LETTER TO THE EDITOR

Structure of supercooled liquid silicon

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Abstract. We report x-ray diffraction measurements of the structure factor $S(Q)$ and the radial distribution function $g(r)$ of levitated liquid silicon in the stable and supercooled states. Supercooling results in a sharpening of the first peak in $S(Q)$ and shift to an 8% higher Q value, the appearance of a double shoulder on the high-r side of the first peak in $g(r)$, a sharpening of the first peak in $g(r)$ and a decrease in coordination number. These changes are consistent with a significantly enhanced degree of covalent bonding.

Most commercial applications of silicon begin with single-crystal growth from the melt via the Czochralski process. Amorphous silicon on the other hand is made from slightly supercooled melts. There are conflicting results in the literature on the macroscopic properties of liquid silicon near the melting point (1685 K). The data of Sasaki *et al* [1] show an abrupt increase in the density on cooling towards the melting point, while more recent data of Rhim *et al* [2] show a gradual increase on cooling, both in the stable and supercooled states. Earlier studies of the viscosity [3] found a sharp increase towards the melting point, while the more recent results of Sasaki *et al* and Sato and Waseda [4] show a gradual increase on cooling. The measured values of electrical resistivity [5, 6] and thermopower [6] indicate nearly free electron behaviour; the temperature dependence of the resistivity shows either a shallow minimum around 1820 K [5] or a small positive coefficient [6]. These unusual results suggest the occurrence of structural changes in the liquid as a function of temperature. In addition, the possibility of polymorphic phase transitions in supercooled liquid Si, Ge and C has recently been proposed [7]. The aim of the present study was to measure the atomic structure of the liquid in the normal and supercooled states and investigate possible structural correlations of the macroscopic properties.

Silicon and germanium exhibit a semiconductor–metal transition upon melting, with a density increase of approximately 10%. Both x-ray [8–10] and neutron [11] diffraction data and theoretical results [12] show that Si and Ge are low-coordination metallic liquids with significant directional bonding. Specifically, a partial splitting of the first peak in the structure factor $S(Q)$ is observed, similar to that found in liquid Ga and Sn. The main features of the diffraction patterns as well as the electronic properties are satisfactorily reproduced by *ab initio* molecular dynamics (MD) [13, 14]. However, all the structural work on liquid silicon to date has been carried out in the normal liquid regime. By using a conical nozzle levitation device in conjunction with laser heating, x-ray diffraction can be carried out on liquids in the supercooled regime, due to the lack of container-induced nucleation [15].

The diffraction measurements were made at the X-6B and X-25 beam lines at the National Synchrotron Light Source (NSLS) at x-ray energies in the range 7–12 keV, using

a solid-state detector coupled to three single-channel analysers. The levitation technique was similar to that used in a recent study of liquid Al_2O_3 [15] and described in detail in [16]. A CO_2 laser was used to heat and melt the specimens; supercooling was achieved by reducing the laser power after melting. Temperatures were measured with two optical pyrometers and applying emissivity corrections obtained previously [17]. Diffraction data were taken at temperatures of 1829 K in the stable liquid (144 K above the bulk melting point) and 1603 and 1542 K in the supercooled liquid state (82 and 143 K below the melting point). The data were corrected for multiple scattering, Compton scattering, fluorescence and attenuation effects using Monte Carlo methods [18]. The form factor [19] was assumed to be independent of temperature.
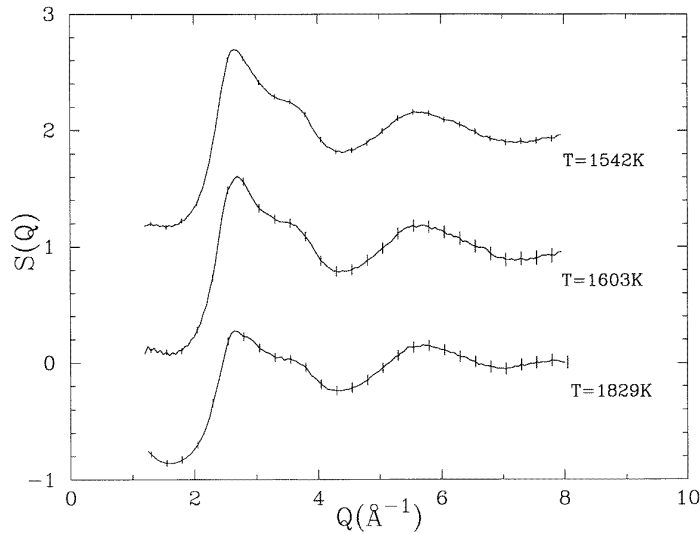

Figure 1. Structure factors for liquid silicon at temperatures of 1542 and 1603 (supercooled liquid) and 1829 K (stable liquid). For clarity, The curves are displaced vertically by 1, 0 and −1 units, respectively. The error bars represent uncertainties in the values of $S(Q)$; their magnitudes are different in the three curves due to differences in counting time.

Table 1. Summary of experimental data for $S(Q)$ and $g(r)$ in liquid silicon.

| Temperature (K) | $S(Q)$ | | | $g(r)$ | | | |
	Q_1 (Å^{-1})	Shoulder (Å^{-1})	Q_2 (Å^{-1})	r_1 (Å)	Shoulder (Å)	r_2 (Å)	C_n
			Experimental results (this work)				
1542	2.65	3.65	5.65	2.41	3.28 3.98	5.22	5.6± 0.5
1603	2.70	3.60	5.70	2.42	3.27 3.95	5.22	5.6± 0.5
1829	2.45	3.55	5.45	2.46	3.45	5.20	6.4± 0.5
			MD results [14]				
1800	2.63	3.54	5.68	2.47	3.64	5.64	6.2

X-ray weighted average structure factors $S(Q)$ for the three temperatures, displayed in figure 1, show a main peak with a pronounced shoulder on the high-Q side in addition to a second peak. The Q values corresponding to these features are given in table 1. The principal effect of supercooling is to move the first peak and shoulder to a Q value about 8% higher at 1542 K compared with 1829 K. This change is much larger than the linear compression (0.6% over the same temperature range [2]) and indicates a substantial change in the intermediate-range order.
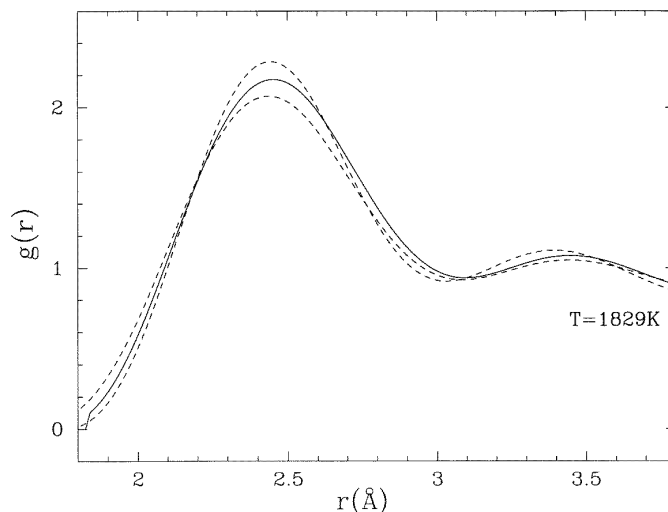

Figure 2. Pair correlation function for liquid silicon at 1829 K in the region around the main peak. The solid line represents the best estimate, derived from the $S(Q)$ data by a maximum entropy method, while the dashed lines represent a measure of the uncertainty in the derived correlation function.

Pair correlation functions $g(r)$ were obtained from the $S(Q)$ results by a maximum entropy method [20]. The region around the main peak obtained for 1829 K is shown in figure 2, along with two additional curves which straddle the best estimate for $g(r)$ and represent the uncertainty in deriving it from the $S(Q)$ data. These curves were obtained by minimizing the first peak in $g(r)$ while maintaining $S(Q)$ within the error bars shown in figure 1. The best estimates for $g(r)$ for all three temperatures are shown in figure 3. Since the same procedure was used for all three temperatures, the uncertainty in changes with temperature is likely to be less than the uncertainty at a single temperature as shown in figure 2. Similarly, while uncertainties in absolute coordination numbers, obtained by integration of the radial distribution function $n(r) = 4\pi\rho r^2 g(r)$ over the limits of the first peak, are estimated as ±0.5, the uncertainties in changes with temperature are probably lower.

Supercooling results in a significant sharpening of the first peak and a reduction in the coordination number from 6.4 to 5.6. There is also a systematic decrease in the r value of the first peak with supercooling: the decrease is approximately 2% between 1829 and 1542 K, again larger than the linear compression. The stable liquid shows a subsidiary peak or shoulder on the high-r side of the main peak which becomes a double shoulder in the supercooled state. The r values corresponding to these features are given also in table 1.

The structure of stable liquid silicon has been interpreted [8–12] as a metallic structure with a coordination number of about 6, indicating a much more open structure than is
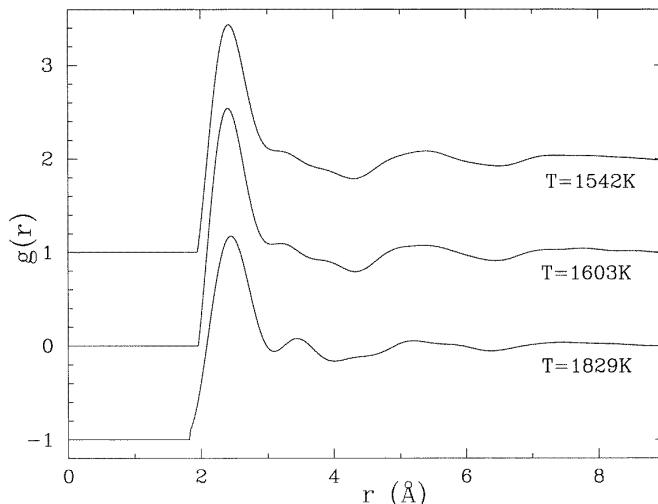
Figure 3. Pair correlation functions for liquid silicon at temperatures of 1542 and 1603 (supercooled liquid) and 1829 K (stable liquid). For clarity, the curves are displaced vertically by 1, 0 and −1 units, respectively.

common in liquid metals, presumably due to survival of directional bonds on melting. Associated with the reduced coordination number is a secondary feature at 3.45 Å. When the liquid is supercooled, this splits into a double shoulder at 3.28 and 3.95 Å. The second coordination shell in crystalline silicon occurs at 3.84 Å and the appearance of the double shoulder may reflect an increased tetrahedral component in the supercooled state. The sharpening and reduction in coordination number of the first peak reflects an increase in the degree of directional bonding on supercooling; it may be expected that, as the supercooling limit (≈ 340 K) is approached, all the atoms become fully covalently bonded into a tetrahedral structure.

There are no MD simulations reported for silicon in the supercooled state: we hope that these will be stimulated by the present results. *Ab initio* MD simulations of stable liquid silicon around 1800 K have been made by Stich *et al* in the local density approximation (LDA) [13, 14] and in the generalized gradient approximation with inclusion of spin (SGGA) [14]. In figure 4, their SGGA result for $S(Q)$ is compared with our measurements in the stable liquid at 1829 K and those of Waseda *et al* [10] at 1793 K. The two sets of experimental data agree reasonably well but the two-peak structure is more pronounced in the MD simulations, especially in the SGGA result shown here. The corresponding $g(r)''$s are shown in figure 5: again there is good agreement between the two sets of experimental data but the first peak is sharper and narrower in the MD result. The discrepancy between the MD and the diffraction data may be due in part to the limited size of the MD cell, which results in the simulation being unable to maintain an angularly oriented structure into the second coordination shell.

Kresse and Hafner [21] have carried out *ab initio* MD simulations for germanium in both stable and supercooled liquid phases. On supercooling from just above the melting point at 1190 K to ~ 500 K below it, the first peak in $g(r)$ sharpens, the nearest-neighbour distance decreases from 2.75 to 2.63 Å, and the coordination number drops from 5.8 to 4.6. Taking the large temperature drop into account, these changes are rather consistent with the ones observed here. A conventional MD simulation of stable fluid silicon with a Tersoff
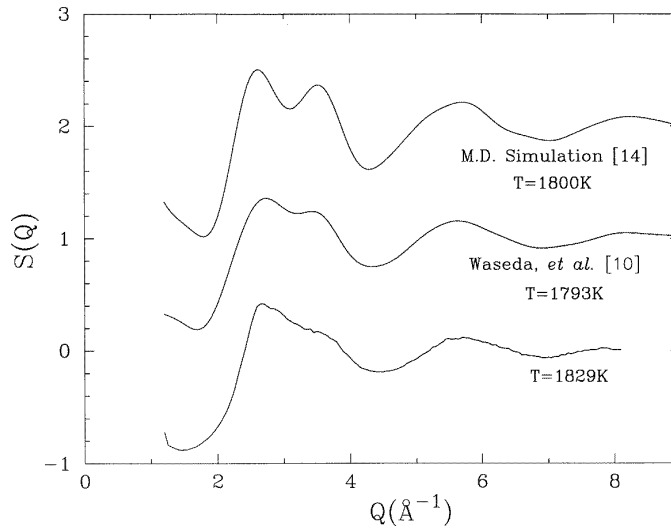
Figure 4. Comparison of structure factors for stable liquid silicon with literature results. Top curve: results of MD simulations of Stich *et al* [14], corresponding to a temperature of 1800 K; middle curve: experimental results of Waseda *et al* [10] at 1793 K; bottom curve: present results at 1829 K For clarity, the curves are displaced vertically by 1, 0 and −1 units, respectively.
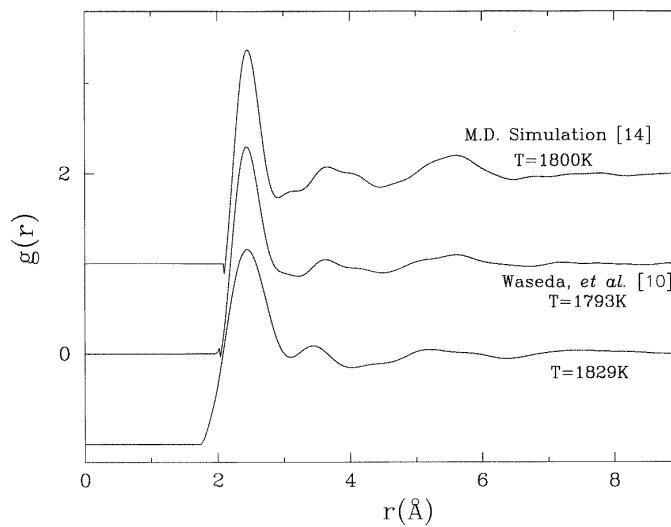

Figure 5. Comparison of pair correlation functions for stable liquid silicon with literature results. Top curve: results of MD simulations of Stich *et al* [14], corresponding to a temperature of 1800 K; middle curve: experimental results of Waseda *et al* [10] at 1793 K; bottom curve: present results at 1829 K For clarity, the curves are displaced vertically by 1, 0 and −1 units, respectively.

potential also shows a correlation between bond length and coordination number [22].

In summary, we have obtained structural data on supercooled liquid Si at temperatures 83 and 143 K below the bulk melting point. Our results for the stable liquid at 144 K above the melting point agree reasonably well with previous measurements. The effects

of supercooling are (i) a sharpening of the first peak in $S(Q)$ and shift to an 8% higher Q value, (ii) the appearance of a double shoulder on the high-r side of the first peak in $g(r)$, (iii) a sharpening of the first peak in $g(r)$ and (iv) a decrease in coordination number from 6.4 to 5.6. These changes indicate a significant enhancement of the degree of covalent bonding on supercooling.

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