

Inelastic x-ray scattering study of liquid Ga: Implications for the short-range orderValentina M. Giordano^{1,2} and Giulio Monaco²¹*Laboratoire de Physique de la Matière Condensée et Nanostructures (LPMCN), Université de Lyon I, 69622 Villeurbanne Cedex, France*²*European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, BP220, 38043 Grenoble CEDEX, France*

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The high-frequency dynamics of liquid gallium is investigated by inelastic x-ray scattering at high pressure using a crystal-like approach for the data analysis to extract the dispersion curves of the quasitransverse and quasilongitudinal acoustic excitations. A strict relation between these dispersion curves and those of solid monoclinic β -Ga is found, confirming the similarity between these two phases already suggested by structural investigations. This result shows that the high-frequency dynamics of liquids holds, similarly to crystals, rich and system-specific information, and establishes a clear connection between microscopic structure and dynamics.

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A snapshot of the microscopic structure of a simple liquid can be interpreted in terms of two extreme pictures: a continuous random network, as well as a collection of crystallites (small enough not to be revealed by diffraction). The latter picture, in particular, naturally emphasizes the role of the short-range order in the microscopic structure. In liquids with a marked short-range order, such as liquid metals, a crystal-like approach has been used in fact to characterize by x-ray diffraction the local atomic structure of the liquid with respect to that of the corresponding crystal,¹ and to carry out similar comparisons for the electronic structure by nuclear magnetic resonance² and inelastic x-ray scattering (IXS).³

For what concerns the high-frequency vibrational properties of liquids, inelastic neutron and x-ray scattering techniques have provided detailed information in the last four decades, revealing the presence of well-defined acoustic excitations well outside the truly hydrodynamic (macroscopic) range:⁴ they appear as peaks in the dynamic structure factor, $S(q, \omega)$, with characteristic frequencies that follow a sinusoidal dispersion curve, $\omega(q)$, q being the momentum exchanged in the scattering process. In these kinds of studies, many details on the short-range order do not play any role. This has to do with the fact that the $S(q, \omega)$ spectra do not show clear qualitative modifications between the macroscopic range and the microscopic (high- q) one (at least for q values well within the pseudo-Brillouin zone). This has in particular led to the development of models (e.g., generalized hydrodynamics⁴) that are largely based on simple hydrodynamics and where the microscopic structure of the liquid is taken into account only via the pair correlation function, $g(r)$ [i.e., the (orientationally averaged) probability distribution of finding an atom at a distance r from a central one placed at $r = 0$]. Liquid alkali metals, for example, have been thoroughly investigated within this framework, and their high-frequency dynamics has been interpreted in terms of two relaxation processes: the structural relaxation, active in the picosecond range and responsible for the viscoelastic effects;^{4,5} and a second relaxation process, dubbed microscopic, active in the subpicosecond range and associated with the structural disorder.⁶

Very recently we have used a crystal-like approach to interpret the high-frequency vibrational spectra of the simplest liquid metal, Na.⁷ We have shown that the microscopic dynamics of a simple liquid can be simply described in

terms of a distribution of acoustic excitations very similar to those of the corresponding crystal. In particular, the spectral region attributed to the microscopic relaxation (which in first approximation gives a broad quasielastic contribution to the spectra) can actually be interpreted in terms of quasitransverse excitations, partly hidden in the spectra of the liquid by an overall disorder-induced broadening. These results are interesting since they establish a close connection between structure and dynamics in a liquid and in the corresponding crystal. Can we exploit in practice these results to learn more of the local structure and microscopic dynamics in liquids that are characterized by a structural arrangement more complex than the simple close-packed one displayed by alkali metals?

In order to give an answer to the previous question, we address here the interesting case of Ga. Indeed, Ga shows a sizable elastic anisotropy⁸ and an extended solid phase polymorphism with complex crystal structures.⁹ As for the liquid, it has a very low melting point ($T_m = 303$ K), and a detailed study of the static structure factor, $S(q)$, clearly denotes a non-close-packed local order.¹⁰ In fact, *ab initio* calculations have suggested that covalent and metallic characters coexist in liquid Ga, and very short-living Ga₂ divalent molecules have been identified.¹¹ While the coexistence of metallic and covalent bonding is a characteristic of the orthorhombic α -Ga phase stable at room pressure and temperature,¹² the local order in the liquid has been suggested to be closer to the one of the metallic metastable monoclinic phase β -Ga,¹³ despite its strongly anisotropic atomic arrangement.

In this Brief Report we utilize IXS to study the connection between dynamics and structure in this interesting system. We present the IXS spectra of liquid Ga collected at high pressure in order to enhance the visibility of the quasitransverse and quasilongitudinal excitations by increasing the speed of sound. We show that also in this case a crystal-like approach can be consistently utilized to successfully describe the measured spectra. Our results establish a clear correspondence between the high-frequency dynamics of liquid Ga and that of the metastable crystalline phase β -Ga, similarly to what is already suggested by structural investigations.¹³ This demonstrates that, similarly to crystals, experiments on the high-frequency dynamics of liquids can be exploited to obtain very detailed information on their microscopic arrangement.

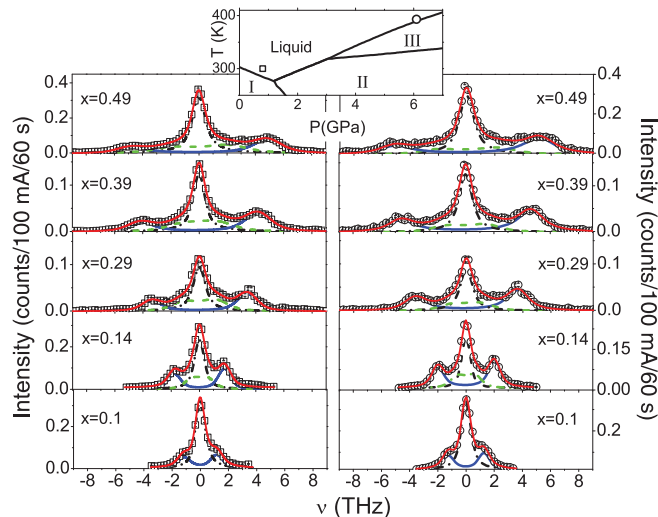


FIG. 1. (Color online) Density-density fluctuations spectra of liquid Ga at 0.8 GPa and 295 K (left, squares) and at 6.1 GPa and 393 K (right, circles) are reported together with the best fitting line shape of model Eqs. (1) and (2) (full red line) at selected $x = q/q_0$ values, where $q_0 = 2.52(2.55) \text{ \AA}^{-1}$ is the main diffraction peak position at the low (high) pressure. The quasielastic (dash-dotted black line), inelastic transverse (dashed green line), and longitudinal (full blue line) components of the fitting model are also reported after convolution with the instrumental function. The location of the two investigated thermodynamic points is indicated in the phase diagram reported in the panel at top, from Ref. 17.

For our IXS experiment, high purity Ga (Sigma-Aldrich) was loaded in a membrane diamond anvil cell in a stainless steel gasket. The cell was wrapped in an external resistive heater, and the temperature measured by a thermocouple cemented to one of the diamonds. The liquid phase was studied in two different conditions: 0.8 GPa at 295 K, and 6.1 GPa at 393 K (see top panel in Fig. 1). The IXS experiment was carried out at the ID16 beamline of the European Synchrotron Radiation Facility (ESRF),¹⁵ using an incident energy of 17793 eV. The spectra were collected in the frequency range (−10–10) THz with a frequency resolution of 0.68 THz full width at half maximum (FWHM), and in the q range (0.24–1.21) \AA^{-1} , with a total integration time of 900 (700) s per point at low (high) pressure. Selected IXS spectra are reported in Fig. 1 for the liquid at the two pressure points. The measured intensity is proportional to the dynamic structure factor $S(q, \omega)$, convoluted with the instrument response function $R(\omega)$. Longitudinal acoustic excitations are clearly visible in the measured spectra, and a shoulder between them and the quasielastic line calls for the presence of quasitransverse excitations.¹⁶

The spectra reported in Fig. 1 look at first sight similar to those collected at the room pressure melting point,^{14,16,18–20} which, despite the previously recalled specificity of liquid Ga, have been analyzed in terms of two universal relaxation processes common to all liquid metals.⁶ More recently, the (partially) covalent character of liquid Ga has been addressed in detailed IXS experiments, which have reported on the existence of quasitransverse excitations in the $S(q, \omega)$ spectra for q values close to the border of the pseudo-Brillouin

zone.^{16,20} Their origin has been ascribed to the instantaneous formation of clusters with a lifetime of ≈ 0.5 ps.

In order to unveil the relation between the microscopic dynamics and the short-range order in this nonsimple liquid, we model our spectra within a crystal-like approach using a Lorentzian function for the quasielastic line and the sum of two damped harmonic oscillators (DHO), representing quasitransverse and quasilongitudinal excitations, for the inelastic part of the spectrum⁷

$$S(q, \omega) = S_{\text{el}} \frac{\Gamma_0}{\omega^2 + \Gamma_0^2} + S_{\text{in}}(q, \omega) \otimes G(\omega), \quad (1)$$

with

$$S_{\text{in}}(q, \omega) = I_L \frac{\Omega_L^2 \Gamma_L}{(\omega^2 - \Omega_L^2)^2 + \omega^2 \Gamma_L^2} + I_T \frac{\Omega_T^2 \Gamma_T^2}{(\omega^2 - \Omega_T^2)^2 + \omega^2 \Gamma_T^2}. \quad (2)$$

Here \otimes represents the convolution operation; $\Omega_L(\Omega_T)$ is the frequency position of the quasilongitudinal (quasitransverse) excitations, and $\Gamma_L(\Gamma_T)$ the corresponding broadening (FWHM); $2\Gamma_0$ is the broadening of the quasielastic line; and S_{el}, I_L , and I_T are spectral weights. In this model the bare DHO FWHM accounts for that part of the broadening of the acoustic excitations related to the local elastic anisotropy (i.e., the one we would observe measuring an orientationally averaged crystal) while an additional broadening contribution specific to the disordered liquid structure is accounted for via the convolution with the Gaussian function $G(\omega)$. The model function Eq. (1) is then multiplied by $\hbar\omega[n(\omega) + 1]/k_B T$ in order to take into account the quantum nature of the measured spectra,⁴ and finally is convoluted with the instrument function $R(\omega)$ prior to being fitted to the experimental data. The spectra collected at both pressures can be well described by this model, as shown for the examples reported in Fig. 1.

In Fig. 2 we compare our results for the frequency and total width (i.e., including the Gaussian broadening contribution) of the inelastic excitations with the corresponding data available at the room pressure melting point from Ref. 16, the other published data^{14,19,20} being in agreement with those. As expected, the speed of sound of both excitations increases with density, while no clear trend appears for what concerns the width. We can investigate the density dependence of the dispersion curves by looking at the behavior of the maximum of the longitudinal dispersion curve ν_{MAX} (see inset of Fig. 2). The density of liquid Ga is 6.095 g/cm³ at the room pressure melting point, and can be estimated to be 6.33 and 6.73 g/cm³ at 0.8 GPa and 295 K and at 6.1 GPa and 393 K, respectively.²¹ ν_{MAX} is found to depend linearly on the density, as predicted by a simple quasiharmonic approximation,²² moreover, the intercept of the best fitting line is compatible with zero, and indeed we have verified that the acoustic dispersions collapse on each other once scaled by the density.

Within a crystal-like approach, we can expect a close correspondence between the frequency of the acoustic modes of the liquid and the orientational average of the branches of the corresponding solid phase.⁷ We can then compare our data for the liquid to the phonon branches measured for the two crystal

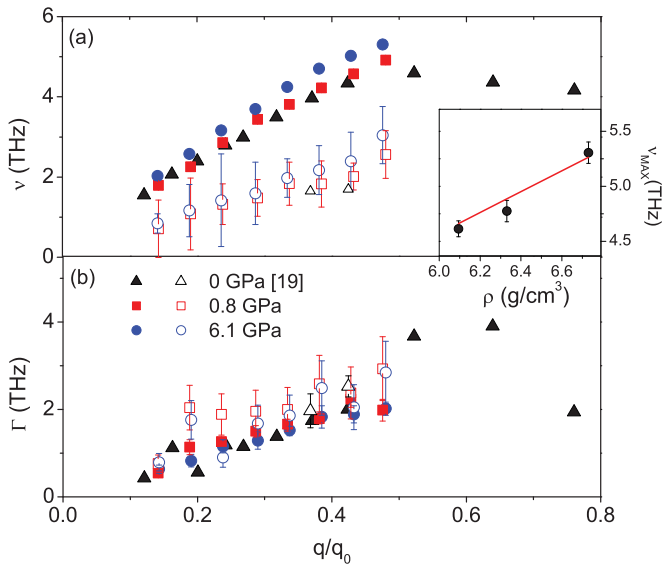


FIG. 2. (Color online) The frequency (a) and full width at half maximum (b) of the acoustic excitations are reported for 0.8 GPa and 295 K (squares) and 6.1 GPa and 393 K (circles), and are compared to literature data for the room pressure melting point (triangles, from Ref. 16) for both longitudinal and transverse polarizations [full (empty) symbols, respectively]. Inset: density dependence of the longitudinal dispersion curve, together with the best linear fit (red line).

phases α -Ga at 77 K and β -Ga at 256.8 K,^{23,24} after scaling the data for the liquid to the densities of the crystals (5.977 and 6.25 g/cm³, respectively). This comparison is shown in Fig. 3 where, together with the scaled data for the liquid, we report the highest and lowest frequency branches (dashed lines) for the two crystal phases. All data are reported in q/q_0 units, q_0 being the main diffraction peak for the liquid and the first diffraction peak for the crystal phases [(110) for β -Ga and (010) for α -Ga]. A clear correspondence is found for the acoustic frequencies of both polarizations between the liquid and the β -Ga crystal. On the other hand, the longitudinal acoustic frequencies scaled at the density of α -Ga remain too high with respect to the average of those corresponding to this crystalline phase, despite a good agreement for the transverse ones.

Additional information is provided by the broadening of the acoustic excitations for the liquid. Our crystal-like model Eqs. (1) and (2) describes the FWHM of the acoustic excitations in terms of two main effects: (i) the local elastic anisotropy, related to the orientational average of the corresponding single crystal phonon branches; and (ii) the smearing of the Brillouin zone, induced by the structural disorder and described by the Gaussian convolution in Eq. (1). We have recently shown for the case of liquid Na that the latter contribution can be grasped, at least in first approximation, by the FWHM, Δ , of the main diffraction peak in the static structure factor of the liquid:⁷ the single crystal phonon branches will spread over bands when plotted against $q/(q_0 \pm \Delta/2)$ as a consequence of the smearing of the Brillouin zone. Figure 3 shows that the same scheme works also in liquid Ga: The error bars for the data corresponding to the liquid represent, in fact, the overall broadening of the acoustic excitations, including

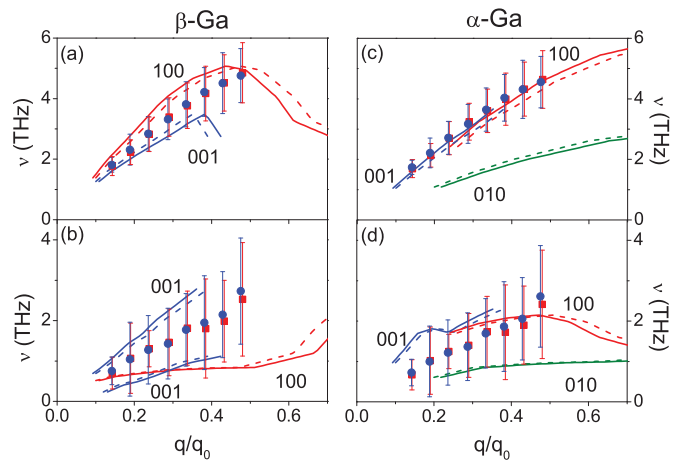


FIG. 3. (Color online) Longitudinal (a), (c) and transverse (b), (d) excitations of liquid Ga at 0.8 GPa and 295 K (red squares) and at 6.1 GPa and 393 K (blue circles) compared to the acoustic branches of β -Ga²⁴ (left) and α -Ga²³ (right) after scaling to the crystalline phases density. Only the highest and lowest frequency branches along high symmetry directions are reported for the solids (dashed lines), together with the corresponding Miller indices (different colors correspond to different indices). The solid lines correspond to the highest (lowest) frequency phonon branch plotted as a function of $q/(q_0 - \Delta/2)(q/(q_0 + \Delta/2))$, where Δ is the FWHM of the main diffraction peak in the liquid. The error bars of the data for the liquid correspond to the full width at half maximum of the corresponding excitations.

also the Gaussian contribution of Eq. (1), and closely match the separation between the highest and lowest frequency phonon branches of β -Ga reported as a function of $q/(q_0 \pm \Delta/2)$, where we have used $\Delta/q_0 = 0.16 \text{ \AA}^{-1}$ at all pressure points (solid lines).

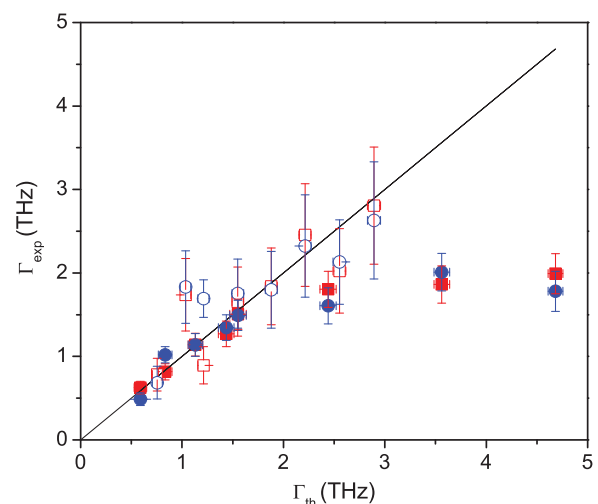


FIG. 4. (Color online) The FWHM of the quasilongitudinal (full symbols) and quasitransverse (empty symbols) excitations in liquid Ga at 0.8 GPa and 295 K (squares) and at 6.1 GPa and 393 K (circles) are reported as a function of the prediction by Eq. (3) worked out using the phonon branches of β -Ga. The line indicates the condition of exact correspondence.

This correspondence between the broadening of the acoustic excitations for the liquid and the dispersion curves for the related crystalline structure can be expressed in very simple terms in the q range where the crystal dispersion curves are approximately linear. If we call $v_h(q)$ and $v_l(q)$ the phonon branches of highest and lowest frequency, the broadening expected for the liquid, to first order in Δ/q_0 , is

$$\begin{aligned} \Gamma_{\text{th}}\left(\frac{q}{q_0}\right) &= v_h\left(\frac{q}{q_0 - \Delta/2}\right) - v_l\left(\frac{q}{q_0 + \Delta/2}\right) \\ &\approx \left[v_h\left(\frac{q}{q_0}\right) - v_l\left(\frac{q}{q_0}\right) \right] \\ &\quad + \frac{\Delta}{2q_0} \left[v_h\left(\frac{q}{q_0}\right) + v_l\left(\frac{q}{q_0}\right) \right]. \end{aligned} \quad (3)$$

The first and second terms in Eq. (3) directly correspond to the contributions (i) and (ii) mentioned above (i.e., to the effects of elastic anisotropy and structural disorder, respectively). Despite the simplicity of this model, we find that Eq. (3) gives a good description of the experimental FWHM of the acoustic excitations for liquid Ga, as shown in Fig. 4.

In conclusion, the clear correspondence between the high-frequency dynamics of the liquid and that of the β -Ga crystal

indicates a close similarity of the short-range order in these two phases, thus confirming similar suggestions obtained from structural studies.¹⁰ This is interesting, because it clarifies that, despite the absence of long-range order, the existence of short-range order in a liquid is enough to give rise to acoustic excitations bearing close resemblance to the phonon branches of the corresponding crystal structure, in the same way as it also gives rise to a similar electronic band structure.^{2,3} The case of Ga is in this sense particularly rich, since we are dealing with an elemental liquid metal with a short-range order similar to that of a monoclinic crystalline phase characterized by a large structural and elastic local anisotropy.

Inelastic scattering studies of the high-frequency dynamics of liquids are thus finally overcoming the stage where it was found with some surprise that liquids share very general universal features, and are reaching a level of maturity where system-specific information can be obtained on the short-range order, as for crystalline structures. While of course we cannot hope to extract information as detailed as for crystals, nevertheless the limits imposed by the intrinsic orientational average and disorder related effects are less severe than one could imagine, and a clear connection between local structure and dynamics can still be extracted from the data.

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