Solidification and fcc- to metastable hcp- phase transition in krypton under variable compression rates

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Understanding the dynamic response of solid under extreme conditions of pressure, temperature and strain rate is a fundamental scientific quest and a basic research need in materials science. Specifically, obtaining an atomistic description of structural and chemical changes of solid under rapid heating and/or compression over a large temporal, spatial and energy range is challenging but critical to understanding material stability or metastable structure, chemical mechanism, transition dynamic, and mechanical deformation. In this regard, developing time-resolved x-ray diffraction applied to solids under dynamic conditions is timely and synergistic to many proposed activities centered at third- and fourth-generation light sources.

Critical to high-pressure kinetic studies is the ability to precisely control pressure and compression rates over a wide range of governing time scales. Solid-state transformations under static high pressures are typically diffusion-limited, occurring in an intermediate time scale of µs to ms and between those of conventional static (<1 GPa/s) and shock wave (>10⁷ GPa/s) compressions. This is the time scale or compression rate that can be obtained, in a controlled way, using dynamic-diamond anvil cells (d-DAC). Hence, in this study we combined d-DAC with time-resolved synchrotron x-ray diffraction to investigate real-time structure changes and transition dynamics associated with melting and phase transitions of krypton under dynamic pressure loadings.

In this run, we have focused on molecular systems on Kr. Time-resolved x-ray diffraction experiments were carried out using monochromatic synchrotron x-rays at 25.7 keV (0.48262 Å) at the Extreme Conditions Beamline (ECB) P02.2 at PETRA III, Deutsches Elektronen Synchrotron (DESY). The incident x-ray beam was focused to a spot size of ~ 2 (H) x 7 (V) μm² using a compound refractive lens system (CRL) and the 2-dimensional diffraction pattern was collected using a Pilatus 1M area detector. Electronic instrumentation was used for synchronization, triggering and monitoring the timing between the x-ray detector and d-DAC; including a piezo-actuator power amplifier, a function generator, a delay generator, and a digital oscilloscope.

Series of x-ray diffraction images were collected with varying exposure times at the frequency range of 2 (500 ms x-ray exposure) to 33 (30 ms) Hz, as shown in Fig. 1. Three selected diffraction images of one diffraction experiment are shown in Fig. 1a. We used the Fit2D program to process the diffraction images and convert them to intensity vs 2θ plots (as shown in Fig. 1b) or a 2D contour plot to examine the lattice response to the pressure variation (in Fig. 1c). For comparison, the solid bars at the top of Fig. 1c represent the calculated peak positions for Cu and fcc- and hcp-Kr at 1.1 GPa using CrystalMaker®. Figure 1c illustrates a series of dynamic loadings of Kr, consisting of five consecutive, one-second-long truncated sine wave pressure modulations. Note that at the beginning of the experiment, Kr is in the liquid state, solidifies into the fcc phase and then transforms into an hcp structure during compression. Upon decompression, both the fcc and hcp phases melt, but only partially; a remnant of fcc phase persists. During the five consecutive pressure modulations, not all of diffraction peaks appear in each cycle. Some diffraction peaks appear and develop after a brief delay.
We analyzed the measured angle-resolved diffraction patterns in Fig. 1b using Jade® (MDI, Jade 9) to index the diffraction peaks of Cu and the high-pressure polymorphs of Kr. Then, we analyzed the spectral shape of each indexed peak using Matlab® to locate the peak position, the intensity at the peak center and the integrated intensity of the peak, for further kinetic analysis. The indexed peak positions give the lattice parameters for Cu, fcc-Kr and hcp-Kr.

We have submitted the major findings for publication, summarized as the following: We present time-resolved synchrotron x-ray diffraction measurements to study kinetics associated with the liquid-solid and solid-solid high-pressure phase transitions in Kr under dynamic loading in a dynamic-diamond anvil cell (d-DAC). The results show a strong compression-rate dependence of the solidification/melting process in liquid Kr. The analysis of the compression-rate dependent melting/solidification, using an Avrami equation with the parameter n=1 indicates a spontaneous nucleation and one-dimensional growth mechanism. In contrast, the fcc to metastable hcp transition in solid Kr occurs rapidly at ~0.8 GPa near the melting line, which has negligible compression rate dependence within the range of compression rates studied (0.004-13 GPa/s).

**Figure 1** (a) Three representative diffraction images during the modulations. The number stated in the image is the scan number of the modulation. (b) the integrated diffraction patterns from the selected images. (c) a 2-D θ-scan_number plot of a series of time-resolved diffraction measurements and the calculated diffraction patterns of Cu (black), Kr-fcc (blue) and Kr-hcp (red) at 1.1 GPa

**References**