Persistence of Covalent Bonding in Liquid Silicon Probed by Inelastic X-Ray Scattering

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Metallic liquid silicon at 1787 K is investigated using x-ray Compton scattering. An excellent agreement is found between the measurements and the corresponding Car-Parrinello molecular dynamics simulations. Our results show persistence of covalent bonding in liquid silicon and provide support for the occurrence of theoretically predicted liquid-liquid phase transition in supercooled liquid states. The population of covalent bond pairs in liquid silicon is estimated to be 17% via a maximally localized Wannier function analysis. Compton scattering is shown to be a sensitive probe of bonding effects in the liquid state.

Silicon (Si) presents a fascinating phase diagram as is the case in other systems that form tetrahedrally coordinated networks. [1] Upon melting, Si transforms into a metal accompanied by a density increase of about 10%. The resistivity of liquid Si (l-Si) at the melting temperature T_m is 0.75 $\mu\Omega$m, which is comparable to that of simple liquid metals such as l-Al. However, the first neighbor atomic coordination number in l-Si remains 5.5–6 [2], which is approximately half that of simple liquid metals, hinting that covalent bonds survive even in the metallic state [3]. In fact, molecular dynamics simulations of molten Si at 1800 K suggest that approximately 30% of the bonds are covalent and that these covalent bonds possess a highly dynamic nature, forming and breaking up rapidly on a time scale of 20 fs [4]. It is remarkable that two completely different types of bonds—metallic and covalent—can coexist in l-Si. In fact, the coexistence of two forms of liquid in a single component substance has been predicted to undergo a phase transition as a function of temperature and/or pressure [5], and many theoretical studies support the existence of a liquid-liquid phase transition (LLPT) [6–8]. A recent study reports that l-Si could undergo an LLPT below about 1232 K and above about −12 kB, separating into a high-density metallic liquid (HDL) and a low-density semimetallic liquid (LDL) [8]. But, 1232 K is far below the melting temperature of 1683 K of Si, and as a result the supercooled state has remained inaccessible to current experimental techniques. Very recently, Beye *et al.* have performed time-resolved x-ray measurements on Si using a femtosecond pulse laser [9] to reveal liquid polymorphs of Si which could support an

LLPT, but these experimental conditions are far from being ideal [6–8] so that the experimental confirmation of an LLPT in Si remains an open question.

A key requirement for the possibility of an LLPT obviously is that the metallic and covalent bonds coexist in l-Si. Although experimental investigations of the atomic configuration hint at the existence of covalent bonds in l-Si, surprisingly, soft x-ray [10] and magnetic susceptibility measurements [11] of electronic properties so far do not support this viewpoint in that all four valence electrons in l-Si appear to behave like free electrons. Emissivity and thermal conductivity of l-Si also exhibit a free-electron-like temperature dependence [12]. It is clear thus that the existence of the covalent bonds in l-Si is not well established. In this Letter, Compton scattering experiments on Si are reported using a levitation technique. Experimental results are interpreted in terms of full quantum mechanical simulations to show the persistence of the covalent bond in l-Si. Moreover, by invoking a number of different first-principles approaches we show that Compton scattering spectroscopy is a sensitive probe of bonding effects even in the presence of disorder induced broadening of the spectrum in the liquid state.

As background, we note that Compton scattering refers to the inelastic x-ray scattering process at large energy and momentum transfers. To date, the technique has been applied primarily to investigate electronic structure and fermiology of solid-state systems, where the measured Compton profile is directly related to the momentum density distribution of the electronic ground state within the impulse approximation [13,14]. The present study shows

how the Compton technique can also provide a novel spectroscopic window on the liquid state. Since no charged particles entering or leaving the sample are involved, the Compton technique is a genuinely bulk probe, which is not complicated by surface effects present in photoemission or electron scattering experiments [15].

Compton profiles of polycrystalline Si (300 K) and molten Si (1787 K) were measured by high-energy (116 keV) inelastic x-ray scattering at the BL08W beam line of SPring-8 [16] with a momentum resolution of 0.16 a.u. The data processing to deduce the Compton profile from the raw energy spectrum consists of the following procedures: background subtraction and energy-dependent corrections for the Compton scattering cross section, the absorption of incident and scattered x-rays in the sample, the efficiency of the analyzer and the detector, and correction for double scattering events; see [17]. Backgrounds of the measured profiles are suppressed in the levitation technique used since no material is present in the immediate vicinity of the sample at the x-ray scattering center.

Molten Si is highly reactive with most crucibles. To hold the sample without contamination, a high temperature electrostatic levitator (HTESL) was used. The HTESL levitates a spheroid sample of 2 mm diameter in a high-vacuum environment (approximately 10^{-5} Pa) using electrostatic forces via a feedback computer control [18,19]. Two separate Be windows (1.5 mm thick) were installed in the HTESL chamber for the entrance and exit of the x-ray beam. The scattering angle was set at 165 degrees. The sample (Si, 99.9999% purity) was heated and melted using the focused radiation of three 50 W semiconductor laser beams emitting at 808 nm. Temperature was controlled within 15 K and measured by pyrometry with wavelengths of 0.90 and 0.96 nm.

Car-Parrinello molecular dynamics (CPMD) simulations [20] were performed with the Quantum ESPRESSO package [21] within the framework of the density-functional theory using the generalized gradient approximation [22]. We employed norm-conserving pseudopotentials with plane-wave expansion of the Kohn-Sham wave functions and charge density up to a kinetic energy cutoff of 24 Ry and 96 Ry, respectively. Spin-unpolarized simulations were done with 64 Si atoms in simple cubic supercells. A time step of 0.097 fs was used with the fictitious mass of electron set to 300 a.u., which is within the suggested range for accurate CPMD simulations [23,24]. The solid Si (s-Si) simulation was performed at 300 K at the experimental density of 2.33 g/cm^3. The l-Si simulation was performed at 1787 K at the experimental density of 2.56 g/cm^3 [25]. The Nose-Hoover thermostat [26,27] on ions was applied in both solid and liquid simulations. We also used an additional Nose-Hoover thermostat on electrons in the liquid simulation due to the metallic character of the system. The solid and liquid simulations lasted for around 9 ps and 13.6 ps, respectively, after thermalization. The s-Si Compton profile was calculated from the average of ten

uncorrelated configurations, equally spaced by 1 ps. The l-Si Compton profile was calculated from the average of ten uncorrelated configurations, equally spaced by 1.5 ps. Both profiles were spherically averaged and convoluted with a Gaussian to match the 0.16 a.u. experimental resolution. In order to estimate disorder effects in the liquid [28], we have performed the simulation on l-Si using the first-principles Korringa-Kohn-Rostoker (KKR) coherent potential approximation (CPA) framework [29]. In these simulations, we adopted the lattice model for l-Si given in Ref. [30]. In particular, we used a body centered cubic structure with lattice constant 5.13 a.u. in which lattice sites are occupied by randomly distributed 50% Si atoms and 50% empty spheres.

The valence-electron Compton profiles of s-Si (300 K) and l-Si (1787 K), obtained by subtracting the theoretical core-electron profile $J_c(p_z)$ from the experimental profiles, are presented in Fig. 1. The theoretical core-electron profiles are based on the free-atom Hartree-Fock simulations [31], where $(1s)^2(2s)^2(2p)^6$ are treated as core electrons.

Figure 2 presents the differences between the Compton profiles for the solid and liquid phases [$\Delta J(p_z) = J_{\mathrm{solid}}(p_z) - J_{\mathrm{liquid}}(p_z)$]. The results of CPMD simulation are obtained by taking the difference of the liquid Compton profile and the spherically averaged profile of the solid. The CPMD results agree very well with the experimental results, establishing the efficacy of the bonding properties of l-Si obtained through CPMD simulation [4]. The difference between the KKR CPA results for l-Si and the spherically averaged s-Si is also shown in Fig. 2. The effect of disorder in the KKR CPA calculation yields a momentum density smearing near $p_z = 1$ a.u. [29] and produces a dip of $\Delta J(p_z)$ at this same location. However, in the experiment $\Delta J(p_z)$ shows a peak near $p_z = 1$ a.u. instead of a dip. We therefore conclude that the features induced by the Si site disorder are overshadowed by competing effects due to the covalent bond breaking.

In order to analyze the bonding character in l-Si obtained through CPMD simulation, the maximally-localized Wannier functions (MLWFs) analysis method is used [32].
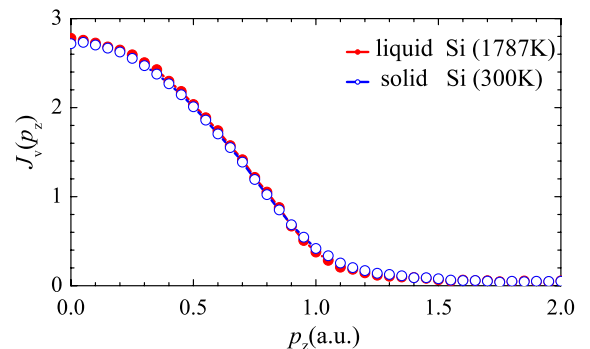

FIG. 1 (color online). Experimental valence-electron Compton profile of solid (blue open circles) and liquid Si (red solid circles). The error bars are less than the symbol size.
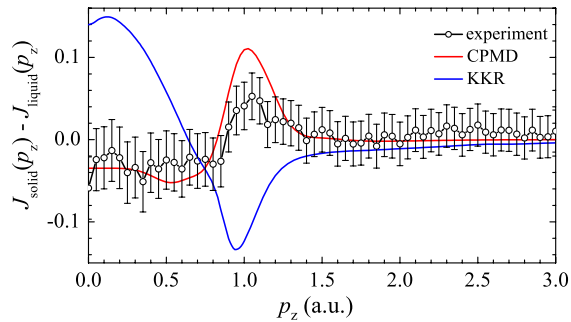
FIG. 2 (color online).   Differences between the Compton profiles for the solid and liquid phases, $[J_{\text{solid}}(p_z) - J_{\text{liquid}}(p_z)]$: experiment (black), CPMD simulation (red), and KKR CPA simulation (blue).

MLWFs are constructed through unitary transformation of Kohn-Sham wave functions such that the average spread (variance) of the Wannier functions is minimized. Same as the Kohn-Sham wave functions, each MLWF represents two electrons in spin-unpolarized calculations. In the *s*-Si simulation, the spreads of MLWFs are all smaller than 1.84 Å² and all the corresponding Wannier centers (WCs) are in the middle between two Si atoms, showing that all electron pairs in *s*-Si are covalent. On the other hand, MLWFs calculated from the *l*-Si simulation exhibit diverse characteristics. In particular, a majority of MLWFs have spreads larger than 1.84 Å², up to over 7.8 Å². The spread is an indicator of the spatial extent of the MLWF. The inability of the MLWF procedure to localize some of the Wannier functions is expected as the system is metallic and the MLWFs with large spreads contribute to the metallic properties of *l*-Si. We refer to such electron pairs as diffuse pairs. The MLWFs with small spreads mostly correspond to the covalent electron pairs in *l*-Si. However, there is a special type of MLWF whose spread is comparable to that of the covalent electron pairs but the WC is not shared by any two Si atoms, so that the corresponding electron pair may be called a lone pair. The lone pair MLWF is computed to have a spread of 2.21 Å² [33].

In order to categorize different types of electron pairs in *l*-Si, we sort the MLWFs into three groups: covalent bond pairs, lone pairs, and diffuse pairs. All electron pairs with a Wannier spread larger than 2.21 Å² are assigned to be diffuse pairs. Among electron pairs with spreads smaller than 2.21 Å², an electron pair is a covalent bond pair if the following two criteria are satisfied: (1) The WC lies between two Si atoms separated by less than 3.1 Å, which corresponds to the first minimum of the Si-Si radial distribution function; (2) The WC lies within 1.36 Å from the midpoint of the two Si atoms. The 1.36 Å equals the square root of 1.84 Å², which is the largest variance of covalent bond pair MLWFs in *s*-Si. With this scheme, we found that on the average, there are 17%, 83%, and less than 1% of covalent bond pairs, diffuse pairs, and lone pairs, respectively [34]. Figure 3 shows a snapshot from the simulation carried out on *l*-Si. Note that the population of different
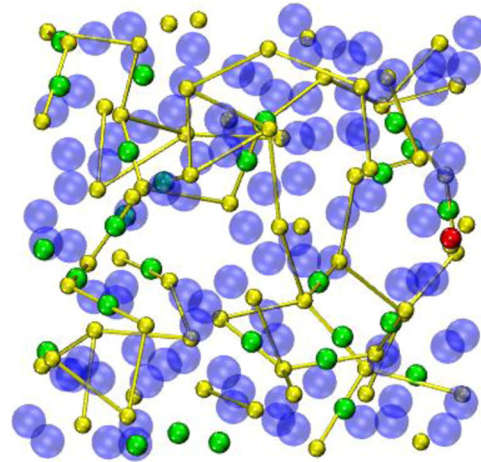

FIG. 3 (color online).   Snapshot from the simulation on *l*-Si at 1787 K exhibiting Si atoms (yellow [light gray]), covalent bond pairs (green [medium-light gray]), lone pairs (red [medium gray]), and diffuse pairs (translucent blue [dark gray]). Note, bonds connecting Si atoms are only guides for the eye as they do not correspond to the chosen cutoff bond length of 3.1 Å.

electron pair types depends on the criteria adopted. The covalent bond pair population of 17% can be taken as the lower bound. This is because the choice of the Wannier spread cutoff of 2.21 Å² is too tight for a bond pair or a lone pair since MLWFs are expected to be more dispersed in the metallic liquid phase.

The key point of our analysis is that the existence of covalent bonds in metallic *l*-Si is clearly confirmed, and that liquid Si is not homogeneous at the atomic scale. The coexistence of two different bonding natures in a single component liquid is a precondition for LLPT [5]. Our study thus supports the possible occurrence of LLPT in deeply supercooled liquid Si.

The temperature of *l*-Si in our study is 1787 K which is far above the predicted LLPT occurrence temperature of 1232 K [8]. To infer what kind of change in *l*-Si could occur and cause LLPT with decreasing temperature, it is useful to look at the temperature dependence of density of *l*-Si. The density of *l*-Si has been measured between 1350 K and 1850 K [25]; a quadratic behavior of the density as a function of temperature in the supercooled region has been observed. This is interpreted as the coexistence of covalent and metallic bonds [35]. Above the melting point, the temperature dependence of the density shows approximate linearity, indicating little heterogeneity in bonding properties. In fact, our study shows that the majority of the electron pairs are in metallic bonds. In supercooled states, the ratio of covalent bonds could gradually increase with decreasing temperature since the temperature dependence of density deviates from linearity and becomes quadratic. The covalent bond pairs could assemble to form LDL domains. When the temperature drops to 1232 K where LLPT could take place, the domain size could exceed a critical size as in the case of nucleation in liquids, separating *l*-Si into HDL and LDL.

Finally, as stated in the introduction, there has been a long-standing controversy related to the interpretation of the nature of bonding in *l*-Si: atomic structure experiments have given indications of the presence of covalent bonds [3,36], while other experiments suggest that all valence electrons behave like free electrons [10–12]. Our study resolves this controversy by establishing the persistence of a significant number of covalent bonds in *l*-Si, even though a majority of valence electrons in *l*-Si exist as diffuse pairs.

To summarize, we have carried out Compton scattering measurements on *s*- and *l*-Si coupled with CPMD and KKR CPA simulations. Comparison with the KKR CPA results shows that Compton scattering remains a sensitive probe of bonding properties despite the smearing of the momentum density induced by disorder in the liquid state. The excellent agreement of the CPMD simulation with the experimental results establishes the existence of covalent bonds in metallic *l*-Si. The contributions of the covalent bond pairs, diffuse pairs, and lone pairs are estimated to be about 17%, 83%, and less than 1%, respectively. Our study thus provides evidence for the coexistence of two distinct bonding species, metallic and covalent, which is a prerequisite for the occurrence of LLPT in deeply supercooled *l*-Si, and thus supports the possibility of such a phase transition. Future Compton experiments with intense x-ray pulses will be needed to probe how the silicon bonding properties evolve from metallic to covalent character and how an LLPT may occur.

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