Supplementary Online Material

The calibration of the temporal axis in the acquired images is measured by recording data for different optical delay line positions and observing how the edge associated with the ultrafast effect moves spatially (Fig. S1). Calibrations are typically 20-30 fs/pixel (depending on the reflection and the placement of the CCD camera), are linear, and are in good agreement with the geometrical propagation times of the x-ray and laser pulses across the sample surface. The scatter in the plot below is mainly a result of fluctuations due to timing jitter between laser and x-rays (~300 fs rms). The time window observed is roughly 8 ps, much larger than this intrinsic jitter.

Fig. S1. Calibration of temporal axis in single-shot images for (220) reflection, obtained by recording the pixel corresponding to the midpoint of the decay in the diffracted intensity for different optical delay line positions.
Time zero has been determined by locating the onset of the sudden drop in diffracted intensity. This choice is justified by previous optical (4-7) and x-ray (8-10) experiments which have shown that the signal changes associated with the phase transition occur directly after the arrival of the excitation pulse.

The pump laser is a Ti:Al$_2$O$_3$ laser running at 800 nm with a pulse duration of 50 fs. It runs at an actively stabilized repetition rate of 102 MHz, a sub-harmonic of the linac RF signal at SLAC. The short-term timing jitter between x-ray and laser pulses has rms < 300 fs. The laser is focused using a cylindrical lens onto the sample at an angle of 25 degrees with respect to the sample surface. Peak fluence for the data shown in Fig. 2 is 0.1 J/cm$^2$. The x-ray undulator is tuned to produce 8.9 keV light. We measure $2 \times 10^6$ x-ray photons/pulse in a 200 x 400 µm spot in a 1.5% bandwidth, set by the acceptance of a series of three multilayer mirrors.

We have estimated the influence of instrumental broadening effects due to the finite pulse duration of the x-rays (80 fs) and laser (50 fs) and due to the accuracy with which we can image the surface topography (80 fs for the (220) reflection and 130 fs for the (111) reflection). A sum-of-squares estimate of the total broadening gives 125 fs for the (220) reflection and 160 fs for the (111) reflection. We have used these values to compute the convolution of the theoretical Gaussian decay in diffracted intensity with an instrument response function of fwhm 125 or 160 fs, compared in Fig. S2. We estimate the 10-90% fall time to change by <10% for the (220) reflection and <6% for the (111)
reflection. The ratio of the time constants $\tau_{111}/\tau_{220}$ changes from a theoretical value of $1.62 (\sqrt{8/3})$ to 1.57, in good agreement with our experimental results.

Fig. S2. Comparison of theoretical time-dependent Gaussian response with and without inclusion of instrumental response.