Real-Time X-Ray Diffraction Measurements of the Phase Transition in KCl Shocked along [100]

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X-ray diffraction measurements and analyses were developed and used to examine the phase transition in KCl shocked to 7 GPa. Diffraction data were obtained below and above the transition stress, and related quantitatively to macroscopic compression in the two phases. Interplanar spacing measurements revealed isotropic compression of the unit cell. Above the transition stress, a diffraction peak from the (110) planes in phase II was observed consistently and the orientation of the transformed crystal structure was determined with respect to the phase I structure. This determination provides a mechanism for the atomic rearrangement from the rocksalt to the cesium chloride structure in KCl shocked along [100].

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A good understanding of the atomistic mechanisms governing shock wave induced phase transformations is a long-standing, scientific challenge [1]. Real time, quantitative, x-ray diffraction data in conjunction with continuum measurements and analyses are needed to determine the transformation mechanisms, and to provide a detailed comparison between shock wave and static pressure results. Because of various experimental limitations, earlier attempts [2–10] to obtain x-ray diffraction in shocked solids are of limited value particularly for quantitative measurements. Recently, we have developed experimental methods [11,12] to overcome these limitations and obtained quantitative data in well characterized, laboratory plate impact experiments. The present work was motivated by the following objective: to determine if these recent developments could be extended to examine atomic rearrangements accompanying shock induced phase changes. Because of significant volume changes and shear deformations associated with shock induced phase transformations, it is not clear that single crystal diffraction data can be obtained on ns time scales from a transformed phase. Also, it is difficult to set up an experimental system to detect a phase which does not exist at ambient conditions.

Potassium chloride (KCl) was chosen for this first study because of the considerable information available from static pressure [13–16] and shock compression [17–19] experiments. Overall, the final P-V values above 3 GPa are in good agreement between the two sets of experiments. Continuum shock wave studies by Hayes [18,19] have demonstrated a strong dependence of the transition kinetics on crystal orientation, and provided a complete equation of state (EOS) which was valuable for our work. Our objectives were to obtain x-ray diffraction data in phase I and phase II, relate these data to continuum results, and determine the atomic rearrangement associated with this transition.

Figure 1 shows the overall experimental configuration. The KCl sample, placed between a buffer (quartz or copper) and a vitreous carbon (VC) x-ray window is impacted by a flyer plate mounted on a projectile accelerated to the desired velocity in a powder gun [12]. The shock wave response of VC [20] is well matched to the KCl phase I response. Hence, wave reflection at the KCl/VC interface is minimal. A 50–70 ns pulse of slightly divergent (500 μm slit), $K\alpha$ x-rays, produced from a 300 kV x-ray tube (Hewlett Packard), is incident on the sample; either a copper anode ($\lambda = 1.54$ Å) or a molybdenum anode ($\lambda = 0.71$ Å) was used. The diffracted signal is recorded using a charge-coupled device detector (Princeton Instruments). Diffraction from planes perpendicular to the shock direction was obtained by satisfying the Bragg condition,

$$\lambda = 2d\sin\theta\,, \tag{1}$$

where λ is the wavelength, d is the interplanar spacing and θ is the Bragg angle. Further details regarding the experimental method are presented elsewhere [12]. In all experiments, a diffraction peak recorded just prior to impacting the crystal served as a reference. All data were obtained on [100] oriented KCl samples (Crystal Growth Laboratory, University of Utah).

The diffraction angle in the shocked state (phase I or II) is obtained from the continuum results using the following procedure. First, the volume change, $\Delta V = V_0 - V$, is obtained from Hayes' work [18,19]; V_0 (0.503 cm^3 g^{-1})

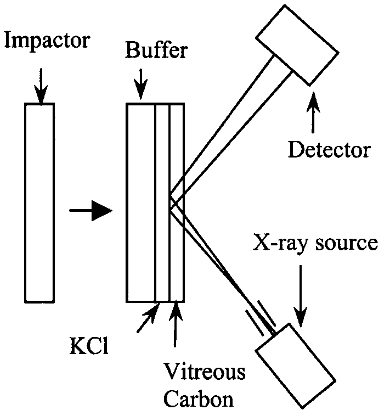

FIG. 1. Experimental arrangement used for x-ray diffraction measurements in shocked KCl.

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is the specific volume at ambient conditions, and V is the specific volume in the shocked state. Next, $\Delta V/V_0$ is used to obtain the lattice parameter, b, in the shocked state. For the NaCl structure below the transition stress (eight atoms or four molecules per unit cell),

$$b = a[1 - (\Delta V/V_0)]^{1/3}, \tag{2}$$

and for the CsCl structure above the transition stress (two atoms or one molecule per unit cell),

$$b = a[0.25(1 - \Delta V/V_0)]^{1/3}, \tag{3}$$

where a (6.2929 Å) is the lattice parameter for KCl under ambient conditions. Equations (2) and (3), as explained later, are written for an isotropic compression of the unit cell [11]. Knowing b, interplanar spacing for the planes of interest is calculated and used in Eq. (1) to determine the Bragg angle, θ. Prediction of θ from continuum results is simplified if the probed depth is uniformly compressed as discussed next.

Schematic views of the KCl compression curve and the corresponding stress-distance profiles are shown in Fig. 2. Below the transition stress of 2.1 GPa, denoted by B, the sample is traversed by a single wave [21]. Above 2.1 GPa, the shock wave is unstable [19] and a two wave structure develops: wave amplitudes, P_1 and P_2, correspond to points B and D, respectively, in the compression curve. Despite the phase change, compression to point E and above results in a single or overdriven wave. Using Hayes' EOS and wave propagation calculations [18,19,22], sample thicknesses and wave amplitudes were chosen appropriately to ensure that, at the time of the peak x-ray intensity, the probed depth is in a state of uniform compression. The good impedance match of VC [20] and KCl phase I was particularly beneficial for experimental design.

A total of six experiments were performed in this study. Three experiments were performed in phase I for peak stresses ranging from 1.4 to 2 GPa. Figure 3 shows typical diffraction data, corresponding to the (200) planes, below the transition stress. The solid curves, representing Gaussian fits to the data, were used to determine the peak shifts. Results from the three experiments are summarized in Table I. Stress and density compression ($V_0/V - 1$) values in Table I were calculated using Hayes' EOS [18,19,22]. Predicted positions of the (200) peaks indicated in Table I are discussed next.

As shown by Rigg and Gupta [11], density compression or macroscopic strain can be related to interplanar spacing changes by considering two extreme (or bounding) cases for unit cell compression: uniaxial compression along the shock propagation direction or isotropic compression. Further details regarding these calculations can be seen elsewhere [11,23]. A comparison of the measured interplanar spacing changes and the two bounding calculations for phase I is shown in Fig. 4. The results clearly indicate that the unit cell compression is isotropic and contradict earlier inferences of uniaxial compression [8]. The predictions shown in Table I are based on an isotropic compression of the unit cell and were calculated using the procedure described earlier; see Eq. (2).

Unlike phase I, determination of θ for phase II is not straightforward because no description of the atomic rearrangements exists *a priori* for shock compression along [100]. Hence, results from continuum calculations need to be combined with various crystallographic considerations to come up with the diffraction peaks likely to be observed in phase II. After considering different possibilities [24], we concluded that diffraction peaks from the (110) planes in the CsCl structure (the shock direction would be normal to these planes) were most likely to be observed. Also, to avoid complications arising from the two wave structure, we first chose to do an experiment at 6.9 GPa. This value corresponds to the overdriven state in Fig. 2. Later, experiments were also performed at 3 and 5 GPa.

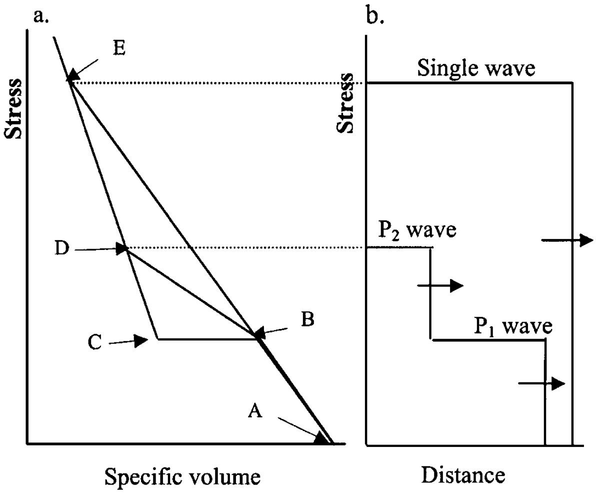

FIG. 2. Schematic representation of (a) compression curve for KCl and (b) stress-distance profiles.

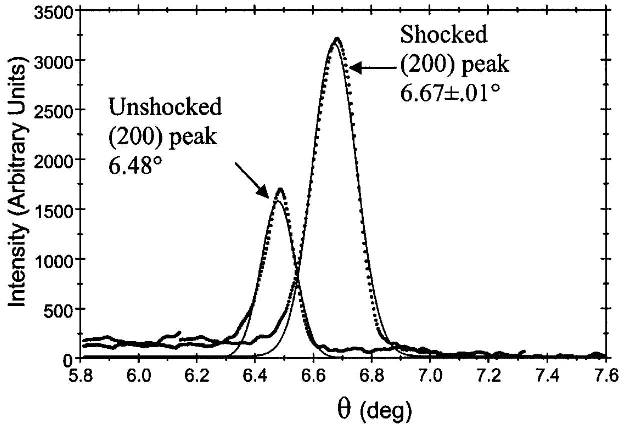

FIG. 3. Diffraction data from a typical experiment on KCl [100] in phase I (2 GPa at the KCl/VC interface). Intensity of the shocked peak was higher because the x-ray tube was positioned closer to the angle expected for the shocked state.

TABLE I. Summary of experiments.

Experiment No.	Impactor material and velocity (mm μs^{-1})	Stress at KCl/VC interface[c] (GPa)	Density compression[d] (percent)	Predicted (200) peak (degrees)	Predicted (110) peak (degrees)	Measurements θ (degree)
1 (98-736)[a]	Al, 0.328	1.40	6.9	14.49	⋯	14.48 ± 0.01
2 (98-726)[a]	Al, 0.332	1.52	7.2	14.50	⋯	14.47 ± 0.01
3 (99-317)[b]	Al, 0.703	2	9.6	6.68	⋯	6.67 ± 0.01
4 (99-324)[b]	Al, 0.702	3.02	25.8	⋯	7.86	7.84 ± 0.02
5 (99-323)[b]	Cu, 0.920	5.03	32.3	⋯	7.99	8.01 ± 0.02
6 (99-318)[b]	Cu, 1.22	6.93	36.9	⋯	8.12	8.14 ± 0.03

[a] Cu $K\alpha$ x rays.
[b] Mo $K\alpha$ x rays.
[c] Stress values at the peak of x-ray output.
[d] Defined as $(V_0/V) - 1$.

Figure 5 shows the diffraction data for the 6.9 GPa experiment. Similar data showing the diffraction peak corresponding to phase II were also obtained at lower stresses (5 and 3 GPa). In all experiments, the diffraction peak observed in the transformed state corresponded to the (110) peak. The shoulder on the right side of the main peak, not observed at lower stresses, is not understood at the present time. Results from the three experiments performed in the second phase are also summarized in Table I. Measured location of the (110) peak for each experiment was in good agreement with the predictions [25] using Eq. (3). These results show that compression in phase II can be monitored through changes in the (110) interplanar spacing. The consistent observation of the (110) peak in phase II is an important result because it relates the orientation of the transformed crystal to the shock direction. When shocked along the [100] direction, the phase change results in the (100) planes of the initial structure being changed to the (110) planes of the CsCl structure. We carried out two experiments to determine if the (100) and (111) planes in the CsCl structure were normal to the shock direction. But, as expected, no diffraction signal was observed in the shocked state.

Based on the relationship between the orientation of the two crystal structures, we provide a description of the atomic rearrangement accompanying the transition. In the initial structure, shown in Fig. 6(a), the first (100) layer can be viewed as squares of side $a/\sqrt{2}$ with K atoms at the corners (labeled 1, 2, 3, 4) and Cl atoms in the middle. The next layer at a distance $d = a/2$ behind the first layer is not visible in this view but consists of Cl atoms at the corners (labeled 1′, 2′, 3′, 4′) and K atoms in the middle. In the final structure shown in Fig. 6(b), the front (110) planes can be viewed as rectangles ($\sqrt{2}b \times b$) with K atoms in the corners and Cl atoms in the middle; the first layer atoms are connected by darker colored bonds. The next layer at a distance $d = b/\sqrt{2}$ behind the first layer is visible in this structure and has Cl atoms at the corners of the rectangle (labeled 1′, 2′, 3′, 4′) and K atoms in the middle. Thus, the second layer in the final structure corresponds to the second layer in the initial structure being shifted along the [110] direction of phase I by a distance $a/2\sqrt{2}$. Hence, the transformation in KCl, shocked along

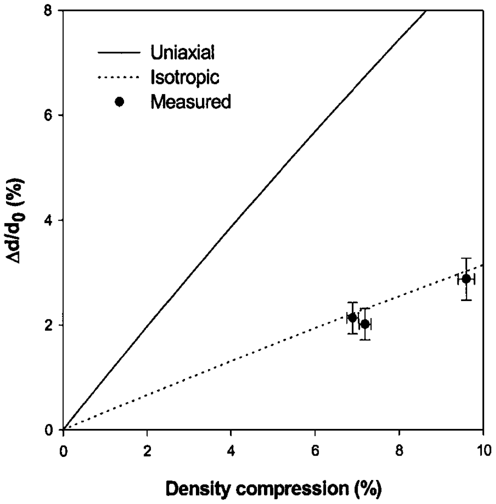

FIG. 4. Change in interplanar spacing versus density compression $(V_0/V - 1)$ in phase I. Predictions based on uniaxial and isotropic compression of the unit cell are shown.

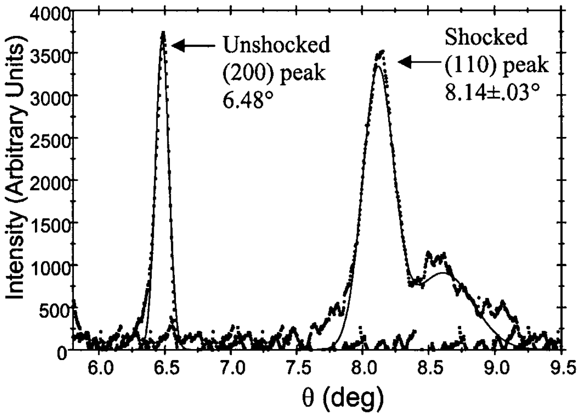

FIG. 5. Diffraction data showing the phase transition in KCl shock compressed along [100] to 6.9 GPa. Solid curves are Gaussian fits to the data.

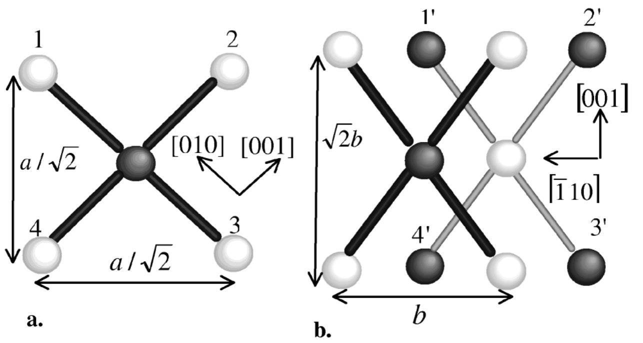

FIG. 6. Atomic arrangements as viewed along the direction of shock propagation. Potassium atoms are shown in light color and chlorine atoms are shown in dark color. (a) Front (100) plane of the NaCl structure along with the [100] axes. (b) First and second (110) planes of the CsCl structure. Atoms in the first plane are linked by darker colored bonds.

[100], can be understood as a combination of compression along [100] directions and shift of the alternate (200) planes of the rocksalt structure along the [110] direction.

The results presented here contradict earlier inferences regarding the shock wave induced phase transition in KCl [8,9]. Earlier inferences that unit cell compression below the transition is uniaxial are incorrect as shown by our results in Fig. 4. Use of incorrect wave speed for the second wave in Ref. [8] resulted in wave separations much larger than anticipated, and the x-ray data were obtained before arrival of the second wave in the probed region [26].

In conclusion, we have obtained real-time x-ray diffraction data from shock compressed KCl below and above the phase transition stress. These data were related quantitatively to macroscopic compression in phase I and phase II. The orientation of the transformed crystal structure with respect to the phase I structure was determined from the x-ray data. Because of this determination, we have provided a mechanism for the atomic rearrangement for the NaCl → CsCl transformation in KCl shocked along the [100] direction. Similar studies are under way for shock compression along the [111] direction.

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[24] M. C. Gupta, G. E. Duvall, and Y. M. Gupta (unpublished); this preliminary work carried out in 1973 utilized simple geometrical models to examine how (100) planes in the NaCl structure may be converted to (100), (110), and (111) planes in the CsCl structure.

[25] Similar to the results for phase I in Fig. 4, both uniaxial and isotropic compressions of phase II unit cell were considered. The data matched only the isotropic compression case denoted by Eq. (3).

[26] We have had extensive interactions with Professor Zaretskii, senior author of Ref. [8], who agrees with our conclusions regarding their work.