LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-411089

Hysteresis and Kinetic Effects During Liquid-Solid Transitions

F. H. Streitz, R. Chau

March 6, 2009

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

FY07 LDRD Final Report

Hysteresis and kinetic effects during liquid-solid transitions

LDRD Project Tracking Code: 05-ERD-014

Frederick Streitz, Principal Investigator

Abstract

We address the fundamental issue of phase transition kinetics in dynamically compressed materials. Focusing on solid bismuth (Bi) as a prototype material, we used a variety of time-resolved experiments including electrical conductivity and velocimetry to study the phase transition kinetics of the solid-solid phase transitions. Simple single shock experiments performed on several low-lying high pressure phases of Bi, revealed surprisingly complex behavior and slow dynamics. Strong hysteresis effects were observed in the transition behavior in experiments where the compressed Bi was allowed to release back across a phase line. These experiments represent the first reported simultaneous use of resistivity and velocimetry in a shock compression experiment, and the first observation of hysteresis effects occurring during dynamic compression and release.

Introduction

A unified description of kinetics of phase transitions under dynamic loading conditions is generally lacking. Problems of kinetics in phase transition have been sporadically examined in specific cases such as iron or carbon, but an overarching framework is nonexistent and remains elusive. For many decades, dynamic loading was limited to simple shock wave studies where the final shock states are described by the Rankine-Hugoniot equations derived from simple conservation laws. The Hugoniot equations, while simple, are powerful in that they fully describe the pressure, density, and total energy of the final shock state. However, this description does not invoke the concept of time dependence of the material state and hence cannot describe the kinetics of the system. If the final shock state of a material places the system in the stability region of a phase different than the ambient state, how (and over what does timescale) does the system transform itself into the new state?

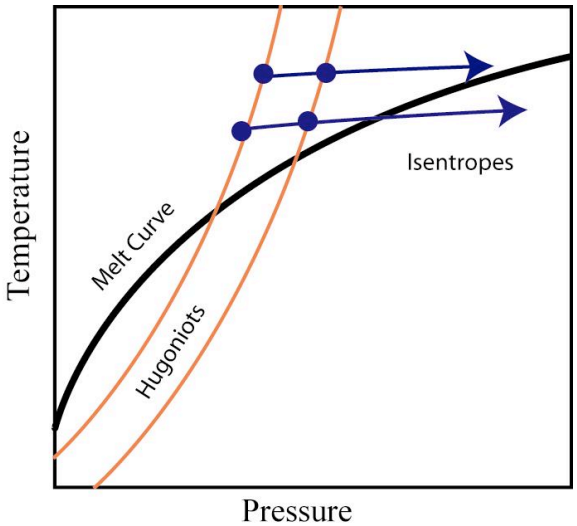

Figure 1: We explore the high P/T part of the melt curve by isentropically compressing from shock melted states, such as the four noted above. We can shock onto different hugoniots by preheating the sample, and can compress on different isentropes by altering the strength of the initial shock.

This is the central question.

The high-pressure phase diagrams of materials are derived from a combination of static high pressure and dynamic shock wave data. This is especially true in the multi-megabar pressure regime at high temperatures, where only dynamic data is available due to limitations in the maximum high pressure attainable with static techniques. In many materials, there is a discrepancy between the static data, dynamic data, and theory. This recurring problem illustrates the difficulty in understanding phase transition kinetics and highlights the current need for progress. The phase diagram of Fe is a classic example. The essential difference between the dynamic data and static is the timescale over which the experiments are performed. Many questions arise from kinetics consideration: how long does it take for a material to transform from one phase to another; are there intermediate metastable phases; how does the thermodynamic history affect the end result?

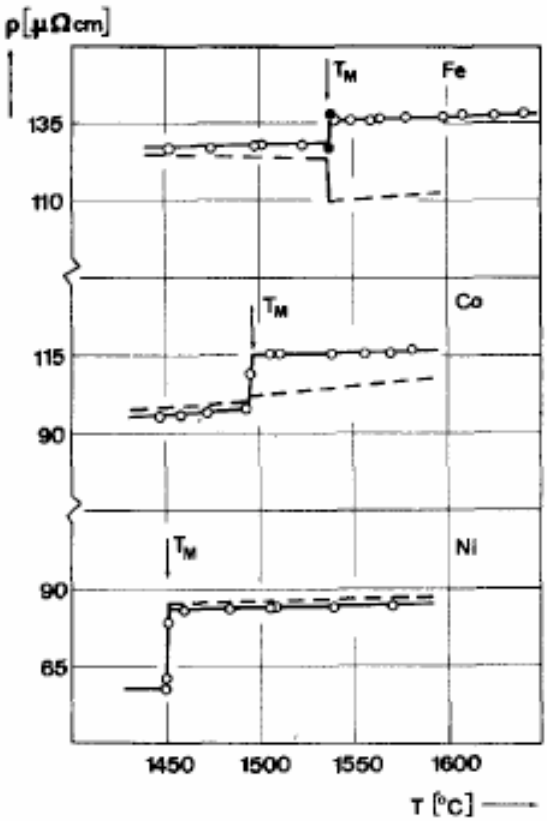

Figure 2: Conductivity is known to be a sensitive measure of phase, discriminating between liquid and solid as well as multiple solid phases. (from H.-J. Güntherodt *et al.,* Phys. Lett. 54A, 291, 1975)

The goals for this project are three-fold: 1) to develop time resolved methods to observe phase transitions, 2) to gain insight into the kinetics of phase transitions as a first step towards developing phase transition models which incorporate dynamics, and 3) to understand how phase transitions are affected by multiple crossings of the melt line, where hysteresis effects might come into play. To investigate the high-pressure phase transitions, we will use single shock compression. This will provide valuable experience for future work using tailored impactors and quasi-isentropic compression. The difficulty in analyzing isentropic compression data would add undue complexity to an already formidable problem at this time. In addition to these experiments, companion calculations will be performed on the hydrodynamic scale (to aid both in the design of the experiment and in the analysis of the results) and at the atomic scale.

The exploration of phase transitions at high pressure and temperature was accomplished in a series of single shock experiments that compress a prototype material from ambient into a different solid phase. Time-resolved electrical conductivity and velocimetry diagnostics were used to track the kinetic changes. Conductivity in particular has been shown to be a useful diagnostic for liquid-solid phase transitions (see Fig. 2), and we leveraged a demonstrated expertise in the making of these measurements during dynamic compression experiments.

Existing electronics available to this project proved sufficiently sensitivity to allow full resolution measurements at the nanosecond timescale.

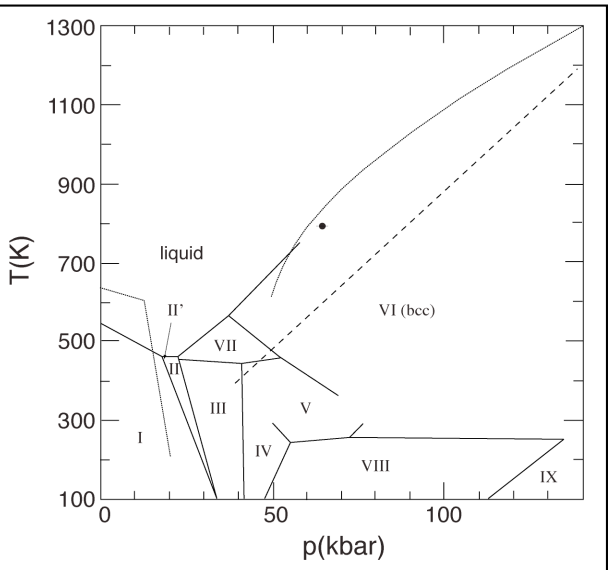

Figure 3: Phase diagram of bismuth.

We chose Bi as the prototype material for these experiments. Bi has a complex phase diagram (see Fig. 3) with numerous low-pressure solid phases. Bi is also one of the few materials with a negative slope in the melt curve. Bi is an ideal test material because it offers easily accessible solid-solid and solid-liquid phase transitions while remaining easy to handle and is non-toxic. Finally, the numerous high-pressure solid phases of Bi display a large change in electrical conductivity thus making time resolved conductivity experiments a viable diagnostic of phase transitions. In fact, much of the early work on the static phase diagram of Bi used the change in electrical conductivity as the evidence for a phase transition.

One of the most important aspects of the kinetic problem was the measurement the kinetic timescale for each phase transition. To address this key issue, we used a relatively simple single shock loading to focus on the Bi I-II and Bi I-III solid-solid transitions. The target design for electrical conductivity introduces a natural pressure release due to the lower shock impedance of the electrical insulator materials. We took advantage of this fact to compress the Bi across a phase line and release back across the same line. These experiments were one of the few to investigate hysteresis effects in phase transitions and to examine the location, extent and strain rate dependence of a multi-phase coexistence region. (This region can be seen on the green path shown in Figure 1.)

Results/Technical Outcome

For the initial phase of this project, we focused on studying the kinetics in a simple shock experiment. Bismuth was chosen as the initial test system because of the many phases accessible in a shock experiment. We focused on the Bi I to Bi II, Bi I to Bi III, and the Bi I to Bi V solid to solid transitions since there are large differences in the electrical conductivity of the three phases. Before we began experiments on Bi, we benchmarked the existing electrical conductivity diagnostic using copper. Copper has one of the highest electrical conductivities and thus is expected to be a worst case in terms of the signal to noise ratio in the experiment. We used a traditional 4-probe design for the conductivity probe, modifying the standard circuit to accommodate a floating ground (thus avoiding interference with the gun firing circuitry). With this experimental arrangement we were able to detect a change in the resistance of the copper on the order of 10% at a signal level of 16 mV, as shown in Figure 4.

In the first set of experiments, the Bi was shocked to a peak pressure, released to a lower pressure and held for a period of time. The electrical conductivity data for peak pressures from 35 kbar to 112 kbar is shown in Fig. 5. The data in Fig. 5 represents three different cases. The lowest pressure data (35 kbar) shows Bi I shocked into Bi II and immediately released back into Bi I. We see the initial drop in resistivity expected for Bi II but then a large increase in resistivity as the pressure is released. In the second case (39, 41, and 47 kbar), the Bi is shocked into Bi III and released down to Bi I through Bi II. The rise in resistivity upon release is suppressed relative to the 35 kbar case, and we observe the emergence of another increase in resistivity at later times. This second feature moves to longer times as the peak shock pressure is increased. In the third case, the Bi is shocked into Bi V and remains in Bi V upon release. The resistivity drops and then remains fairly constant.

The static high-pressure phase diagram of bismuth remains controversial. The phase lines for many of the high-pressure solid phases such as VII vary from study to study and the structures for many of the high-pressure phases are unknown. Our interpretation of the data is highly dependent on the choice of phase diagram and Hugoniot of bismuth. The discussion above is based on the phase diagram shown in Fig. 3.

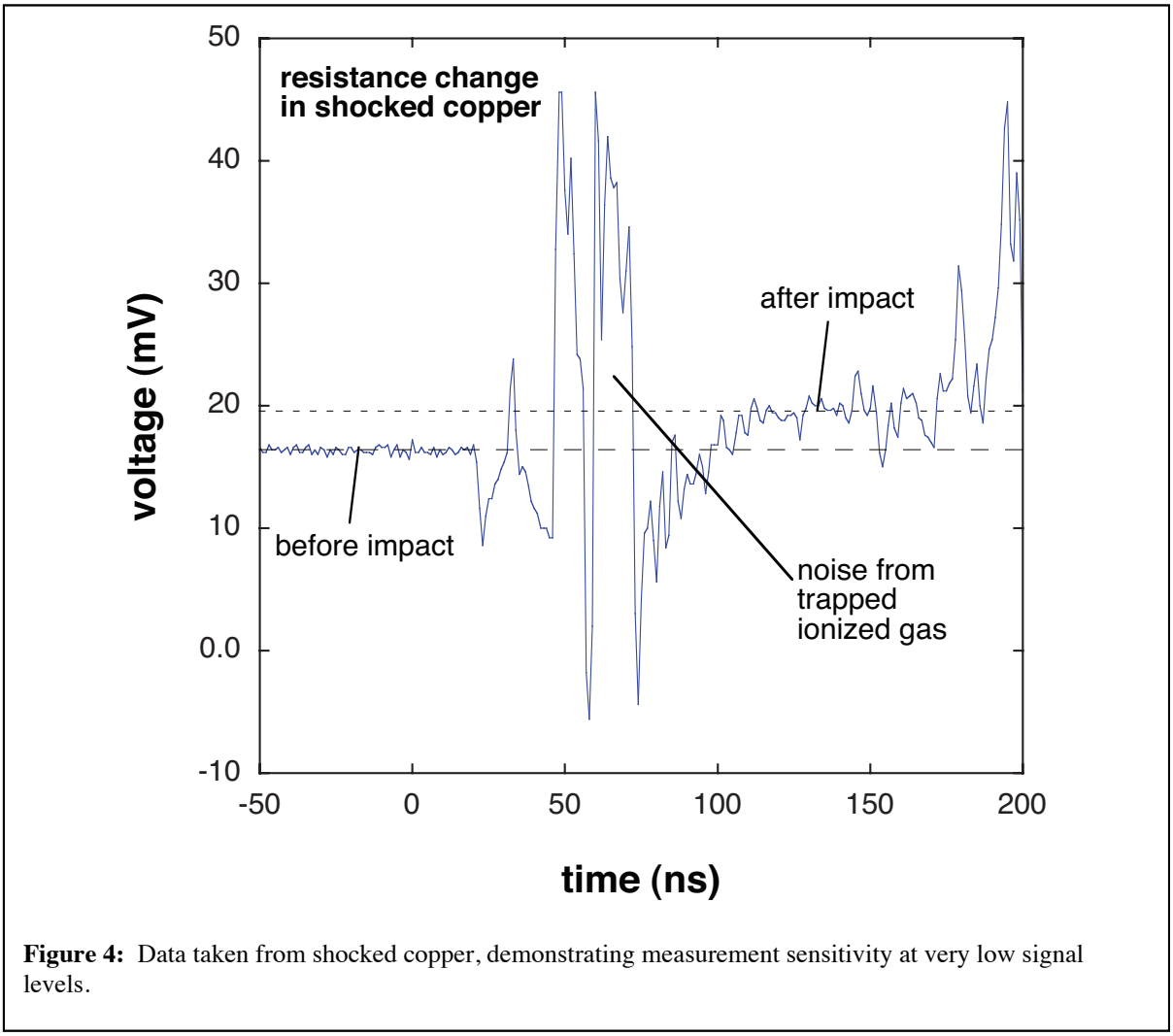

Figure 4: Data taken from shocked copper, demonstrating measurement sensitivity at very low signal levels.

The initial target design was conservative and included extra electrical insulation of the bismuth samples. However, this insulation introduced extra shock wave reflections in the bismuth and hence introduces a more complex hydrodynamic history. We performed comparison experiments without the extra insulation. Shown in Fig. 6(a) is a comparison of the two experiments taken under identical shock loading conditions but with and without the extra kapton insulation. The data without the kapton has a drop in resistivity and then returns to the ambient resistivity after the release in pressure. This is consistent with the bismuth going from Bi I to Bi II and then releasing cleanly back into Bi I. With the kapton, the resistivity increases after the pressure release. The additional reflected waves from the kapton may have caused the bismuth to cross the phase boundary multiple times. The kinetic response time of the bismuth is likely longer than the reverberation time of reflected waves. The kapton insulation appears to have no effect on the resistivity at the highest peak shock pressures. In those experiments, the bismuth is shocked into phase V and remains there. This drastic difference suggests strong hysteretic effects in the solid-to-solid phase transitions.

The thin 25 μm samples give the best resistivity signals due to their high sample resistance. However, the wave interactions with the lower impedance anvil/insulator materials lead to a pressure profile that is changing as a function of time within the bismuth for significant periods of time. To alleviate this problem and to test the effects of bismuth thickness, we performed a series of resistivity measurements on 250 μm thick bismuth. This is a ten-fold increase in thickness over the thin bismuth samples. The tradeoff was an increase in signal to noise due to the much lower sample resistance. Shown in Fig. 6(b) is a plot of the electrical resistivity of the 250 μm thick bismuth at three different pressures. The 4.5 GPa and 6.5 GPa data is consistent with the behavior observed in the thinner bismuth samples at comparable pressures. The 4.5 GPa data shows a slight drop in resistivity and then increases. The 6.5 GPa data shows a decrease in resistivity over 200 ns and then remains constant. At the lowest shock pressure, the

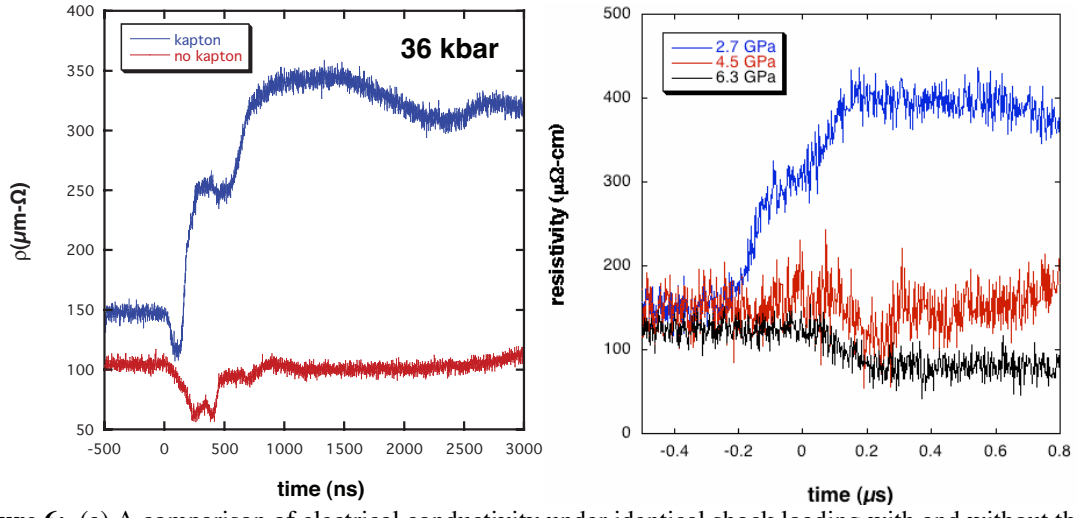

Figure 6: (a) A comparison of electrical conductivity under identical shock loading with and without the kapton insulation, (b) A comparison of electrical resistivity of 250 μm thick bismuth at three different pressures.

resistivity increases, and the behavior is similar to the thin bismuth samples with the Kapton. The hydro simulations of the 250 μm bismuth experiments still show considerable wave interactions between the sample and insulating materials. The pressure inside the bismuth at 2.7 GPA is shown in Fig. 7 and shows the variation in pressure within the sample. The variation in the pressure can be correlated to the changes observed in the resistivity. It is unclear why the resistivity increases at this pressure regime. Based on the variations in the resistivity shown in Fig. 7, it would appear that the bulk response time for the resistivity is on the order of tens of ns. How this bulk time scale for changes in the electrical transport property relates to the actual changes in phase at the microstructure level is an open question.

Electrical resistivity serves as an adequate diagnostic to examine the kinetics of the solid-to-solid phase transition. However, the need for a thin bismuth sample to get an acceptable signal to noise ratio introduces a very complex hydrodynamic response of the bismuth conductivity target. This makes clear interpretation of the resulting data difficult. It is clear that the behavior of bismuth is highly dependent on the thermodynamic history. The drastic differences shown in Fig. 5 are a clear indication of strong hysteretic effect.

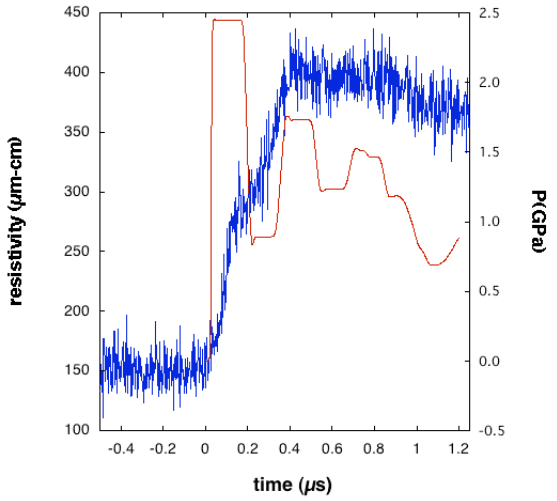

Figure 7: A comparison of electrical resistivity of 250 μm thick bismuth at 2.7 GPa and a hydro simulation showing the variation of pressure within the sample.

The large differences in the response of the bismuth due to additional reflected shock waves pointed out the need to velocity profile experiments. We performed velocimetry experiments with and without simultaneous electrical conductivity measurements. For the velocimetry, we used the LLNL developed heterodyne velocimeter. Fig. 8 shows the velocity profile of shocked bismuth in Fourier space. To eliminate the problem of additional wave interactions in the bismuth, the dedicated velocimetry experiments used 2 mm thick bismuth to simplify the hydrodynamic response. For these experiments, a 5 mm thick sapphire window was used for all experiments. The pressure profile is steady in the sample for the duration of the experiment. The velocity profiles of bismuth for five different pressures are shown in Fig. 9. The velocity profiles show a dramatic evolution with increasing pressure. The lower peak pressure velocity profiles (40 kbar and below) show a single jump in velocity at impact followed by a pressure release. Increasing the shock pressure results in the development of a second jump in the velocity. There is a large time delay from shock arrival till the onset of the second velocity jump. This time lag decreases with increasing shock pressure. It is striking to note that the velocity of the first velocity jump due to shock arrival is the same for shock pressures below 90 kbar. However, the second velocity increases with increasing shock pressure. It would appear that the mass velocity of bismuth is kinetically limited in this pressure regime. This begs the question as to physical state of the bismuth for the first few hundred nanoseconds after shock arrival. Our measurements give no information on the local structure of

the bismuth.

The time between shock arrival and second velocity jump is plotted as a function of shock pressure in Fig. 10. The data in Fig. 10 is well described by a sigmoid function of the following form:

$$base + \frac{max}{1 + exp(\frac{x_{half} - x}{rate})}$$

Where base=512.26±7.49, max=-508.54±8.04, xhalf=70.9±0.43, and rate=12.658±0.29 for the data in Fig. 8. The red line in Fig. 8 is a fit to the sigmoid function based on only the points in black. The green points were experiments performed after the fit and they nearly perfectly on the fit.

At this point, there is insufficient data to draw any strong conclusions from the behavior of the time lag in the second velocity jump. However, sigmoid distributions are quite common in nucleation and growth phenomena. In many of these processes, the slow initial growth is due to the lack of some parameter such as nucleation sites or high initial energy barrier for transformation. This is followed by a period of rapid growth and then a slow down as saturation is reached. Such a picture would be quite natural for the solid-to-solid phase transition in bismuth. One can argue that the long initial time for transition could be due to a kinetic limitation imposed by the lack of sufficient free energy and/or entropy flux for the nucleation of the new phase. As the initial shock pressure increases, the amount of available energy for the transition increases. At an initial shock pressure of 144 kbar, the velocity profile once again only displays a single velocity jump followed by a release consistent with a thickness of the sapphire window used in the experiment. This suggests that the phase transition can be overdriven. Another possibility is that at 144 kbar, the bismuth is shocked into phase VI the kinetics associated with the I-VI transition is very different than I-II or I-III. The observed behavior of the Bi draws no immediate parallels with any other material whose phase transitions have been studied dynamically. One of the inherent difficulties of understanding dynamically driven phase transition kinetics is that the behavior between different material systems varies dramatically.

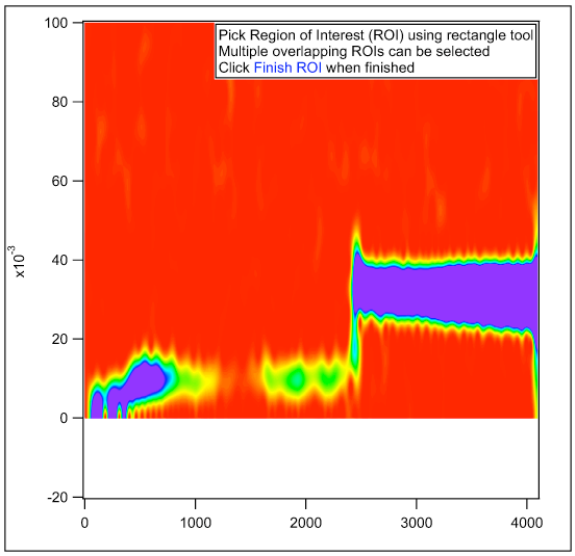

Figure 8: PDV velocimetry (in Fourier space) of shocked bismuth, showing (a) the ramp-like nature of compression wave in the kapton layer and (b) the appearance of multiple velocities as the transition proceeds0.

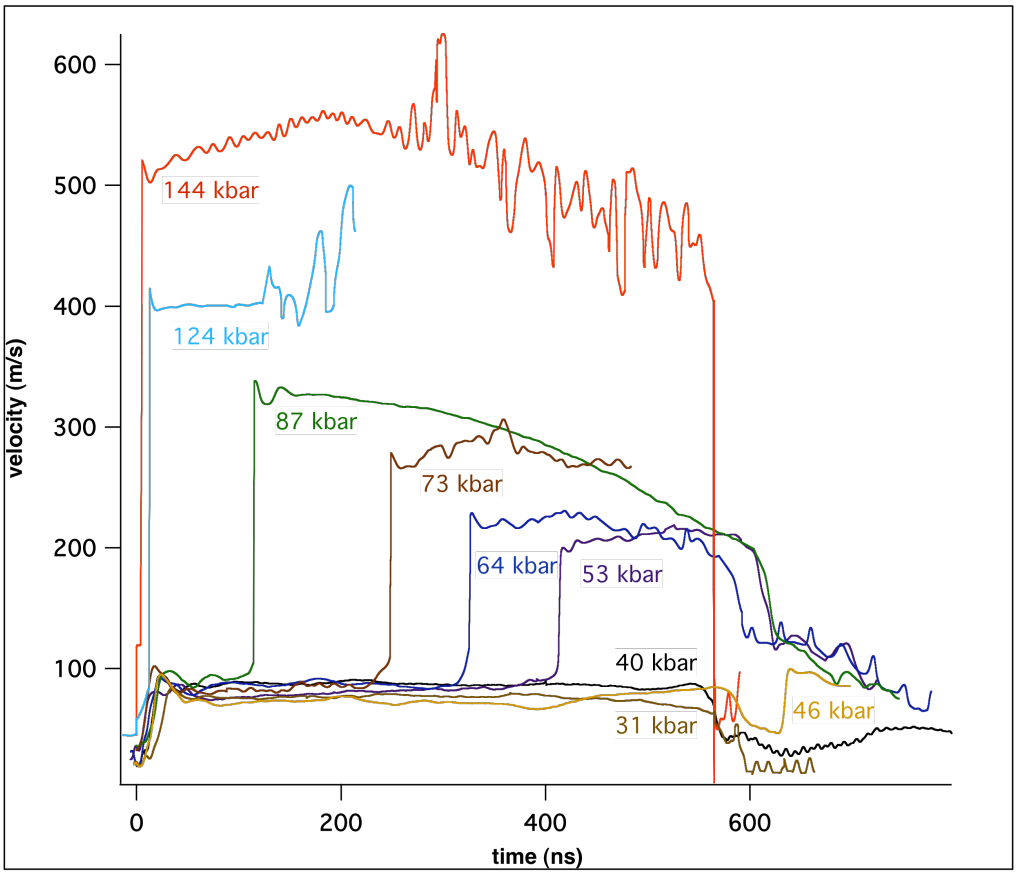

Figure 9: The velocity profiles of shock bismuth at five different pressures.

Summary

The results of this study show that time resolved dynamic experiments provide insight into the general problem of kinetics and hysteresis in phase transitions. This current work showed that the solid-solid phase transitions in Bi under shock loading displays both slow kinetics and fast kinetics depending on the specific phase transition. Under more complex loading that involve multiple crossings of a phase line, strong hysteretic effects were observed in the Bi. Because of the complexity of the hydrodynamic loading in the electrical conductivity experiments, the way the hysteresis occurs in the Bi could not be determined. Our results do show that the behavior of the Bi was strongly dependent on the thermodynamic history. The Bi I-III transition showed a curious kinetically inhibited mass velocity. The associated time lag between initial shock and the second velocity jump is well described by a sigmoid type function that naturally suggest a growth model that is not unlike the growth pattern of a cancer tumor.

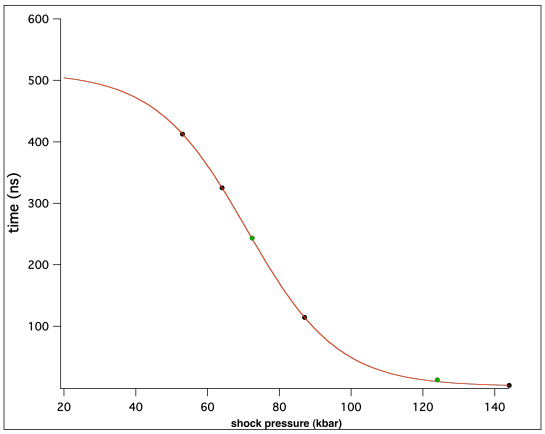

Figure 10: The second velocity jump time as a function of shock pressure. Time is measured from shock arrival. The red line is a fit of the time to a lognormal function.

The general problem of understanding kinetics under dynamic compression is a very daunting problem. This work revealed several key limitations in our approach to the kinetics problem. Our current suite of experimental diagnostics is limited in their ability to provide information on a local scale. In this study, the electrical conductivity and velocimetry measurements provide time-resolved data but no information on the local structure of the Bi. We have no way to determine the exact phase of the Bi or even if the Bi is single phase or in a metastable phase. A phase diagram constructed from the dynamic compression data bears little resemblance to the static phase diagram, which is also not fully understood. New time-resolved diagnostics will be needed, especially structural probes like x-ray diffraction.

In addition to improvements in experimental diagnostics, a new theoretical framework needs to be developed. The problem of kinetics in a dynamic compression experiment is inherently a nonequilibrium thermodynamics problem. Any theoretical framework needs to treat time on the same footing as traditional thermodynamic variables such as pressure and temperature. In particular, the flux of entropy (or a nonequlibrium generalization of entropy) is likely the central parameter that governs the development of any kinetics.