Supporting online material

Materials and Methods:

Conceptually, the time-resolved electron diffraction method is similar to an ultrafast optical pump-probe experiment; the new ingredient is that the probing is done by electron diffraction (Fig. S1). Dynamics are initiated with an ultrafast light pulse and then, at various delay times, the sample is probed with an electron pulse from a photoactivated electron gun. Synchronization of the two pulses is ensured (to better than 100 fs), since they are generated from a single laser pulse. By recording diffraction patterns as a function of delay time between the pump and the probe pulses we are able to follow the real-space atomic configuration as it evolves.

In the present case, we studied an ultrafast, laser-induced (70 mJ/cm$^2$) solid-liquid phase transition in polycrystalline Al samples that were 20 ± 2 nm thick. To avoid ground-state contamination of the diffraction patterns (from material not undergoing the phase-transition), the diameter of the pump laser beam ($\omega_l = 500 \mu m$) was chosen to be a factor of 2.5 larger than that of the probe electron beam ($\omega_e = 200 \mu m$). The Al in the excited volume evaporated at the high temperature induced by the laser excitation, which necessitated sample translation between laser shots and hence the somewhat low repetition rate of 3 Hz. Even at these repetition rates, however, data collection for each time delay took only 50 s (for 150 laser shots). Given the finite sample dimensions (2.5 cm x 1.25 cm) and nonreversible nature of the experiment, it was essential to use ~10 000 electrons per pulse to accumulate diffraction patterns of a quality sufficient for accurate structure determinations and still allow for many pump-probe time delay points from a single sample. This requirement placed demands on the electron gun design to avoid
space-charge-induced electron pulse duration broadening. This pulse broadening mechanism is severe for such beam parameters (10,000 electrons/pulse, 200 µm beam diameter) and propagation distances greater than 5 cm; femtosecond (30 keV) electron pulses of this charge density will broaden into the picosecond range over this distance (Fig. S2A). The photoactivated electron gun used in these experiments was specially designed to minimize space-charge-induced pulse broadening and was placed close to the sample, with only 4.2 cm of propagation in the drift region (that is, the propagation distance after the initial acceleration to 30 keV).

_Determination of the Electron Pulse Duration_

Currently, the only method available for determining the duration of an ultrashort electron pulse is to use the techniques employed by streak cameras (S1-S3), which involves sending an electron pulse through a pair of deflection plates to which a ramped voltage is applied. In this way, information on the temporal duration of the pulse is mapped onto a spatial dimension at the detector. In most configurations (including ours), the voltage ramp is applied to the deflection plates by triggering a pair of GaAs photoconductive switches with a laser pulse (the laser pulse that normally excites the sample (Fig. S1) is used to trigger the photoconductive switches when we are performing pulse duration measurements). The ramp rate available from our system is 4.5 kV/ns, and using 4 cm long deflection plates spaced 5 mm apart we were able to obtain beam sweep speeds at the detector of \( v_s = 1.5 \times 10^8 \) m/s. In single shot mode, the temporal resolution, \( \tau \), of such a deflection system is determined by the sweep speed and the detected beam size, \( w \), according to \( \tau = \frac{w}{v_s} \). When operating with 6000 electrons/pulse, \( w \approx 200 \) µm.
space-charge effects influence the ability to focus the beam at the detector), the temporal resolution is $\tau \approx 1.3$ ps for this system. Defocusing effects through the deflection plates reduce this temporal resolution somewhat, and we typically obtain $\tau \approx 2$ ps. This temporal resolution represents the state-of-the-art, but is insufficient to directly measure the femtosecond pulses available from our electron source at the sample. The best temporal resolution ever reported for a streak camera operating in single shot mode is $\approx 350$ fs ($S1$), but this streak tube operated at only 10 keV and had $w = 35$ µm. Temporal resolution of 800 fs is far more typical from these devices ($S2$), but even this requires very small beam sizes ($\sim 40$ µm) at the detector. Such focusing conditions cannot be obtained with the electron gun presented here, since this source is configured to provide femtosecond electron pulses in a well collimated, high-brightness beam through the sample and not a tight focus at the detector. The pulses produced by this high-brightness source are also intrinsically difficult to measure in this manner, because space-charge effects broaden the pulses so rapidly. For example, propagating an electron pulse containing 6000 electrons through a pair of 4 cm long deflection plates placed at the sample position would more than double its duration from 600 fs to 1.45 ps ($S2A$). A measurement conducted in this manner would not accurately determine the pulse duration at the sample, which is the quantity of interest, even if the temporal resolution were adequate. To overcome these difficulties, we use the numerical N-body simulation and analytical model discussed in the text (and presented in detail in ref. ($S4$)) to determine the electron pulse duration at the sample ($S2B$). These calculations are checked by carrying them forward in propagation time to where space-charge induced broadening lengthens the pulses into the several picoseconds range. Pulses of this
duration can be accurately measured with our deflection plate system and compared with the results of the simulations. The agreement between the measurements and both models is excellent (Fig. S2A), providing confirmation of their validity. The observation of subpicosecond changes to the diffraction pattern of Al presented in Fig. 1 further corroborates these results.

**Determination of Temporal Overlap between Electron and Laser Pulses**

There is currently no simple procedure for temporally overlapping the pump and probe pulses at a solid-state sample; it requires the observation of photo-induced changes to the diffraction pattern. Fortunately, during a strongly-driven solid-liquid phase transition these changes are dramatic, unambiguous and readily observed (Fig. 1). By measuring and equalizing the pump and probe path lengths it is possible to determine temporal overlap to within ± 30 ps (± 1 cm of path length). From this initial position we use a systematic binary search procedure to move towards the onset of the phase transition. This involves determining whether the initial delay line position is before or after the onset of the phase transition (by observing the diffraction pattern in a pump-probe experiment), and then resetting its position appropriately 1 cm longer or shorter. At this new position, another determination is made regarding ‘before or after’, and the delay line position is reset to appropriately, 0.5 cm longer or shorter. Continuing this iterative procedure, halving the distance moved at each iteration, it is possible to converge to a position $T = 0 ± 1\text{ ps}$ within 5 moves ($S_5$). Once temporal overlap is determined to this degree of accuracy, we record diffraction patterns in a stroboscopic fashion at pump-probe delay intervals of 500 fs near the onset of the solid-liquid phase transition (so that
the time origin can be determined to an accuracy of ± 0.25 ps by the onset of photoinduced changes to the diffraction pattern) and coarser 1 ps time steps thereafter.

**Sample Preparation**

Samples were prepared by thermal evaporation of a 20 ± 2 nm layer of Al (ESPI, 5N purity) onto optically polished NaCl flats (2.54 cm x 2.54 cm in dimensions). Optically polished substrates where chosen over cleaved salt crystals as the latter inevitably contained large step defects on the prepared surfaces. These step defects resulted in less robust films that disintegrated more readily when being removed from the substrate and mounted on the sample holder by conventional floating techniques. The sample holder consists of electroformed copper mesh (15 µm bars, 110 µm holes, 70% transmission) held under tension on a stainless steel frame with a 1.5 cm x 3 cm clear aperture. To fit over this clear aperture, the deposited films were scored before floating. Each substrate thus produced two films of dimensions ~ 1.25 cm x 2.5 cm. The mounted samples were attached to an XYZ sample manipulator with one rotational axis (Fig. S1) inside the high vacuum chamber.
Fig. S1. Schematic of the femtosecond electron diffractometer. The light source for the system is a conventional Ti:Sapphire chirped pulse amplification laser system, based on a frequency doubled Er:Fibre oscillator (775 nm). The repetition rate is easily controllable from 0 – 1kHz, but is normally operated at 3 Hz during the experiments to allow adequate time for translation to a new sample position between shots. Each laser pulse is divided in two parts (one to drive the photoactivated electron gun, and one used to photoexcite the sample), which ensures that the pump and probe pulses can be synchronized at the sample with very low jitter (< 100 fs). Not shown in this figure is the home-built Faraday cup, which can be translated into and out of the electron beam path to make accurate measurements (together with a Keithley electrometer) of the average beam current.
**Fig. S2.** Propagation dynamics of femtosecond electron pulses. (A) Space-charge-induced pulse duration broadening in the drift region (after acceleration) of the electron gun as configured for these experiments. The electron pulse duration at the start of this region is ~ 280 fs, due to the temporal broadening induced by the photoelectron kinetic energy distribution during extraction (SI). Coulomb repulsion acts to further broaden the electron pulse as it propagates and therefore the dynamics are strongly dependent on the number of electrons contained in the pulse. There is precise agreement between the pulse duration calculated with the two independent models presented in ref. (S4) and the duration measured after 2 ns of propagation (1 ns ≡ 10 cm for 30 keV electrons). (B) The space-charge-induced pulse broadening over short propagation times. The drift region propagation time (that is, to the sample) in these experiments is 0.42 ns. Thus, pulses containing 6000 electrons have a duration of 600 ± 100 fs at the sample. Pulses containing 3000 electrons are only 450 ± 50 fs in duration.
References and Notes


S5. Using this systematic technique for temporal overlap, one can obtain a precision, \( T \), within \( N \) moves according to \( 2^N = (30 \text{ ps})/T \). For \( T = 1 \text{ ps} \), we would use \( N \approx 5 \).