Following a Structural Phase Transition in Real Time with Atomic Spatial Resolution

Constructing atomic scale mechanisms for chemical, biological, and physical transformations of matter represents a critical goal for numerous scientific and technological challenges that face modern society. The natural length and time scale for atomic dynamics dictate that the scientific tools needed to construct these mechanisms possess Ångström (Å) spatial resolution with femtosecond (fs) temporal resolution. Ultrafast x-ray pulses provide the necessary spatial and temporal resolution, but generating sources intense enough for detailed structural studies has been a significant challenge.

The Sub-Picosecond Pulse Source (SPPS) represents the first utilization of a linear electron accelerator to generate fs duration pulses of Å wavelength light for studying structural dynamics. The per pulse fluence at the SPPS exceeds that of all previous ultrafast hard x-ray sources by roughly two orders of magnitude,[1] allowing structural transformations to be investigated with unprecedented dynamical detail.

We have investigated the first steps in the laser driven solid-liquid transition of an InSb semiconductor crystal. Intense fs laser excitation of semiconductor crystals provides a pathway to crystal melting where the time dependent evolution of the atomic structure can be monitored directly with ultrafast x-ray diffraction [2-7]. While pioneering fs x-ray diffraction experiments utilizing ultrafast laser plasma sources have shown that crystals

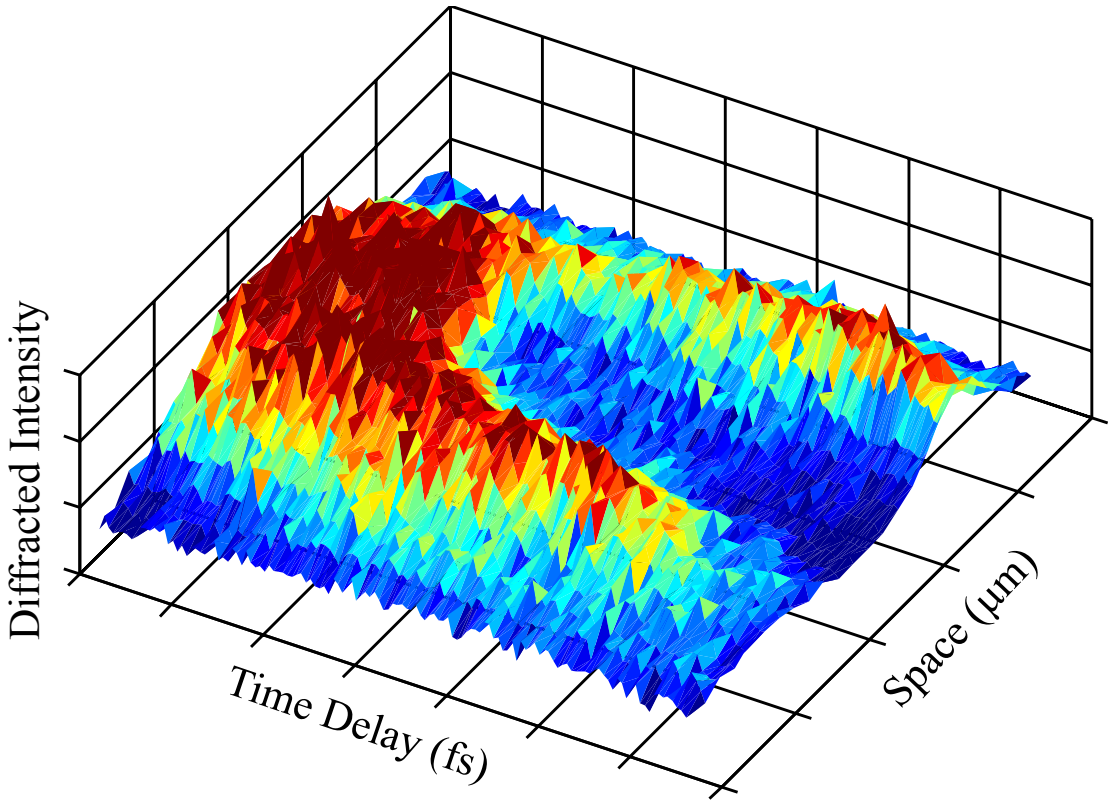

Fig. 1: Single shot image of x-ray diffracted intensity from the (111) Bragg peak of an InSb crystal. The ultrafast drop in diffracted intensity along the central region of the diffracted image results from intense laser induced disordering. The disordering occurs faster than the rate of energy transfer from the excited electronic system to the crystal lattice, indicative of an electronically driven melting mechanism, often termed non-thermal melting.

disorder faster than the rate of electron-phonon coupling [5, 6] and ultrafast optical measurements have observed liquid-like reflectivities on the sub-picosecond time scale,[2, 8] the time needed to generate liquid-like structure and dynamics remained unclear.

The comparatively large x-ray fluence and high time resolution at the SPPS has greatly improved the data quality and led to an increased understanding of the dynamical events that take place during the initial stages of electronically driven melting. While the structural pathway followed during the crystal to liquid phase transition has not been completely identified, the measurements to date at the SPPS have been sufficiently detailed to bring into question the theoretical models and molecular dynamics simulations that have provided the primary description of electronically driven melting and support the commitment to high brightness, ultrafast x-ray sources such as the Linac Coherent Light Source (LCLS).

Studies of ultrafast laser melting at the SPPS demonstrate that the initial stage of crystal disordering results from inertial motion on a laser softened potential energy surface. The atoms initially sample the modified potential with velocities determined by the lattice temperature prior to laser excitation. These inertial dynamics dominate for the first half picosecond following laser excitation, indicating that inter-atomic forces minimally influence atomic excursions from the equilibrium lattice positions, even for motions in excess of an Å. These inertial dynamics result in a linear increase in the root mean square (rms) displacement, as clearly shown in Figure 2. This also indicates that the atoms disorder initially without losing memory of their lattice reference. Interestingly, the time scale for inertial dynamics coincides with the time scale for the increase in optical reflectivity in InSb,[8] indicating that the increase in reflectivity results from band gap collapse prior to the formation of a liquid structure. This highlights the challenges present in utilizing the electronic response of a material to access information about the atomic structure and the utility of ultrafast x-ray diffraction.

Following the inertially driven decay in the diffraction intensity, we observe an exponential decay. These biphasic dynamics occur for both Bragg peaks we measured and for laser fluences ranging from 50 to 130 mJcm^{-2}. This exponential decay of the diffraction intensity

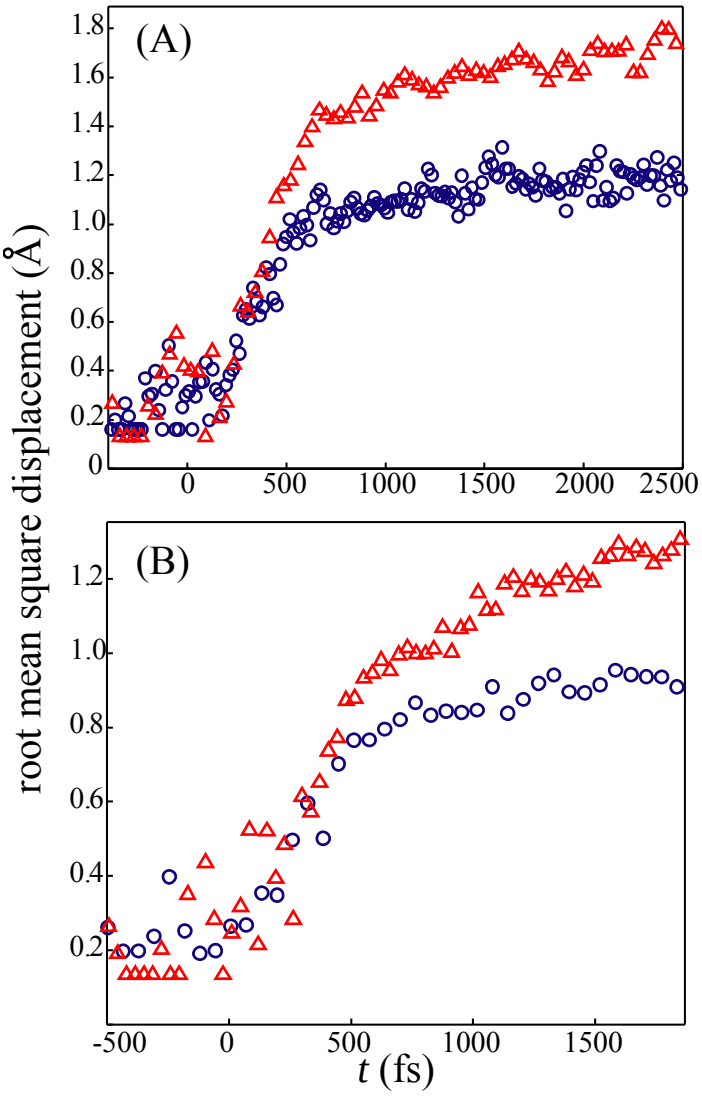

Fig. 2: Time dependent root-mean square displacement measured with the (111) (Δ) and the (220) (○) Bragg reflections. Data collected with laser fluences of 130 mJcm^{-2} (A) and 50 mJcm^{-2} (B).

corresponds to a rms displacement that increases with a square root temporal dependence, consistent with diffusive atomic motion. The experimental observation of diffusive motion provides a signature for liquid-like motion.

While atomic diffusion could be signifying the initiation of liquid formation, coherent Bragg diffraction will never definitively identify the time scale for liquid formation, since a liquid with long range disorder will not generate coherent Bragg diffraction. This will require time resolved measurements of the liquid structure factor via x-ray diffuse scattering [9].

The measurements of electronically driven melting at the SPPS also demonstrate that the disordering proceeds anisotropically. After the first 500 fs, the rms displacement (rmsd) in the [111] direction increases with a rate larger than the rate in the [110] direction. This anisotropy cannot be explained with a hard sphere model of atomic collisions, because the [111] direction disorders faster despite the shorter inter-atomic distances. These observations have provided an initial glimpse at the potential energy surface on which this phase transition occurs. The initial results appear inconsistent with the expected dynamics and anisotropy predicted by the theoretical model potentials used to describe electronically driven melting [3]. These measurements at the SPPS represent the most thorough experimental test to date of these theoretical and simulation studies of non-thermal melting and demonstrate the importance of high brightness, ultrafast x-ray probes of structural dynamics.

Primary Citations:

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