In situ High-Energy X-Ray Diffraction Study of the Local Structure of Supercooled Liquid Si

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Employing the technique of electrostatic levitation, coupled with high-energy x-ray diffraction and rapid data acquisition methods, we have obtained high quality structural data more deeply into the supercooled regime of liquid silicon than has been possible before. No change in coordination number is observed in this temperature region, calling into question previous experimental claims of structural evidence for the existence of a liquid-liquid phase transition.

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The structure of supercooled liquid Si, and its transition from a metallic dense-packed structure at high temperatures to a semiconducting open network at lower temperatures, has remained a controversial topic for several decades. Much of the controversy has focused on the existence of a first-order liquid-liquid (*L*-*L*) phase transition in the supercooled state first proposed by Aptekar based on studies of the extrapolated Gibbs free energies of the liquid and amorphous solid phases [1]. Subsequent computer simulations have indicated that the occurrence and nature of the *L*-*L* and liquid-amorphous (*L*-*A*) transitions are sensitive to the form of the assumed interatomic potential. For example, only a glass (*L*-*A*) transition, but no *L*-*L* transition, is predicted if a general Keating-type potential is used [2]. A Stillinger-Weber (SW) potential, however, yields a discontinuous *L*-*L* transition at 1060 K, but no *L*-*A* transition [3–5]. A more recent calculation, using semiempirical potentials from the environment dependent interatomic potential model, predicted both a first-order *L*-*L* transition (1135 K) and a continuous *L*-*A* transition (843 K) [6].

Like most studies of liquids, structural studies of deeply supercooled liquid Si have been hampered by the need for a container to support the liquid, severely reducing the range of supercooling that could be attained. Recently, however, techniques have been developed to process liquids under high-purity environmental conditions in the absence of a container using aerodynamic, acoustic, electromagnetic, and electrostatic levitation techniques. Nevertheless, containerless x-ray studies of supercooled liquid Si have largely produced contradictory results. For example, x-ray measurements made using conical nozzle levitation [7,8] have provided structural information for a supercooling of 230 K below the melting point ($T_M \approx 1685$ K) and identified a decrease in the coordination number from 6.3 at 1767 K to about 5.6 at 1458 K. This result is consistent with the predicted decrease in coordination number obtained from simulations using the SW potential as the temperature is reduced below T_M, and was argued to provide strong evidence for the existence of an underlying first-order *L*-*L* transition. However, other x-ray measurements by Kimura *et al.* [9] employing electromagnetic levitation (EML) for a supercooling of 290 K below the melting point found an increase in the average coordination number from 5.5 at 1793 K to 6.1 at 1403 K. Recent measurements by Higuchi *et al.* [10], using EML to a supercooling of 150 K, found no change in coordination number with temperature, but obtained a rather low value for the coordination number ($N = 5$) relative to previous investigations. The discrepancies between these results and the fact that none of the groups found evidence of a discontinuous change in the structure, indicative of a first-order *L*-*L* transition, leaves the matter of a *L*-*L* transition in supercooled liquid silicon an open question.

To resolve these questions, we have performed time-resolved *in situ* high-energy x-ray diffraction measurements of liquid Si using the containerless electrostatic levitation (ESL) technique. These measurements offer important improvements over the previous investigations. First, through the use of high-energy x rays (125 keV), the experiments are performed in a transmission geometry ensuring that the volume structure is probed. The use of high-energy x rays also minimizes data corrections due to sample absorption and multiple scattering required for lower energy measurements [10]. Second, a distinct advantage of ESL over electromagnetic and aerodynamic levitation is that even for nonmetallic samples, the processes of heating and positioning are decoupled, obviating the need for cooling or levitating gases. The high-vacuum environment of ESL minimizes environmental contamination of the sample that can lead to heterogeneous nucleation and, therefore, allowed structural measurements to be extended to a more deeply supercooled liquid state, 316 K below T_M. Finally, the use of fast area detector technology combined with high-energy x rays permits rapid data acquisition (≈ 100 ms for a complete pattern) over a reasonably wide range of momentum transfer ($q_{\max} \approx 10$ Å^{-1}), allowing us to take advantage of the deep supercooling obtained in ESL without the need to hold the sample at a set temperature for a prolonged period of time. Rather than obtaining only 5–10 data sets spaced over the entire temperature range, we were able to continuously monitor changes in the structure over a temperature range from 1815 K down to 1369 K.

We find that the coordination number of liquid Si remains unchanged ($N = 6.0 \pm 0.5$) throughout the temperature range accessible in this measurement. In agreement with previous measurements, no signal of a sharp transition in the liquid phase is observed down to the onset of crystallization. However, close inspection of the reduced radial distribution function, $G(r)$, reveals subtle continuous changes in the higher order coordination shells that indicate a continuous evolution of the liquid structure with decreasing temperature. Perhaps most importantly, these new results are not consistent with the structural predictions of simulations of supercooling using the SW potential [11].

The data presented here were obtained using the recently developed beam line electrostatic levitation (BESL) technique that has been described in detail elsewhere [12]. Small spheres (2.2–2.5 mm diameter) of high-purity Si, prepared by arc melting in a high-purity argon atmosphere, were levitated in an ESL chamber in high vacuum (10^{-7}–10^{-8} torr). The levitated samples were heated and melted using 30 W diode and 30 W CO_2 lasers. Optical pyrometers with a 1.45 to 1.8 mm wavelength range were used to measure the sample temperature to a relative accuracy of ±1 K.

Diffraction data were obtained from the levitated samples on the MUCAT beamline 6ID-D at the Advanced Photon Source in a transmission geometry using an incident beam energy of 125 keV. With the GE Revolution 41-rt area detector, data were obtained over a momentum transfer range of $0.5 \leq q \leq 10$ Å^{-1}, at an acquisition rate of up to 30 full diffraction patterns per second. This allowed structural measurements on the liquid to be obtained through the onset of recalescence. Because of the high thermal conductivity of liquid silicon, the sample was in thermal equilibrium over the measured temperature range; the maximum difference between the temperature of the center of the sample and the surface was less than 1 K. The diffraction images were integrated to produce one-dimensional powder diffraction patterns which, in turn, were processed to correct for background scattering from air and the Be windows of the chamber, absorption effects (minimal), multiple scattering (minimal), and Compton scattering contributions using the PDFGETX2 analysis package [13].

Figure 1 shows the derived x-ray structure factors, $S(q)$, and reduced radial distribution functions, $G(r)$, for liquid Si as a function of temperature from data obtained at a rate of 1 Hz (1 frame per second) from the sample cooled at a rate of 13 K/s. The trends observed in the evolution of $S(q)$ over the temperature range are in substantial agreement with previous measurements. A primary peak is observed at approximately 2.6 Å^{-1} with a shoulder on the high-q side that becomes better resolved as temperature is lowered [inset in Fig. 1(a)]. The reduced radial distribution function in Fig. 1(b) was calculated from the Fourier transform of the data in Fig. 1(a) ($G(r) = (2/\pi) \times \int q[S(q) - 1]\sin(qr)dq$ from $q = 0.5$ to $q_{\max} = 10$ Å^{-1}). The same data range and treatment were used at each temperature point. The first peak in $G(r)$ appears to change little in position or profile with decreasing temperature (2.50 Å at 1815 K and 2.49 Å at 1382 K). The

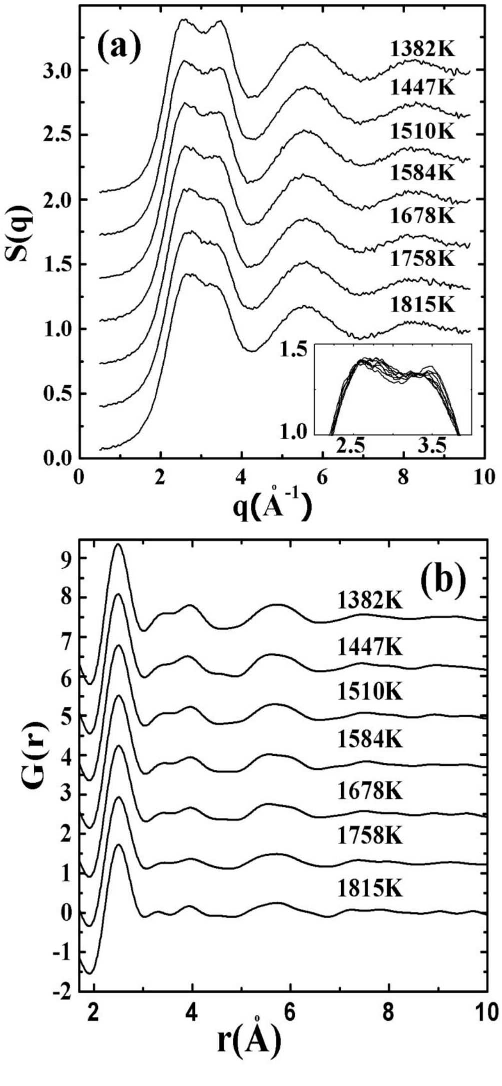

FIG. 1. (a) Structure factors and (b) reduced radial distribution functions for liquid Si, obtained from diffraction patterns taken at a frame rate of 1 Hz during cooling at 13 K/s.

second peak in $G(r)$ is actually composed of two subpeaks, at approximately 3.45 and 4.0 Å. We note that a similar distribution of peaks was predicted from simulation studies using the Stillinger-Weber potential [3,14,15]. With supercooling, both subpeaks in $G(r)$ increase in intensity, signaling a change in the local order of the liquid upon cooling, consistent with the changes observed in $S(q)$.

The 1 Hz data allowed us to collect diffraction data down to approximately 300 K below T_M during a controlled cooling of the sample. To obtain structural data even closer to sample recalescence, diffraction patterns were also obtained at a frame rate of 10 Hz (100 ms per pattern) as the sample was free-cooled to 316 K below T_M. The structure factors calculated at selected temperatures prior to and during recalescence are shown in Fig. 2. Beyond the expected degradation in the signal-to-noise ratio, reflecting poorer counting statistics due to the shorter data collection times, the data reliably reproduce the $S(q)$ data taken at 1 Hz [Fig. 1(a)] over the same temperature range. The features in the $G(r)$ data (not shown) for the 10 Hz data are identical to those shown in Fig. 1(b).

The coordination number, N, of the first shell as a function of temperature obtained from the 10 Hz data is shown in Fig. 3(a). For direct comparison, the results of previous x-ray measurements are reproduced in Fig. 3(b) [7–9]. For liquids, the first shell coordination number is poorly defined, and several methods for determining N can be found in the literature [16]. The method chosen in previous experiments [7–10] on liquid Si was to integrate the radial distribution function, $R(r)$, up to the first minimum after the main peak. Here, $R(r) = 4\pi r^2 \rho_0[1 + G(r)/4\pi r\rho_0]$ and ρ_0 is the average number density. For consistency with previous measurements, we adopted this method as well. The average density at each temperature was derived from ESL density measurements by Rhim *et al.* [17] and increases smoothly by approximately 2.3% from 1815 to 1370 K, the temperature range of our measurement. From Fig. 3, the data clearly show a constant coordination number of approximately 6.0 ± 0.5 over the entire temperature range from above T_M down to a supercooling of 316 K.

Our results for the temperature independence of the coordination number are in conflict with the results of several previously published experimental studies and with expectations from most simulation studies based upon the SW potential. Using the conical nozzle technique for sample levitation and diffraction measurements for x rays in the energy range of 7–25 keV, Ansell *et al.* [7] and Jakse *et al.* [8] have reported that the coordination number decreases with decreasing temperature. Working in a reflection geometry using relatively low energy x rays requires significant data corrections for the scattering geometry as well as absorption and multiple scattering. The use of a gas stream for levitation, together with the decreased sample penetration, raises some concerns about the impact of surface contamination upon these results. Energy dispersive x-ray diffraction studies [9] and angular dispersive measurements at 50 keV [10] on electromagnetically levitated samples 8–10 mm in diameter have found either an increasing or a constant, but lower, coordination number with decreasing temperature, respectively. The present measurements provide a more precise determination of the structure of supercooled liquid Si because of the high-vacuum environment of ESL and the use of high-

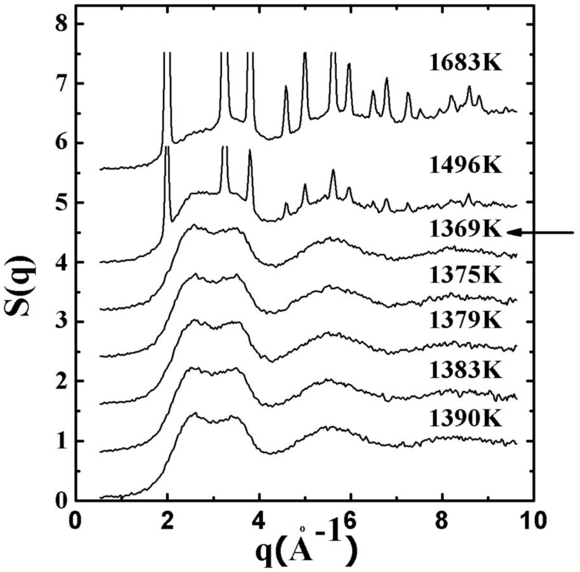

FIG. 2. Structure factors for supercooled liquid Si obtained from diffraction patterns taken at a rate of 10 Hz during free cooling. Note that upon recalescence (indicated by the arrow), the sample temperature rises.

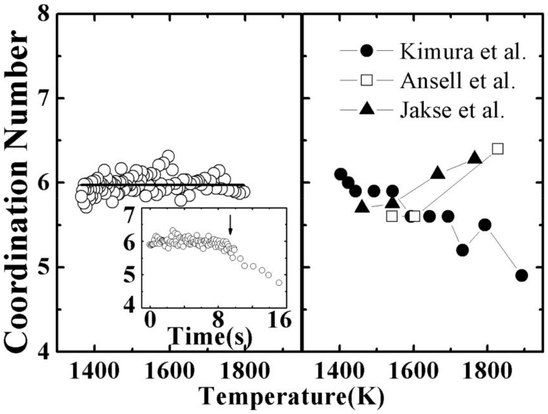

FIG. 3. Left: The coordination number of supercooled liquid Si calculated from the 10 Hz data (0.1 s exposure time data). In order to show the change in coordination during recalescence, a time series is displayed in the inset. The arrow denotes the onset of recalescence. Right: Temperature dependence of the coordination number obtained by previous measurements as described in the text.

energy x rays, minimizing the impact of any surface contamination and the effects of sample absorption and multiple scattering. For the present study, we point out that the deviation of the coordination number over the entire temperature range is small, as indicated by the scatter of the data points in Fig. 3(a). Furthermore, as the sample is cooled below 1369 K, recalescence occurs, and there is a marked decrease in the coordination number to approximately 4.5, approaching a value appropriate to tetrahedral coordination in crystalline silicon [inset of Fig. 3(a)].

Even though the coordination number in the first shell remains constant, both the $S(q)$ and the $G(r)$ data do indicate changes in the structure of supercooled liquid Si. The evolution of the intensities of the two subpeaks that constitute the second peak of $G(r)$ indicates that this involves primarily changes in the second and higher order coordination shells. Some insight may be gained from a dominant-cluster-based view of the short-range order. For example, it has been noted previously that the fundamental cluster of the A5 (white tin) structure that characterizes metallic liquid Si can be distorted continuously by an internal rotation to the A4 (diamond) structure, characteristic of semiconducting Si [18]. Our preliminary calculations show that the small changes observed here in $S(q)$ and $G(r)$ correspond qualitatively to a partial ($\sim 15\%$ of the total) A5-A4 rotation. More fundamental structural studies using *ab initio* potentials are currently underway.

In summary, we have demonstrated that, in contradiction to several existing experimental studies and many simulations using the Stillinger-Weber potential, there is no evidence for a change in the coordination number of liquid Si, down to the recalescence temperature corresponding to the nucleation and growth of the crystal phase. This is inconsistent with a nearby liquid-liquid phase transition as has been widely predicted. The existence of a liquid-liquid transition at a much lower temperature, such as has been recently predicted by *ab initio* molecular dynamics simulations [3] to occur at approximately 300 K below our recalescence temperature, cannot be ruled out. However, our data conclusively show that, if present, it has no impact on the first neighbor coordination within the experimentally accessible temperature range down to recalescence (at least at standard pressure). Further, while the first-order liquid-liquid phase transition predicted to occur at lower temperature could be the source of the observed transformation of the higher order coordination shells, the fact that these changes are continuous is intriguing and warrants further investigation.

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