests that the vibrational states of the boson peak belong to *acoustic* branches. Indeed, an alternative attribution of the boson peak to *additional* modes would face a problem to explain the $\sim 35\%$ deficit of acoustic states in the glass.

Application of pressure causes the transformation of the reduced DOS of the glass towards the reduced DOS of the crystal (Fig. 1d): The boson peak decreases in height and shifts to higher energy, moving towards the TA singularity. Fig. 1d also suggests the mechanism of this: The height of the boson peak decreases consistently with the decrease of the Debye level, staying approximately two times higher. The same ratio holds also for the height of the TA singularity and the Debye level of the crystal. Because the Debye level is defined by the elastic medium, this suggests that (i) the effect of pressure on atomic vibrations of the glass and (ii) the difference of atomic vibrations of the glass and the crystal are controlled mainly by the elastic medium.

The measured (Supplementary Material) density and sound velocity are shown in Fig. 3. The density shows the usual increase with pressure. The sound velocities reveal an anomaly: The transverse velocity decreases, reaches a minimum at ~ 2.5 GPa, and then increases. At the same pressure, the longitudinal velocity changes its slope.

Using the density and sound velocities data, the Debye energies E_D were calculated (Supplementary Material). Fig. 4 shows the reduced DOS in Debye units. This corrects the data for differences in the elastic medium [15, 16]. Except for the 2.8 GPa data, the boson peaks are

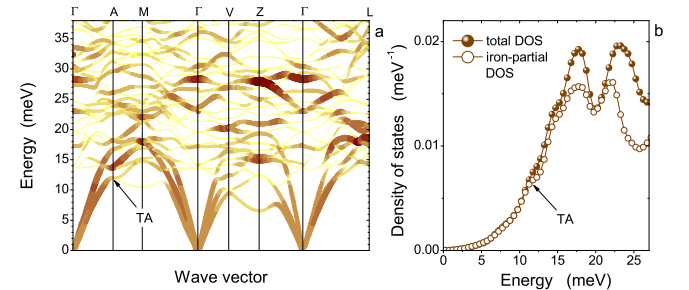


FIG. 2: (a) The calculated dispersion relations for the aegirine crystal. The size and intensity of symbols is proportional to the fraction of vibrational energy related to iron atoms. (b) The calculated iron-partial and total DOSs. In order to emphasize the match of the two DOS at low energy, the iron partial DOS is divided by the mass-ratio coefficient $m_{Fe}/\langle m \rangle$ (Supplementary Material). The arrows show the positions of the transverse acoustic (TA) van Hove singularity.

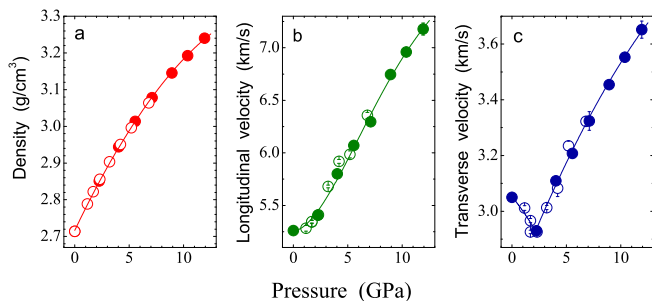


FIG. 3: The pressure dependence of (a) density, (b) longitudinal and (c) transverse sound velocity of the sodium silicate glass. The solid and open circles show the results of two independent measurements. The lines are to guide the eye.

identical both in energy and height. This means that the evolution of the boson peak with pressure is controlled mainly by the elastic medium. The same trend has been observed in other experiments [15–19] and suggested by theory [10]. Some deviations were also reported: For high-temperature measurements [20, 21], they are apparently related [20] to anharmonic effects. For high-pressure studies of polymers [22, 23], they could be possibly attributed to significant pressure dependence of the glass transition temperature.

At 2.8 GPa, the boson peak in Debye units is lower than the others (Fig. 4a). At this pressure, the TA velocity decreases (Fig. 3c). This anomaly is commonly attributed to frequency-dependent relaxation effects [24]. They affect the measured sound velocity at the \sim GHz frequencies but do not change much the sound velocity at the frequencies of the boson peak [20]. Assuming that the \sim THz transverse sound velocity stays the same as at ambient pressure, the height of the boson peak at 2.8 GPa will increase by 8% and match all other curves.

Fig. 4b compares the results for the glass and the crystal: The corrections for the elastic medium eliminate entirely the initial (Fig. 1b) \sim 400% difference in height and almost completely remove the initial \sim 200% difference in energy. The residual \sim 20% mismatch in energy of the boson peak for the ambient glass and the TA singularity of the crystal seems to disappear with the increase of density: At 11 GPa, the reduced DOS of the glass develops a shoulder at the position of the TA singularity (Fig. 4b). This indicates an eventual match of the boson peak and the TA singularity both in *height* and *energy*.

The equivalence of boson peak and TA singularity in Debye units (Fig. 4b) suggests that the boson peak originates from the piling up of the acoustic states near the boundary of the pseudo-Brillouin zone. To check this, we estimate the size of the pseudo-Brillouin zone required to provide the boson peak at the observed energy. Assuming that the energy of the dominant contribution to the *reduced* DOS in glasses can be, similar to crystals, approximated by a sinusoidal dependence on the wave-number (Fig. 5b), the effective size q_0 of the average (for

crystal) and pseudo- (for glass) Brillouin zone is given by the transverse sound velocity v_T and the energy of the peak E_0 as $q_0 = \pi E_0 / 2\hbar v_T$. In order to account for changes in density, we express q_0 in units of the Debye wave number $q_D = (6\pi^2 n)^{1/3}$, where n is the molecular number density. Fig. 5a shows that q_0 is only slightly (\sim 8%) affected by the glass density. The small continuous growth is consistent with the expected steepening of the dispersion curves with density [9]. The extrapolation of the estimated q_0 to the density of the crystal matches the size of the Brillouin zone in aegirine (Fig. 5a). Thus, the suggested piling up of the boson peak states in the glass should occur at nearly the same wave-numbers as the piling up of the TA states in the crystal.

The assumed model for the q -dependence of the dominant contribution of the TA branch to the *reduced* DOS (Fig. 5a) is justified by the observations of the *transverse* modes in glasses [25–27]. It is also consistent with the precise measurements of the *longitudinal* dispersion relations [28–30]. Moreover, it follows from the results of molecular dynamics simulations [9, 31]: The q -differential components of the *reduced* DOS are given by the dynamic structure factors $S(q, E)$ (Eq. (6) in Ref. [28]). Fig. 5c shows the current correlation functions $J_T(q, E)$ for silica from Ref. [31]. Using these data, we calculated the corresponding $S_T(q, E) \propto J_T(q, E)/E^2$ (Fig. 5d). The q -dependence of the peak positions for $J_T(q, E)$ and $S_T(q, E)$ are shown in Fig. 5e together with the results from Ref. [9] processed in the same way. The behavior of the $S(q, E)$ peaks (Fig. 5e) is close to the assumed model (Fig. 5b).

The suggested assignment of the boson peak to the TA branch does not mean that one can understand the boson peak in terms of only transverse waves. The vibrational states along the TA branch are pure transverse waves only for small wave vectors. Approaching the boundary of the Brillouin zone of crystals or pseudo-Brillouin zone of glasses, the pattern of atomic displacements changes. In silica, the boson peak is associated with librations of

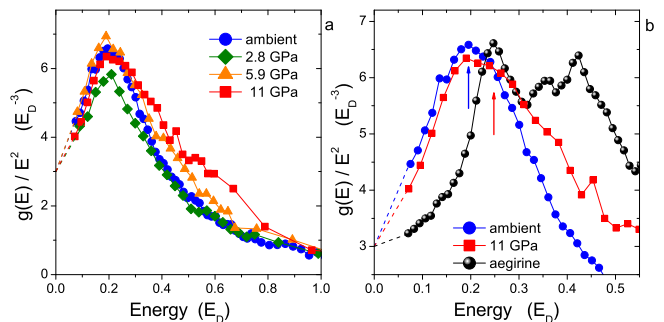


FIG. 4: Reduced density of states of the sodium silicate glass at various pressures and of the aegirine crystal in Debye units. The dashed lines emphasize the consistency of the reduced DOS with the Debye level $3E_D^{-3}$. The blue arrow in (b) shows the boson peak at ambient pressure. The red arrow in (b) emphasizes the shoulder of the reduced DOS at 11 GPa.

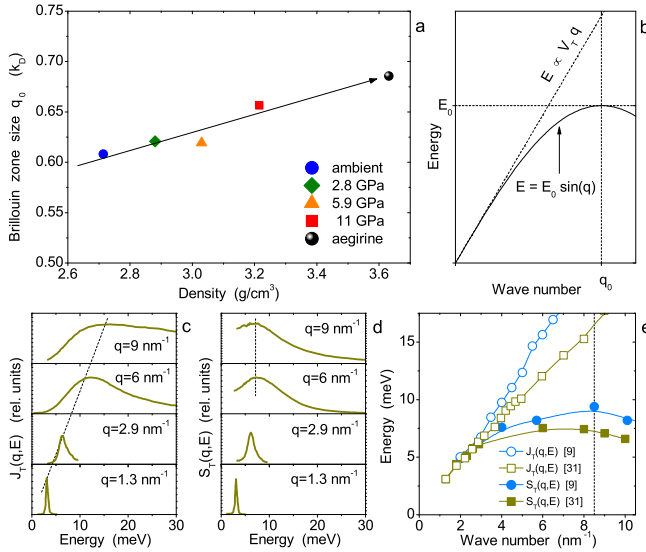


FIG. 5: (a) The effective size q_0 of the pseudo- (for the sodium silicate glass) and of the average (for the aegirine crystal) Brillouin zone. The line shows the linear fit to the glass data only. (b) The model used to calculate q_0 . (c) The current correlation functions $J_T(q, E)$ from Ref.[31]. (d) The dynamic structure factors $S_T(q, E)$ recalculated from $J_T(q, E)$ shown in (c). The dashed lines emphasize the dispersive (c) and non-dispersive (d) behavior of the $J_T(q, E)$ and $S_T(q, E)$ peaks, respectively. (e) The energy positions of the peaks in $J_T(q, E)$ from Refs.[9, 31] and in the recalculated $S_T(q, E)$. The vertical dashed line shows the boundary of the pseudo-Brillouin zone (half of the first sharp diffraction peak position [31]).

SiO_4 tetrahedra [4]. The same can be expected for our glass, because its network consists of the same tetrahedra. Should this be the case, the boson peak and the TA singularity are common also in the pattern of atomic motion: For the TA singularity of aegirine, our *ab initio* calculations show nearly transverse displacements of iron and silicon accompanied by librations of almost undistorted SiO_4 tetrahedra (Supplementary Material).

In summary, the obtained experimental results reveal (i) the *equal number of states* for the boson peak of the glass and TA singularity of the corresponding crystal; (ii) the *equal excess of states* of the two features relative to the Debye levels; (iii) the *gradual transformation* of the boson peak to the TA singularity with pressure, and (iv) the equivalence of these two features in *energy* and in *height* after corrections for the difference in the elastic medium. In addition, *ab initio* calculations indicate that the boson peak of the studied glass and the TA peak of its crystalline counterpart might be common also in the pattern of atomic motions - librations of SiO_4 tetrahedra.

These observations suggest that: (i) The DOS of the glass does not contain *additional* modes in the low-energy region. Similar to the crystal, it consists of acoustic modes, though modified by disorder. (ii) The boson peak appears higher than the TA singularity not because of the larger *excess* of states, but because these states are

located at *lower* energy. (iii) Though the acoustic states in the glass are no longer plane waves, their energy spectrum does not differ qualitatively from that of the crystal: Apart from additional broadening, they transform into each other by corrections for the parameters of the elastic medium. (iv) Similar to the TA singularity, the boson peak originates from the piling up of the acoustic states near the boundary of the pseudo-Brillouin zone.

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be located lower than the shown dispersion relations.

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