COLLECTIVE EXCITATIONS IN LIQUID Si

The structurally simplest ‘semiconductor’, Si, is manufactured by growing the crystal directly from the ‘metallic’ melt. This interplay between a metallic disordered phase and the semiconducting crystalline state has stimulated much theoretical and experimental interest in the static and dynamic properties of this system. For example, the influence of covalent bonds on the dynamics of the metallic melt was investigated in an early first-principles molecular-dynamics simulation by the originators [1]. However, the experimental investigation of the microscopic dynamics has yet been hindered by the fact that the collective longitudinal modes in liquid Si are out of reach of thermal neutrons due to the high sound velocity (~ 4,000 ms^{-1}) and the kinematic restrictions of this technique. High-resolution inelastic X-ray scattering (IXS) is another technique that permits the study of Q dependence of excitations in the meV range, but in contrast to neutron scattering, it has no kinematic restrictions and the scattered radiation is entirely coherent within the energy range of interest. Combined with a suitable high-temperature sample environment, we were able to measure for the first time the dynamic scattering law $S(Q, \omega)$ of liquid Si [2].

The experiments were carried out at beamline **BL35XU** using a horizontal IXS spectrometer [3] (energy resolution: ~1.8 meV FWHM at 21.8 keV). The hot sample (T = 1733 K) was located in a sapphire container, which was a slight modification of the so-called Tamura-type cell [4]. It was placed in a vessel equipped with continuous Be windows [5] capable of covering scattering angles between 0° and 25°.

Figure 1 shows selected spectra normalized to the respective intensity. Also given is a typical example of the resolution function (dashed line). The data clearly prove the existence of longitudinal collective short wavelength modes, which appear

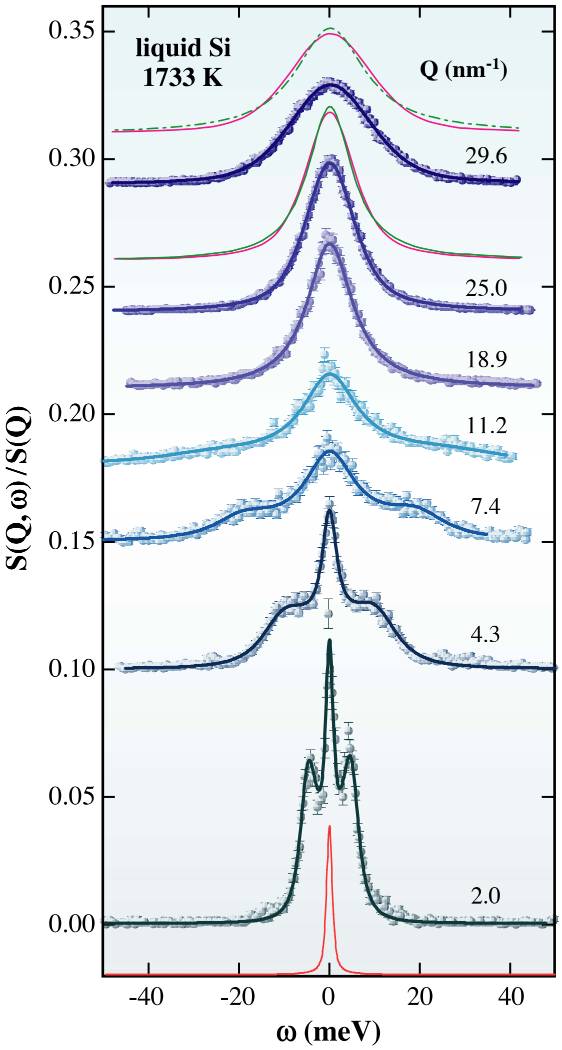

Fig. 1. Selected $S(Q,\omega)$ spectra normalized to $S(Q)$. Experimental data are given by circles with error bars, and thick solid lines represent fits of the DHO model convoluted with the resolution function (dashed line). Dot-dashed lines show the best convoluted fits for the quasielastic lines using a Lorentzian in comparison to the quasi-Voigt fits (thin solid lines, shifted from the data).

as peaks or shoulders in the lower Q range. For the resolution correction, a model $S(Q, \omega)$ function convoluted with the resolution function was fitted to the data. For this model, we approximated the central line by a Lorentzian at lower Q values or by a pseudo-Voigt function at higher Q values (see text below), and the inelastic contribution by a damped harmonic oscillator (DHO). Using the fitted results (thick solid lines), the excitation energy ω_c and the line width Γ_Q were determined as shown in Fig. 2 . The dashed line represents the dispersion of hydrodynamic sound, and its slope is given by the bulk adiabatic sound velocity $v_s = 3952$ ms^{-1}. The frequencies of the short wavelength modes increase noticeably faster (~17%) with Q than predicted by classical hydrodynamics. This so-called 'positive' dispersion was already found earlier in liquid alkali metals and also in liquid Hg. The collective modes are highly damped at higher Q values compared to those in liquid alkali metals.

The usual choice, in which a quasielastic line is modelled by a Lorentzian, is not suitable for liquid Si beyond Q = 20 nm^{-1}. Instead we used a quasi-Voigt function, *i.e.*, a linear combination of a Gaussian and a Lorentzian. Dot-dashed lines in Fig. 1 show convoluted fits using a Lorentzian in comparison to the quasi-Voigt fits (thin solid line, the same as the thick ones). The quasi-Voigt function fits the data well, whereas the deviation of the Lorentzian fits is considerable. Circles and triangles in Fig. 3 represent the line width Γ_0s and the Gaussian fraction c of the quasielastic lines. The Gaussian contribution becomes noticeably important at about 20 nm^{-1} and reaches about 50% at Q ~ 30 nm^{-1}. Around the Q value where the maximum in $S(Q)$ is located, a minimum in Γ_0

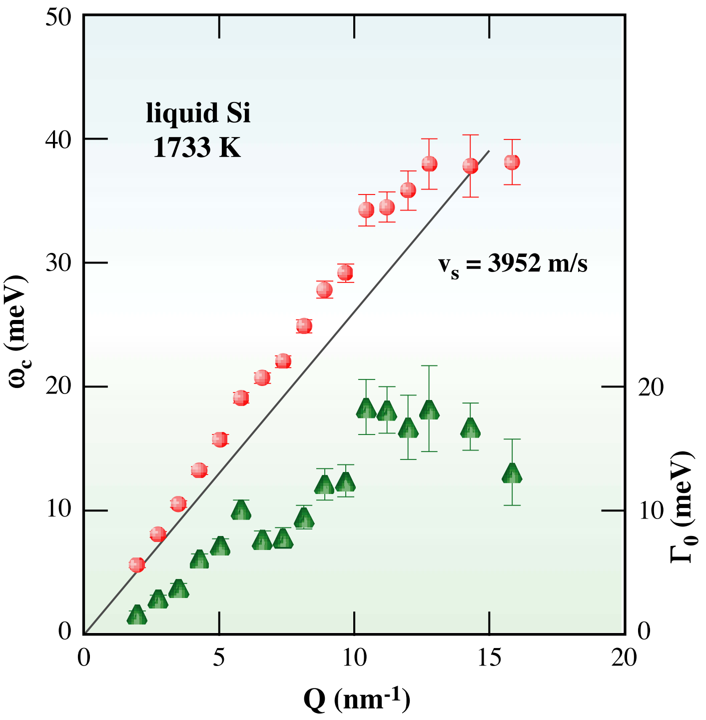

Fig. 2. Dispersion relation (circles) and line width (triangles) of the collective modes in liquid Si.

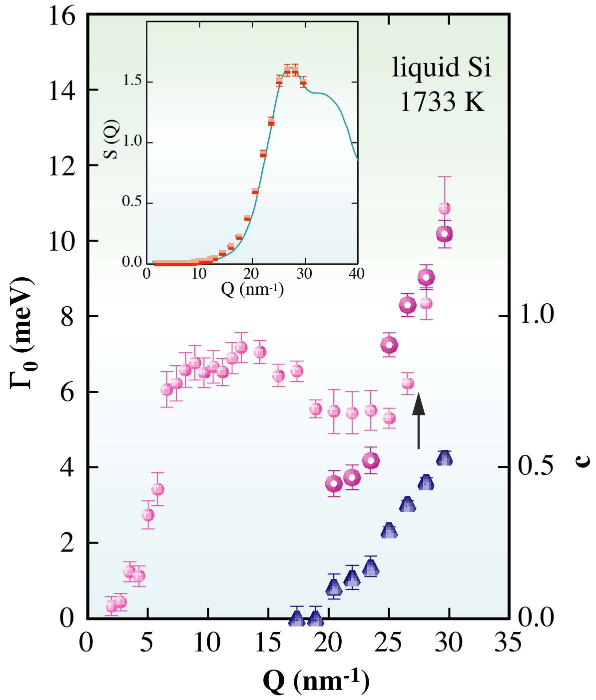

Fig. 3. Q dependence of the quasielastic line width Γ_0 (circles). With increasing Q, a Gaussian component (open circles) is needed in addition to the Lorentzian (full circles) to model the central line. Triangles give the Gaussian fraction, c. The arrow indicates the Q position of the first maximum in S(Q). Inset: S(Q) determined from the zero frequency moment of the present experiment (squares) together with the result from elastic X-ray scattering [6].

(usually Γ_{0L}) is expected, which is the well-known *de Gennes* narrowing. However it is worth noting that the minimum of Γ_{0L} is found at about 22.5 nm^{-1}, while the maximum in $S(Q)$ is located at 27.3 nm^{-1} (arrow in Fig. 3, see also $S(Q)$ given in the inset).

Besides the damped phonon modes and the anomalies in the quasielastic line, however, direct evidence for the existence of covalent bonds in liquid Si (*e.g.* localized modes) was not observed. A detailed analysis using *e.g.* a mode-coupling theory would be useful for a further understanding of the present results, and is now in progress.

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