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Abstract

In this project we studied the series of structural phase transitions that occurs in the alkali earth metal Ca as it transforms to increasingly complex arrangements with pressure. The experiments were designed specifically for the ultra-bright X-ray source of the LCLS and the optical capabilities of the MEC nanosecond drive laser. We studied in detail the unusual structural behavior near the minimum of Ca's melt curve along the Hugoniot and investigated possible metastable phase formation as an explanation for large discrepancies in pressure-volume data from previous shock and static experiments. In total 200 data shots were taken. Using the laser pulse shaping capabilities for the MEC nanosecond laser permitted two thermodynamic compression paths to be explored: (i) Along the principal Hugoniot within the solid and liquid phases, (ii) along a double-shock path to access a cooler P-T compression path within the solid state. Probing the compressed Ca sample with the LCLS XFEL permitted structural determination of the Ca through x-ray diffraction. Pressure was determined with Doppler Interferometry (MEC VISAR diagnostic) and the known equation-of-state of Ca. These data represent the first direct measurements of lattice level rearrangement in Ca under shock compression. We observe the onset of melt, structure within the liquid and an evolution of crystal structure along off-Hugoniot paths up to 100 GPa. These experiments yield important insights into non-equilibrium phase formation under dynamic loading and the deviation away from nearly free electron like behavior, which has been found to be ubiquitous among the elements.

Project Summary

Pressure-driven structural phase transformations can fundamentally alter the chemical, strength and transport properties of a material. For example, carbon arranged in the graphite or diamond structure leads to a 1.6x difference in density, 10x difference in compressibility, 40x in thermal conductivity and a 500x difference in strength. As such crystal structure determination at high pressure has been an intense area of research for decades. In recent years there has been a paradigm shift in our understanding of atomic packing at high pressure. The long-standing assumption that materials will tend to more closed packed structures with pressure has been shown over the last 20 years through theoretical and experimental results to be wholly incorrect. Deviation from nearly free electron like behavior has been predicted in some cases to culminate in the localization of the materials valence electron density in the interstices of the atomic lattice which then behave like massless anions in a pseudo-ionic structure. Exotic electronic behavior is tied to structural complexity, as open structures with increasingly large numbers of atoms in the unit cell become more favorable at high-pressure coinciding with dramatic changes in the materials electronic properties. This behavior had been predicted to be remarkably ubiquitous among the elements with even aluminum reported to transform to an incommensurate host-guest "electride"

structure with 16 atoms per unit cell at 3.2 TPa. Dynamic compression is the only technique capable of reaching these extreme conditions in the laboratory. However, the considerable experimental challenge of using nanosecond *in-situ* X-ray diffraction in this pressure regime have made structural studies of such behavior experimentally challenging. The key to understanding pressure induced complexity may lie in another group of metals which have been predicted to exhibit similar behavior at much lower P-T conditions - the heavy alkali Earth metals.

The focus of our study, calcium, is an ideal analogous candidate for the study of high-pressure electride structures at P-T conditions ideally suited for using the nanosecond drive laser at MEC. Its high pressure behavior is intriguing - characterized by simple structural transitions at low pressure followed by remarkable structural complexity at higher pressure (atoms per unit cell increases 1->12->16->40->128). However, despite the vast amount of research on Ca, theoretically and in diamond anvil cells (DAC), its structural behavior had never been studied directly under dynamic compression. As such, our understanding of if, and how complex phases form under rapid loading is severely limited. In our experiments on MEC, we shock, and double-shock compress Ca and directly diagnose the evolution of crystal structure for the first time.

Traditional shockwave experiments rely on changes in the shock wave profile to diagnose phase transformations and as such, do not give any structural information. The interpretation of these measurements can become very complicated when several distinct phenomena are occurring in close vicinity to each other, such as solid-solid phase transformations and melting - as is the case in Ca. This is a wider problem in the field of shock physics with several discrepancies reported in other complex systems such as Si and Bi and so it is generally uncertain if the same phases observed in the DAC also form under shock compression. If an equilibrium transformation cannot be completed in the timescale of the compression experiment, non-equilibrium structures can form, with potential novel material properties as in Si.

The high-brightness of LCLS is uniquely suited to perform in-situ x-ray diffraction experiments to directly diagnose the crystal structure of Calcium under dynamic (< ns) loading. To access high-pressure low-temperature states, well below the melt, in our experiments we implemented a double-shock design. Here one arm of the MEC drive laser was used to deliver an initial weak shock into the Ca sample. The second arm of the MEC is then used to deliver a second stronger shock. Timing of the two laser beams is set so nearly the full volume of Calcium is at this double-shock state – which is characterised by a much cooler P-T compression path (over a single strong shock) prevents the sample from melting. The pressure and timing of the double-shock state was diagnosed with the MEC Visar system. The ability to control the strength of the initial shock allowed us to probe P-T above 100 GPa completely within the solid phase and also paths from an initial liquid state, for P > 35 GPa.

In our experimental setup the target design and pulse duration were optimized for both single and double-shock experiments by performing 1-D hydrodynamic simulations using the radiation simulations package HYADES. Our targets were prepared by our team at JHU/LLNL who are world experts in deposition/polishing techniques using non-standard materials. 50 µm layers of Ca was deposited onto polyimide ablators and so our targets were highly repeatable which is essential for performing in detail, pressure / time scans of phase space. Crucially, Ca is much less reactive than many of the other materials which exhibit similar behavior, making the production of many repeatable targets straightforward.

For the single shock studies, the MEC drive laser delivered up to 20 J in a 15 ns quasi flat-top pulse within a 250 µm spot onto the front of a 75 µm polyamide ablator on which, 50 µm of Ca was directly deposited.

Using the MEC laser, single-shock pressures of > 25 GPa were readily accessible which was sufficient to access the liquid phase. The MEC VISAR diagnostic recorded the LiF/Ca interface velocity history during each experiment and the sample pressure-time history was then extracted by using standard impedance techniques and knowledge of LiF and Ca equations-of-state (EoS's). Our simulations guided our pulse shape and target design to produce a steady shock wave (i.e. amplitude not changing with time) in the sample -- which is highly desirable to minimize pressure gradients which can complicate the interpretation of the resulting diffraction patterns. The VISAR also gives precise timing of shock break out which is essential in informing the XFEL snapshot delay which should be chosen.

By introducing a second 20 J drive pulse of the same duration, 15 ns after the first, the sample compression followed a much more isentropic compression path up to ~100 GPa. Diffraction was collected using several in-vacuum CS-Pads placed in the standard set-up in the MEC chamber. By varying the timing of XFEL delay / laser energy several different phases of Ca were observed at pressures ranging from the ambient crystal up to highest solid pressures of 30 / 150 GPa in the single / double-shock experiments.

While during these experiments there were a number of difficulties with MEC laser performance - in terms of pulse shaping and energy delivery on target - we successfully directly measured, at the atomic lattice level, polymorphism in Ca both along the Hugoniot to melt and along a cooler double shock path within the solid phase to ~100 GPa. In total the analyzed experimental data pertained to 200 data shots. For every shot the following data was obtained: (1) X-ray diffraction data recorded on CSPAD detectors, (2) Velocity Interferometer data (to determine sample pressure), (3) Laser pulse shape and energy data, and for representative shots. Each velocimetry record provided direct information on the Calcium/LiF window particle velocity history, up(t). The measure of up(t), in turn, provided the necessary information needed to constrain the sample pressure in time and in space. The step requires matching the VISAR measured up(t) with hydrocode simulations which contain the equations-of-state descriptions of the constituent materials in the target: CH, Ca and LiF.

In conclusion, by combining high quality, in situ X-ray diffraction and velocimetry at MEC, we have elucidated for the first time the response of Ca to shock and double-shock compression and upon pressure release over nanosecond timescales. Our results provide the first direct measure of crystal structure evolution along the Hugoniot and into the high-T liquid phase and then along a cooler compression path with the solid phase. On pressure release, we obtain an atomistic view of reverse transitions. This work is currently being prepared for publication.