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Supplementary Materials for

Transient lattice contraction in the solid-to-plasma transition

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Supplementary Materials and Methods

Experimental Setup

Advances in ultrafast x-ray and electron diffraction have allowed for the study of high resolution, time-resolved transient behavior of systems where optical excitation drives mechanical properties (25,26). We have extended this approach so that intense hard x-ray pulses provide the pump energy and probe the evolving lattice dynamics with femtosecond resolution. The experiment was performed in the 100-nm focus chamber of the CXI instrument at the Linac Coherent Light Source (LCLS) (23,24). To measure time-dependent x-ray induced dynamics two 10 fs x-ray pulses were produced using the recently developed double-pulse operating mode at the LCLS (8). Twin electron bunches radiating at slightly different energies in the LCLS undulator produce two high intensity x-ray pulses in the experimental endstation. The x-ray pulses were separated by up to 80 fs, with a photon energy separation of ~70 eV straddling the nickel k-edge at 8.33 keV. The first x-ray pulse, with photon energy above the nickel K-edge and a pulse energy of ~300 μJ, diffracts off the Xe cluster and begins to induce dynamics in the system. The second x-ray pulse, with photon energy just below the nickel K-edge and a pulse energy of 700 μJ, Bragg scatters off the disintegrating Xe cluster and passes through the nickel filter. Bragg peaks from the second x-ray pulse are recorded on the Cornell-SLAC Pixel Array Detector (CSPAD) located 70 mm downstream of the interaction region. A time-of-flight spectrometer is used to measure ions in coincidence with Bragg scattering. Structural and electronic information is obtained with coincident detection of x-ray photons and ions. Clusters with a diameter of 70 nm were produced with a pulsed valve via supersonic expansion of Xe through a 200 μm nozzle with an opening half angle of 4°. The clusters were sent through two differentially pumped skimmer stages and a set of movable slits to produce a defined, localized target and ensure less than one Xe cluster in the interaction region per FEL pulse.

Bragg Peak Analysis

The data has been carefully filtered for events in which all Bragg peaks belonging to one reflection plane are visible, *i.e.*, in which the Ewald sphere is perfectly intercepting the reciprocal lattice, so that phase mixes or twinned particles do not distort the data analysis. In particular, for the fcc (111) and (220) peaks we separate hits that have an angular spacing between Bragg peaks

of 120 and 60 degrees, respectively. In the case of the (111) reflection, Bragg peaks on the x-ray detector at a scattering angle near $2\theta=25.5^{o}$ are filtered on the criteria that two additional Bragg peaks are located 120 degrees from this peak. This filtering procedure ensures no peak distortion from suboptimal exiting of the Ewald sphere. A similar procedure is followed for the (220) Bragg reflection, but with 60 degree angular separations at a scattering angle near $2\theta=44^{o}$.

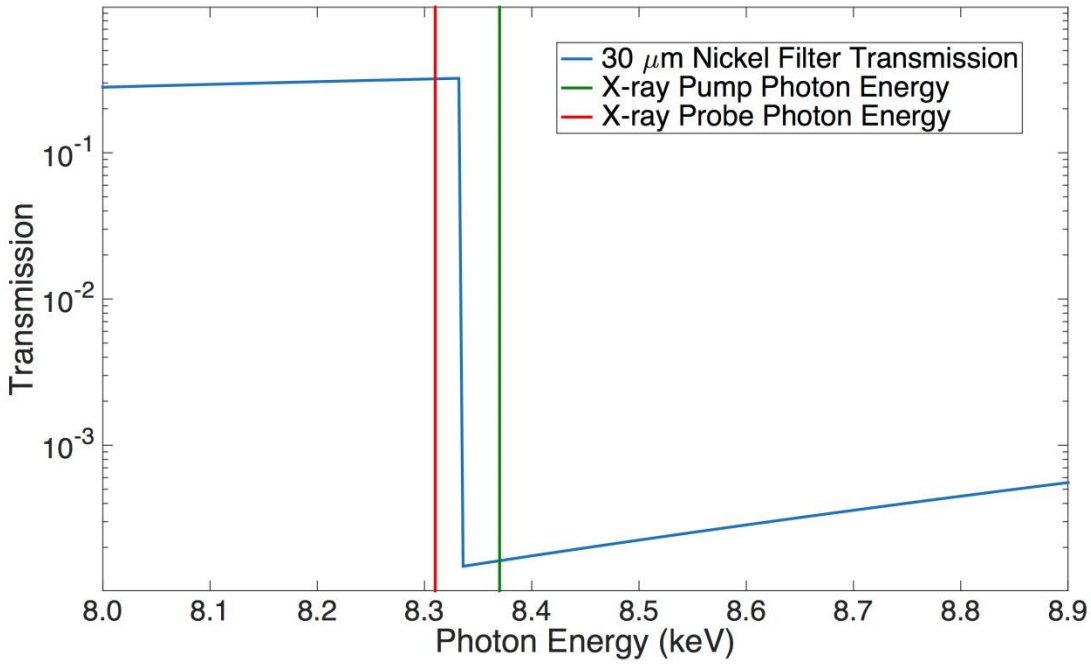

Fig. S1. Transmission of the 30-µm nickel filter around the nickel K-edge. At photon energies about the k-edge (pump pulse) the transmission through the filter is very low (~10^{-4}). Above the k-edge (probe pulse) the transmission is much higher (~$3\cdot10^{-1}$), a more than 3 order of magnitude difference, allowing Bragg scatter from the probe pulse to be visible on the x-ray detector while Bragg peaks from the pump pulse are fully absorbed by the filter.

Time-of-Flight Simulation

From atomic reference data taken during the experiment, a maximum Xe charge state of Xe^{25+} was observed, with more than 98% of ions have a charge state of Q = 20 or lower. Ionization processes in the cluster are similar to those in pure atoms. To simulate the charge state and kinetic energy distributions of ions produced from the cluster—x-ray interaction we use the SIMION ion optics simulation program. SIMION is a simulation software package that calculates electrostatic fields from a given set of electrodes and trajectories in this field using

numerical integration techniques. The program models ion optics problems with 2D or 3D electrostatic potential arrays, which allows users to simulate time-of-flight instruments and other physical systems. Kinetic energy distributions for various charge states were input into SIMION to match TOF spectra from the experimental data. For Xe^{20+} an average and maximum kinetic energy of 10 and 45 keV, respectively, fit the experimental data.

Electron and Ion Temperatures

Taking Xe^{20+} with a maximum kinetic energy of ~45 keV and an average kinetic energy of ~10 keV we deduce a plasma speed of sound $c_s = 1.2 \cdot 10^5$ m/s. The speed of sound defines the electron temperature as

$$T_e = \left(\frac{c_s}{9.79 \cdot 10^3}\right)^2 \frac{\mu_i}{Q\gamma}$$

which is approximately 600 eV, where μ_i is the ion mass in amu (131 for Xe), γ is the adiabatic index $\gamma = 1 + 2/n = 1.67$, and Z is the ion charge state Q = 20.

The ion temperature of the cluster core during exposure is deduced from the DWF, where the average lattice movement leads to a velocity of ~10^3 m/s. With a velocity of 10^3 m/s we calculate an ion temperature of ~1.5 eV.

Debye Length Calculation

To calculate the Debye length we used a modified Debye length equation (27) which is valid when the electron and ion temperatures are not equal. Specifically, the equation for Debye length is given by:

$$\lambda_D = \left[\frac{1}{4\pi n_e e^2}\left(\frac{1}{T_i} + \frac{1}{T_e}\right)^{-1}\right]^{1/2}$$

where n_e is the electron density, e is the charge of an electron, T_i and T_e are the ion and electron temperatures, respectively. Using an electron temperature of T_e = 600 eV and ion temperature of T_i = 1.5 eV we calculate a Debye length of $\lambda_D \approx 1$ Å.

Metallic Xe Bond Length

It is possible to estimate the atomic spacing of metals from basic free electron theory, which is derived from the assumption that free electrons can move through a crystal undisturbed. In the classical approach, the higher the free electron density, the tighter the bonding will be. This leads to an overall smaller interatomic spacing. To better fit known parameters of metals, basic free electron theory is modified under the assumption that ions have a finite size and valence electrons cannot enter the same space as occupied by the ionic cores. This leads to a system potential known as the "Finnis-Sinclair Potential" given by (28,29):

$$U = \frac{3}{10}\frac{Z\hbar^2{k_F}^2}{m} - \frac{Z^2e^2\alpha k_F}{(18\pi Z)^{1/3}} + \frac{2Z}{3\pi}e^2{r_C}^2{k_F}^3 - \frac{3Ze^2k_F}{4\pi}$$

where k_F is the well-known "Fermi wave vector." The Finnis-Sinclair potential leads to a nearest atomic neighbor distance of $d_0 = \left(9\sqrt{3}\pi^2/4\right)^{1/3}{k_F}^{-1}$ (29). The Fermi wave vector describes the distance over which a point charge placed in an electron gas with uniform background charge (jellium) has potential that varies. Namely, this potential varies slowly over a distance of order $\frac{1}{k_F} = \lambda_F$. In a plasma environment the Debye length describes the distance over which a charge is shielded in a plasma and the effective potential appears uniform (28), similar to the Fermi length in a metal. Thus we substitute the inverse Debye length for the Fermi wave vector (30). Using the Debye wave vector, given by ${\lambda_D}^{-1}$, we obtain a nearest neighbor distance of 3.4 Å, and an fcc unit cell length of 4.8 Å.

We can also crudely estimate the metallic Xe bond length without the need for electron temperature and actual electron density. In the simplest case the Fermi wave vector is given by:

$$k_F = \left(\frac{9\pi Z}{4}\right)^{1/3} \cdot \frac{1}{r_0}$$

where Z is the number of valence electrons in each atom, and r_0 is the atomic radius (108 pm for Xe). In the limit where each atom in the cluster is only singly ionzed (Z = 7), the Fermi wave vector is k_F = 3.4 Å^{-1}, leading to a unit cell length of 1.4 Å. This is much shorter than the observed 5.90 Å unit cell length, but highlights the same directionality of the system.