# A new approach for analyzing electronic properties of high-temperature liquids using high-energy inelastic X-ray scattering

The levitation technique has been developed over the last decade so as to hold a liquid sample stable and steady without a sample container, and its use with X-ray or neutron diffraction has enabled progress in research on atomic-level structural properties of high-temperature and undercooled liquids. In this study, in order to investigate the electronic properties of liquid silicon (Si), we have combined a newly developed levitation technique with high-energy, inelastic X-ray scattering, so-called Compton scattering, for the first time. We found, with the help of molecular dynamics simulations, that covalent bonding persists to some degree in the liquid phase. Compton scattering is a bulk-sensitive probe because the incident X-ray energy is as high as 116 keV, and thus the experimental data is not affected by the liquid surface, the temperature of which is difficult to control owing to the occurrence of thermal convection and evaporation. The present study demonstrates how X-ray Compton scattering can provide a novel spectroscopic window on the liquid state [1].

Si transforms into a metal accompanied by a density increase of about 10% upon melting. The resistivity of liquid Si (*l*-Si) at the melting temperature $T_m$ is 0.75 Ωm, which is comparable to that of simple liquid metals such as *l*-Al. Molecular dynamics simulations of liquid 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 rapidly on a time scale of 20 fs [2]. 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. A recent study reports that *l*-Si could undergo a liquid-liquid phase transition (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) [3]. However, 1232 K is far below the Si melting temperature of 1683 K, and as a result, the supercooled state has remained inaccessible to current experimental techniques, so that the experimental confirmation of an LLPT in Si remains an open question.

A key requirement for the occurrence 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, soft X-ray and magnetic susceptibility measurements of electronic properties so far have not supported this viewpoint in that all four valence electrons in *l*-Si appear to behave like free electrons.

Liquid Si is highly reactive with most crucibles. To hold the sample without contamination, a high-temperature electrostatic levitator (HTESL) was used (Fig. 1). The HTESL levitates a spheroid sample of 2 mm diameter in a high vacuum environment (approximately $10^{-5}$ Pa) using electrostatic forces with feedback computer control [4]. The sample (Si, 99.9999% purity) was heated and melted using the focused radiation of three 50 W semiconductor laser beams with emission at 808 nm. Temperature was controlled within 15 K and measured by pyrometry.

Compton profiles of polycrystalline Si (300 K) and liquid Si (1787 K) were measured with high-energy (116 keV) inelastic X-ray scattering at **BL08W** beamline. In order to analyze the Compton profiles, Car-Parrinello molecular dynamics (CPMD) simulations were performed with the Quantum ESPRESSO package within the framework of the density-functional theory using the generalized gradient approximation. Figure 2 presents the differences between the Compton profiles for the solid and liquid phases [$\Delta J(p_z) = J_{solid}(p_z) - J_{liquid}(p_z)$]. The results of CPMD simulation were obtained by taking the difference between the liquid Compton profile and the spherically averaged profile of the solid. The CPMD results agree very well with the experimental results. In order to analyze the bonding character in *l*-Si obtained through CPMD simulation, the maximally localized Wannier functions

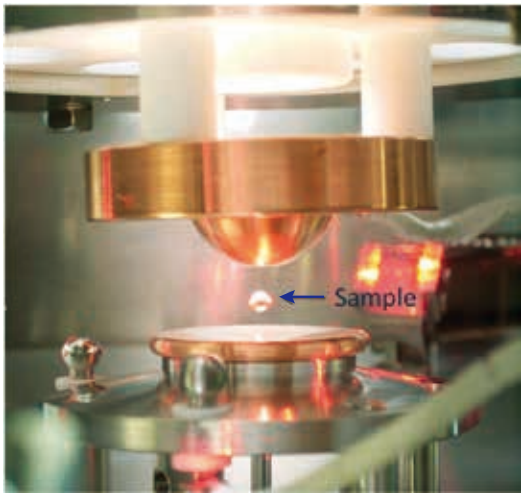


Fig. 1. Interior of electrostatic levitator. A sample of 2 mm diameter is levitated using electrostatic forces via feedback control.

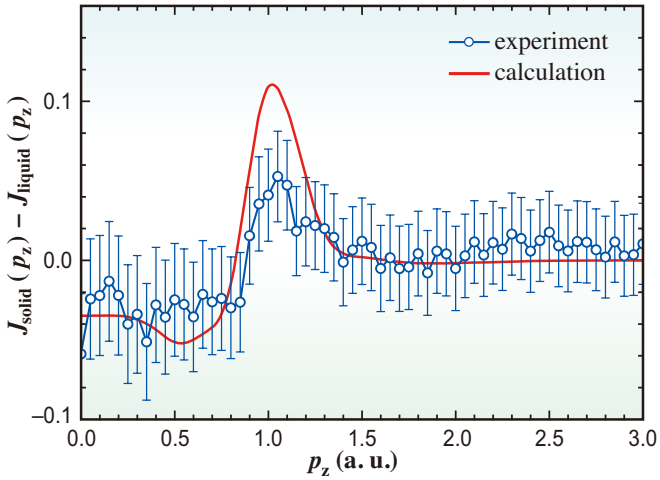


Fig. 2. Difference between the Compton profiles for the solid and liquid phases [$\Delta J(p_z) = J_{solid}(p_z) - J_{liquid}(p_z)$]: experiment (blue) and CPMD simulation (red).

(MLWFs) analysis method is used. We sort the MLWFs into three groups to categorize different types of electron pairs in *l*-Si: covalent bond pairs, lone pairs, and diffuse pairs. We found that, on the average, there are 17%, 83%, and less than 1% of covalent bonds, diffuse pairs, and lone pairs, respectively.

Figure 3 shows a snapshot from the simulation carried out on *l*-Si. The key point of our analysis is that the existence of covalent bonds in metallic *l*-Si is clearly confirmed, and that *l*-Si is not homogeneous at the atomic scale. The coexistence of two different bonding natures in a single-component liquid is a precondition for the occurrence of the LLPT. Our study thus supports the possible occurrence of LLPT in supercooled *l*-Si. Future Compton experiments with intense X-ray pulses will be needed to probe how the silicon bonding properties evolve from the metallic to covalent character and how an LLPT may occur.

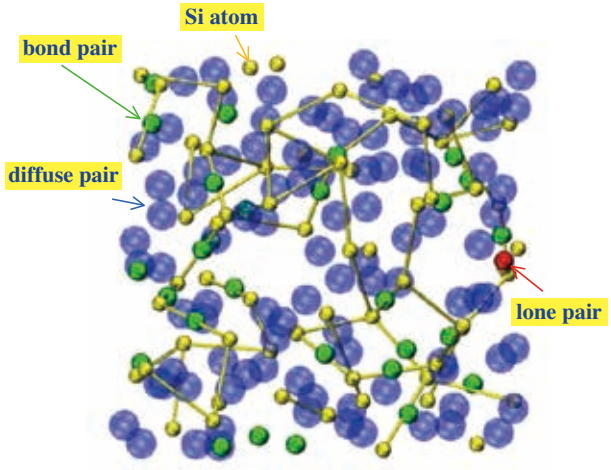


Fig. 3. Snapshot from the simulation on *l*-Si at 1787 K exhibiting Si atoms (yellow), covalent bond pairs (green), lone pairs (red), and diffuse pairs (translucent blue). Bonds connecting Si atoms are only guides for the eyes.

Junpei T. Okada[a,b,*] and Patrick H.-L. Sit[c]

[a] Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency
[b] JST-PRESTO
[c] Dept. of Chemistry, Princeton University

*Email: okada.junpei@jaxa.jp

**References**

[1] *J.T. Okada, P. H.-L. Sit, Y. Watanabe, Y. J. Wang, B. Barbiellini, T. Ishikawa, M. Itou, Y. Sakurai, A. Bansil, R. Ishikawa, M. Hamaishi, T. Masaki, P.-F. Paradis, K. Kimura, T. Ishikawa and S. Nanao: Phys. Rev. Lett.* ***108*** *(2012) 067402.*
[2] I. Stich *et al.*: Phys. Rev. Lett. **63** (1989) 2240.
[3] P. Ganesh and M. Widom: Phys. Rev. Lett. **102** (2009) 075701.
[4] W.K. Rhim *et al.*: Rev. Sci. Instrum. **64** (1993) 2961.