Liquid–liquid phase transition in molten cerium during shock release

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ABSTRACT
The identification of the liquid–liquid phase transition (LLPT) in liquids under shock compression is a long-standing challenge. In this Letter, by designing shock-release experiments in shock-driven molten Ce, we observe a first-order LLPT along the release path. The volume change associated with the transition is less than 6%, much smaller than the one (14%) obtained in static compression experiments, indicating that the LLPT in molten Ce is strongly rate dependent. The identified timescale for the LLPT is on the order of 200 ns. Our results, therefore, provide kinetic information of the LLPT in an unprecedented manner, which is extremely valuable for the construction of a non-equilibrium phase diagram.

Understanding the structural change and related physical properties of liquids under dynamic compression has been a long-standing challenge in materials science. However, it has been widely recognized that the liquid–liquid phase transition (LLPT) occurs in materials with the melting curve of a negative slope, such as water and silicon, where the molten state has a higher density than the corresponding solid phase at the same pressure. However, LLPT has rarely been observed in shocked liquids in part limited by rapidly evolving extreme conditions under shock compression (high temperature, high pressure, and high strain rate) or deep supercooling. So far, no diagnostic method has been well developed to characterize the structural change in liquid or molten states in such extreme conditions although great effort has been devoted to this topic.

Cerium (Ce), as an f-electron occupying metal, exhibits a complex phase diagram at high pressure and high temperature, in which the well-known isostructural phase transition in solids (that is, γ–α phase transition) with a density difference of 17% has been extensively studied in the last few decades by either static or dynamic compression experiments. The proposed LLPT on the extrapolation line of the isostructural phase boundary above the melting curve, however, remains elusive although a few works argued the presence of this transition. Based on the Mott transition model, ab initio calculations suggest that the pressure-induced delocalization of f electrons plays an important role in such a transition. By measuring the equation of state (EoS) of liquid Ce at 1100 K using x-ray radiography, Lipp et al. observed an inflection point at 3.5 GPa, thus suggesting a transition with the volume collapse of 14% in liquid Ce, similar to the γ–α phase transition. But the evidence of LLPT is not convincing, and the kinetics of LLPT has been unexplored yet.

Inspired by the steep liquid–liquid phase boundary proposed in Ref. 19, in this work, we design shock-wave experiments to study the kinetics of the LLPT in molten Ce, in which the isentropic release from a shock-induced melted state crosses over the liquid–liquid boundary, resulting in the transition from the high-density liquid (HDL) into the low-density liquid (LDL). Such a transition is well characterized by the observed abrupt change in the bulk sound velocity along the release path. The transition rate and density change associated with LLPT have also been determined. The experimental findings, thus, provide insight into the transformation kinetics of liquids under shock compression.

Shock-wave experiments employ a direct reverse-impact configuration, as schematically shown in Fig. 1(a), in which a polyurethane
foam backed up Ce flyer is launched by a two-stage gas gun to impact the 12-mm-thick LiF[100] window covered by a 10 μm Al film on the front surface. The impact-induced shock wave compresses the Ce flyer into molten states and then, upon arriving at the flyer/foam interface, reflects a rarefaction wave to isentropically unload the shocked state. Figure 1(b) presents the wave propagation in the Lagrangian diagram. The Ce flyer, which is also the sample studied here, is made of high-purity Ce (99.9%, Alfa Aesar) with an initial density of 6.743 ± 0.015 g/cm³. Both the Ce flyer and the LiF window are finely polished to have the 3–5 μm depth of parallelism. In each shot, the impact velocity is measured using a magnetic-induced diagnostic system with an uncertainty of 1%. 1550 nm Doppler pin system (DPS) interferometry with the frequency-conversion technique has been used to catch every detail in the particle velocity profile at the Ce/LiF interface.

Two shots of direct reverse-impact experiments have been carried out with experimental parameters listed in Table I. Figure 1(c) shows the obtained particle velocity profiles corrected with the index of refraction of LiF. The Hugoniot state of the Ce flyer, given in Table I, is determined by the impedance matching method with the known Hugoniot parameters of Ni. Using the particle velocity profile, together with the sample thickness, the sound velocity in the Hugoniot state is calculated by

\[ C^L = \frac{d}{\Delta t_2 - \Delta t_1}, \]  

where \( d \) is the flyer thickness, \( \Delta t_2 = t_2 - t_0 \), and \( \Delta t_1 = t_1 - t_0 \). As shown in Fig. 1(b), \( t_0 \) is the impact time and \( t_1 \) and \( t_2 \) are the arrival time of the shock wave at the foam/flyer interface and the followed rarefaction wave at the flyer/window interface, respectively. Since the Hugoniot pressure is over 20 GPa, Ce has been driven into an utterly molten state, as shown in Fig. 2. It is also supported by the absence of the elastic–plastic transition during the release [see Fig. 1(c)]. The sound velocity obtained, therefore, is the bulk one. Along the release path, we notice a significant feature that an abnormal S-shaped wave structure shows up in particle velocity profiles marked by arrows in Fig. 1(c), which has not been observed yet in other metals during unloading. We suspect that it may be related to the large volume change associated with LLPT in Ce. To better understand the mechanism responsible for such an abnormality, we quantitatively calculate the Lagrangian sound velocity along the release path from the measured particle velocity profile by the

**TABLE I.** Experimental parameters and the Hugoniot state of Ce under shock compression. \( d \), sample thickness; \( w \), impact velocity; \( P_H \), shock pressure; \( U_p \), particle velocity; \( U_s \), shock velocity; \( C^L \), the Lagrangian bulk sound velocity; \( \rho \), density; \( T_H \), shock temperature. The initial density of the Ce flyer is 6.743 g/cm³. The shock temperatures were taken from Ref. 27.

<table>
<thead>
<tr>
<th>Shot no.</th>
<th>( d ) (mm)</th>
<th>( w ) (km/s)</th>
<th>( P_H ) (GPa)</th>
<th>( U_p ) (km/s)</th>
<th>( U_s ) (km/s)</th>
<th>( C^L ) (km/s)</th>
<th>( \rho ) (g/cm³)</th>
<th>( T_H ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>1.605</td>
<td>2.395</td>
<td>23.12</td>
<td>1.122</td>
<td>3.048</td>
<td>5.883</td>
<td>10.671</td>
<td>1570</td>
</tr>
<tr>
<td>02</td>
<td>1.430</td>
<td>2.499</td>
<td>24.59</td>
<td>1.163</td>
<td>3.133</td>
<td>5.961</td>
<td>10.729</td>
<td>1690</td>
</tr>
</tbody>
</table>
incremental impedance matching between the sample (i.e., the flyer) and the window.\textsuperscript{30,31} For each increment of the sample/window interfacial velocity, the increment of \textit{in situ} particle velocity in the sample is calculated by

\[ D_{up} = \frac{Z_s(t) + Z_w(t)}{2Z_s(t)} \Delta u_p, \]  \hspace{1cm} (2)

where \( Z = \rho_0 C^l \) refers to the impedances at each increment and the subscripts \( s \) and \( w \) represent the sample and the window, respectively. The sound velocity in each release state is determined by

\[ C(t) = \frac{d}{\Delta t} \text{up} - \Delta t, \]  \hspace{1cm} (3)

With \( \Delta t(\text{up}) = t - t_0 \), the increment of pressure and volume in each release state can also be calculated by\textsuperscript{29}

\[ \Delta P = \rho_0 C^l(\text{up}) \Delta u_p, \] \hspace{1cm} (4a)

\[ \Delta V = -V_0 \frac{\Delta u_p}{C^l(\text{up})}, \] \hspace{1cm} (5a)

where \( \Delta P \) and \( \Delta V \) are the pressure and corresponding volume increment at each step and \( V_0 = 1/\rho_0 \). A continuous pressure–density \((P–\rho)\) relation that quantifies the release path is, thus, given by

\[ P = P_i + \rho_0 \left( C^l(\text{up}) \right) \text{d}u_p, \] \hspace{1cm} (4b)

\[ V = V_i - \rho_0 \left( \frac{\text{d}u_p}{C^l(\text{up})} \right), \] \hspace{1cm} (5b)

Here, \( P_i \) and \( V_i \) are the initial pressure and specific volume, respectively.

Figure 3 shows the calculated Lagrangian sound velocity as a function of the particle velocity or shock pressure (in the inset) in Ce, in which an obvious kink exists in each curve. In principle, materials with a single phase exhibit a monotonic decrease in the Lagrangian sound velocity with the decreasing particle velocity.\textsuperscript{33,34} The kink observed, thus, suggests a possible phase transition. Here, we can safely exclude the unloading-induced resolidification of the molten state because it would result in a jump in sound velocity, corresponding to the transition from bulk to longitudinal sound velocities.\textsuperscript{17,27,29} Since the release path passes only through the liquid region, the abrupt change in bulk sound velocity corresponds to the change in bulk modulus, which is usually associated with the transition of a nonnegligible volume change. The transition pressures are 5.8 GPa at the shock pressure of 23.12 GPa and 8.0 GPa at the shock pressure of 24.59 GPa. Except for the transition pressure, one can further quantify the volume change associated with the LLPT by calculating the EoS using Eqs. (4) and (5). However, we have to note that the EoS of each phase should be separately integrated from different starting points because of the different \( P_i \) and \( V_i \) values for two different phases. In the case of the HDL phase, the release starts from the Hugoniot state, that is, \( P_i = P_H \) and \( V_i = V_H \). Figure 4 shows the obtained \( P–\rho \) curve of the HDL phase. The second-order Birch–Murnaghan equation was used to fit the curve to deduce the zero-pressure density of the HDL phase. The obtained values, 7.01 and 6.93 g/cm\(^3\), for two shots are much larger than the high-temperature density data of liquid Ce at zero pressure,\textsuperscript{35–37} further indicating that the LLPT accompanies a large volume change and is a first-order transition.
In the case of the LDL phase, identifying its \( T_m \) and \( V_l \) along the release path is the key to calculate the EoS since the Hugoniot curve does not pass through the LDL region unless preheating the sample. Considering the reversibility of the isentropic unloading process, it would be feasible to obtain the EoS of the LDL phase by knowing its density at the residual temperature after the shocked Ce releases down to zero pressure.

The residual temperature can be estimated as follows. We extrapolate the Lagrangian sound velocity of the LDL phase to zero pressure to have the zero-pressure Lagrangian sound velocity (see the dashed lines in the inset of Fig. 3) and then convert it to the Euler sound velocity by

\[
C^\text{E} = \frac{\rho_0}{\rho_0^0} C^\text{I},
\]

where \( \rho_0 \) is the initial density and \( \rho_{00} \) is the density at the residual temperature.

It is worth noting that the Euler sound velocity \( (C^\text{E}) \) is the isentropic adiabatic one \( (C^\text{S}) \). The ratio between the isentropic and isothermal sound velocities is

\[
\frac{C^\text{S}}{C^\text{T}} = \frac{C_P}{C_V},
\]

Here, \( C_P \) and \( C_V \) are the heat capacity at constant pressure and constant volume, respectively. In liquid Ce, \( C_P/C_V \approx 1.26 \). The density\(^{16}\) and isothermal sound velocity\(^ {38} \) at the ambient pressure exhibit a linear dependence on temperature as

\[
\rho(T) = a + b(T - T_m),
\]

\[
C_T(T) = c + d(T - T_m),
\]

where \( T_m = 1073 \) K is the melting temperature for Ce. The parameters \( (a, b, c, \) and \( d) \) used in this work are listed in Table II. Using Eqs. \((6)-(9)\), the calculated residual temperatures are \( 1230 \pm 150 \) K and \( 1350 \pm 250 \) K for shot-01 and shot-02, and the corresponding zero-pressure densities are about 6.28 and 6.18 g/cm\(^3\), respectively. Using these values as the starting point of the LDL phase, the \( P-\rho \) relation of the LDL phase, shown as the purple solid line in Fig. 4, was obtained by integrating the \( C^\text{S} \) data of the LDL branch. The purple dashed line is an extrapolation using the second-order Birch–Murnaghan equation. With two EoS segments available, we determined the volume change of \( \sim 6\% \) in two-shot experiments. This first-order LLPT probably results from the band structure change in which f-electrons in Ce are itinerant in the LDL phase and then become localized in the LDL one.\(^ {19,22} \)

For comparison, static compressed data are also shown in Fig. 4, and the volume change determined in these two shots is obviously much smaller than the one \( (14\%) \) observed in static compression experiments.\(^ {23} \) We attribute the difference to the rate dependence of the LLPT. Compared with static compression measurements, dynamic compression experiments can access non-equilibrium processes on the ns–\( \mu \)s timescales. Here, the average strain rate during the release is about \( 6.0(5) \times 10^{12}/\)s, and thus, the timescale for the LLPT is on the order of 200 ns. On this timescale, the volume change associated with the LLPT might be somehow kinetically suppressed, as observed in iron.\(^ {41} \)

In summary, shock-wave experiments have been carried out to study the possible LLPT in shock-driven molten Ce. An abrupt change observed in Lagrangian sound velocities along the release path suggests the presence of the LLPT. By constructing the equations of state of two liquid phases from sound velocity data, the volume change and the timescale associated with the LLPT have been well determined, which were inaccessible in previous shock-wave measurements. The density difference between two liquid phases is less than \( 6\% \), much smaller than the reported one in static compression experiments, indicating that the LLPT in molten Ce is rate sensitive. Our results, therefore, provide insight into the kinetics of phase transformations in liquids under shock compression and are extremely valuable for the construction of a non-equilibrium phase diagram.

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### Table II. Density and isothermal sound velocity of liquid Ce at melting point and its temperature coefficients.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>g/cm(^3)</td>
<td>6.41</td>
<td>(^ {37} )</td>
</tr>
<tr>
<td>( b )</td>
<td>g/cm(^3)/K</td>
<td>-8.31</td>
<td>(^ {37} )</td>
</tr>
<tr>
<td>( c )</td>
<td>km/s</td>
<td>1.60</td>
<td>(^ {39} )</td>
</tr>
<tr>
<td>( d )</td>
<td>km/s/K</td>
<td>3.25</td>
<td>(^ {39,40} )</td>
</tr>
</tbody>
</table>

\(^ {a} \) Ce shows a positive temperature coefficient below \( \sim 2800 \) K. The temperature coefficients are \( 2.0 \times 10^{-6} \) km/s K in the range of \( T_m \sim 2800 \) K and \( 3.25 \times 10^{-6} \) km/s K in the range of \( T_m \sim 1500 \) K.
DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES