Real-Time Observation of a Metastable State during the Phase Transition in Shocked Cadmium Sulfide

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A method was developed to perform ps time-resolved electronic spectroscopy in shock wave experiments, and used to examine the initial stages of the phase transition in CdS. Changes in the electronic spectra were observed with 100 ps resolution in single crystals shocked to stresses between 3.6–8.8 GPa. The absorption results suggest that the initial stage of the transition is characterized by a very rapid transformation to an indirect band gap material. Along with earlier ns continuum data, these results make a strong case for a metastable state during the phase transition in shocked CdS. [S0031-9007(98)07264-0]

The ability to obtain real-time information, with sub-nanosecond resolution, at the atomic/molecular level, is an important need for understanding the mechanisms governing shock-induced structural and chemical changes. Time-resolved continuum measurements, such as stress and particle velocity histories, have provided the thermodynamic states and kinetics associated with these phenomena [1–5]. However, other types of experimental data such as electronic spectroscopy are needed to examine the changes at the atomic/molecular level. In particular, the dependence of the absorption edge on photon energy can distinguish between direct and indirect transitions, and provide an estimate of the band gap energy of a material [6]. This information can be related to the crystal structure. Hence, picosecond time-resolved electronic spectra in plate impact experiments can permit real-time examination of structural and chemical changes in materials subjected to very well defined deformation conditions. In this Letter we report the development of a method to obtain picosecond time-resolved electronic spectra in plate impact experiments, and the use of this method to examine the initial stages of the shock-induced phase transition in cadmium sulfide (CdS) single crystals. To the best of our knowledge, these are the fastest time-resolved optical spectroscopy measurements performed in single-event, plate impact experiments.

The pressure-induced wurtzite to rock salt phase transition in CdS, occurring at about 3 GPa, has been examined under both static high pressure [7–14] and shock compression [2–5]. Although considerable information concerning this transition has been obtained in various static high pressure studies, questions regarding time-dependent mechanisms cannot be addressed through such studies. The time and orientation dependence of the transformation was examined through time-resolved, continuum measurements by Tang and Gupta [4], and Sharma and Gupta [5]. Their findings suggest that the transformation proceeds by a two-step process. However, the time resolution (10—15 ns) in their work could not resolve the initial stages of the transformation.

Because of the significant difference in the electronic structure of the two phases, the phase transition in CdS is well suited for examination using fast electronic spectroscopy; the wurtzite and rock salt phases exhibit a direct and indirect band gap with band gap energies of 2.5 and 1.5–1.7 eV [7,12–14], respectively. Absorption/transmission measurements between 500 and 800 nm probe only the shocked material; thus, electronic spectroscopy with 100 ps time resolution permits examination of the initial stages of the transition and the electronic structure of the crystal directly behind the shock front.

The present method to obtain picosecond time-resolved absorption/transmission measurements builds upon previous work used to obtain nanosecond time-resolved measurements [15,16]. However, due to the faster time resolution and the considerably shorter duration of these experiments, several issues not relevant on the nanosecond time scale become important at the picosecond time scale. In particular, considerable effort went into addressing the experimental challenges associated with the synchronization of the light source, the detection equipment, and the arrival of the shock wave at the sample within the 12.7 ns time window of these experiments. Details of the experimental developments will be presented in a future publication.

Figure 1 shows a schematic view of the experimental configuration. Shock waves were generated by the impact of an optically transparent impactor (sapphire, α-quartz, or fused silica), mounted on a projectile accelerated by a light gas gun [17], on the sample assembly. The latter consisted of two optically transparent buffer windows (sapphire or α-quartz) backed by a single crystal CdS sample. Three piezoelectric trigger pins (Dynasen, Inc., CA-1135), located concentrically around the probed region of the sample, were placed behind the front buffer window to provide both a trigger pulse and a fiducial for the arrival of the shock wave at the interface between the buffers. The second buffer window provided a traversal delay to offset the insertion delays of the experimental components,
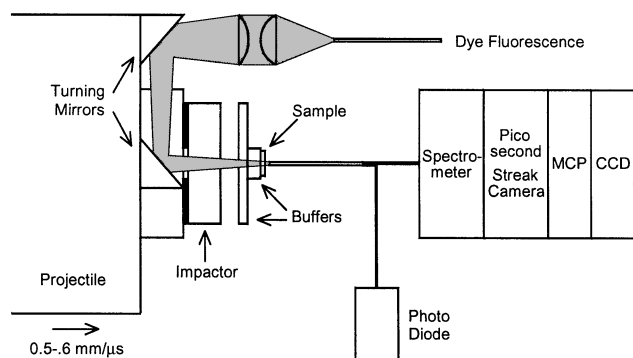
FIG. 1.　The experimental configuration used to obtain time-resolved, picosecond absorption/transmission measurements in plate impact shock wave experiments.

FIG. 2.　Results from the fast photodiode showing the integrated intensity of transmitted light through the sample in an experiment on the c axis, CdS shocked to 8.8 GPa. The reproducibility of the reference pulse is on the order of 5%.

enabling synchronization of the light source, detection equipment, and the arrival of the shock wave at the CdS sample.

Fluorescence from a Nd:YAG (continuum, custom built laser) pumped dye solution, consisting of a mixture of Coumarine 500 and DCM laser dyes, was used as the light source for the experiment. The 12 ns FWHM fluorescence pulse covered the wavelength spectrum between 500 and 700 nm. Two flat mirrors, located on the projectile, directed the light through the sample into an optical fiber bundle, consisting of two fibers. This arrangement provided single pass, absorption/transmission through the sample. One fiber directed the signal to a fast photodiode (Thorlabs, Inc., DET2-SI), which was used as a timing diagnostic. The second fiber delivered the transmitted signal to the picosecond detection system. The signal was spectrally dispersed by a spectrometer (SPEX 500M, 150 grooves/mm grating). The output of the spectrometer was then incident on a fast streak camera (Hadland Photonics, Imacon 500), which provided temporal dispersion. The streak camera output (intensity versus wavelength versus time) was intensified with a microchannel plate (MCP) image intensifier (Photek, MCP140), and digitally recorded on a charge-coupled device (CCD) detector (Princeton Instruments, LN/CCD-1024 TKB/1). The CCD image was binned along the time axis into 127 spectra, each separated in time by 100 ps.

Experiments were performed on CdS single crystals shocked along both the crystal a and c axes. Stresses in these experiments were determined from the known shock response of the various materials [4,5,18] and the measured projectile velocity; the values ranged from 3.6 to 8.8 GPa. Figure 2 shows the photodiode results for a c-axis crystal shocked to a stress of 8.8 GPa, well above the phase transition threshold stress of 3.3 GPa reported by Tang and Gupta [4]. In this figure, the integrated intensity of light transmitted through the sample is displayed for both the shock experiment and a reference pulse taken just prior to the shock experiment. The arrival of the shock front at the CdS sample, determined from the trigger pin
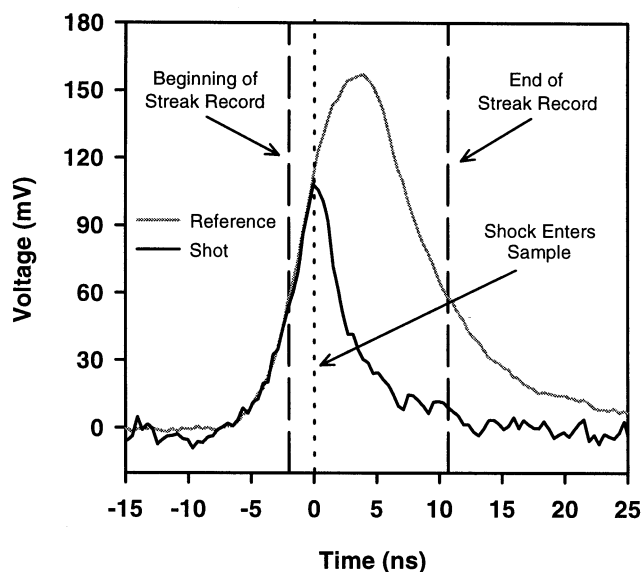
records and the calculated traversal time through the second buffer window (uncertainty of approximately ± 1 ns), is indicated in the figure by a dotted line. Immediately following the arrival of the shock front, there occurred a dramatic decrease in transmission. Also indicated in the figure, by dashed lines, are the beginning and the end of the streak record for this particular experiment. This figure illustrates the synchronization needs due to the very-short time duration of the streak record and the light pulse.

Time-resolved, spectral information was obtained from the picosecond detection system. The top half of Fig. 3 displays the results as a plot of absorbance versus wavelength and time. Absorbance values were determined by comparing the intensities of the streak record obtained during the shock experiment with a reference streak using the expression

$$\text{Absorbance} = -\ln(I/I_0),$$

where I and I_0 are the intensities obtained from the shock experiment and the reference streak, respectively. In accordance with the photodiode results, once the shock front reached the CdS sample, indicated by $t = 0$ in the streak record, the absorbance increased dramatically. The time dependence of the absorbance behind the shock front can be seen more easily in the bottom half of Fig. 3, which displays absorbance versus time for several different wavelengths. It was found that the absorbance at a given wavelength increases linearly with time, with a slope which increases with decreasing wavelength. The linear increase in absorbance with time reflects the propagation of the shock front through the sample; as the shock front propagates through the CdS sample, more
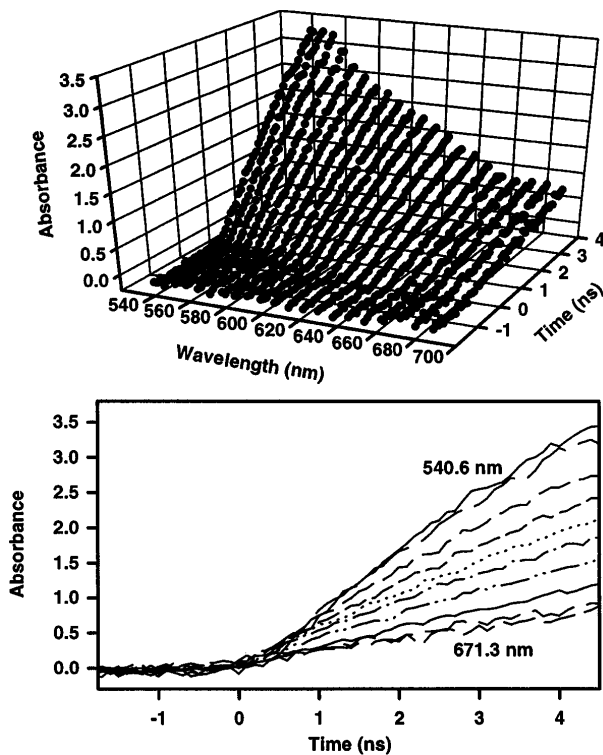
FIG. 3. Results from the picosecond detection system for an experiment on the c axis, CdS shocked to 8.8 GPa.

FIG. 4. Absorption coefficient as a function of wavelength and photon energy for an experiment on the c axis, CdS shocked to 8.8 GPa.

material is subject to uniaxial strain. Thus the linear time dependence suggests that behind the shock front the absorption coefficient, though wavelength dependent, is time independent, at least for this experiment.

Using a value of 4.3 mm/μs for the shock velocity through the CdS sample [4], the slope of the absorbance increase was used to determine the absorption coefficient for the material behind the shock front [19]. The resulting absorption coefficient as a function of wavelength is shown in the top half of Fig. 4. Also plotted in the bottom half of Fig. 4 is the square root of the absorption coefficient versus photon energy. The linearity of the data in the lower figure suggests that the observed absorption in the material behind the shock front is due to an indirect band gap [6]. Extrapolation of the curve to $\alpha = 0$ provides an estimate of 1.52 ± 0.03 eV for the band gap energy. This value is within the range of values (1.5–1.7 eV) reported in the literature for the band gap energy of the high pressure rock salt phase [7,13,14].

A total of six experiments were performed on both a- and c-axis crystals shocked to stresses above 5.9 GPa. Similar results were obtained for all of these experiments, with measured band gaps ranging from 1.49–1.53 eV (similar uncertainties). Experiments on both crystal orientations were also performed at lower stresses. However, we limit our discussion here to the high stress experiments, and only state that an orientational dependence was observed for changes in the electronic spectra for stresses
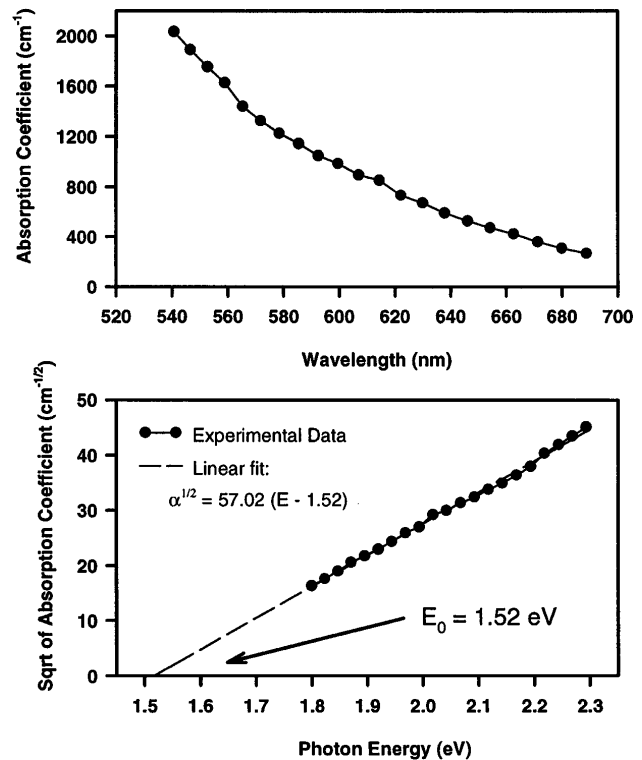
below 5.9 GPa. Further discussion of the low stress experiments will be presented at a future date.

The results of the present experiments provide strong evidence that when shocked to sufficiently high stress, regardless of the orientation along which the crystal is shocked, CdS undergoes a significant change in crystal structure in less than 100 ps. Although the energy gap of the new structure is comparable to that of the rock salt phase of CdS, we do not believe that the material directly behind the shock front has transformed to the final rock salt phase. First, it is unlikely that the transformation to the final rock salt phase can occur in less than 100 ps, considering the large volume change ($\sim$20%) associated with the transition [9,10]. Second, the results of quartz-gauge, stress-time measurements in shocked CdS, performed by Tang and Gupta [4] and Sharma and Gupta [5], show that 100–200 ns is required before an equilibrium stress value, corresponding to the rock salt phase, is reached at the impact surface. Further, the results of their studies suggest that the transformation proceeds by a two-step process; the first step being very rapid (faster than the time resolution of their experiments), followed by a slower (100–200 ns) relaxation to the final rock salt phase. Based upon this evidence, and in accordance with the conclusions of Tang and Gupta [4] and Sharma and Gupta [5], we propose that the state of the material observed behind the shock front in the

present high stress experiments is a metastable structure of CdS. The transformation to this metastable structure is very rapid, occurring in less than 100 ps when shocked to sufficiently high stress.

Although we are unable, at present, to directly determine the structure of the material behind the shock front from the absorption data, some conclusions can be drawn concerning the crystal structure from the experimental results. First, in accordance with the rapid nature of the transition, the transformation mechanism to the metastable structure must proceed through correlated atomic motions, and thus there must be a definite relationship between the metastable and initial wurtzite structures. Second, as is the case in most martensitic-type transformations, the volume of the metastable phase is likely comparable to that of the initial wurtzite phase. Finally, the electronic structure of the metastable state exhibits an indirect band gap with a gap energy comparable to that of the final rock salt phase. Possible intermediate lattice structures for the metastable state, which satisfy the above features, are currently being explored through *ab initio* periodic Hartree-Fock linear combination of atomic-orbitals total energy and electronic structure calculations. The results from this investigation, along with a more detailed discussion of the transformation mechanism, will be presented at a future date.

We note that Sharma and Gupta [5] put forth a mechanism for the first step of the transformation. The proposed mechanism was based upon the rapid nature of the transition, and is characterized by a coupling between a uniaxial strain and a soft phonon mode to bring about a transition from the initial wurtzite structure to a metastable face-centered orthombic (fco) structure. However, with information regarding only the kinetics, the proposed mechanism and metastable fco structure are speculative. The present work provides additional information concerning the electronic structure which can be used to better determine the atomic mechanism governing this phase transition.

In conclusion, we have developed a method to perform picosecond time-resolved electronic spectroscopy in single-event, plate impact shock wave experiments. This method was used to examine the initial stages of the shock-induced phase transition in CdS single crystals with 100 ps time resolution. The results of experiments performed at stresses above 5.9 GPa, along with earlier nanosecond continuum data [4,5], suggest that the initial stage of the shock-induced transition in CdS consists of a very rapid transformation to a metastable state. This metastable state exhibits an indirect band gap (1.52 ± 0.02 eV), similar to that of the final rock salt phase.

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[19] At a given wavelength the absorbance data corresponding to $t > 0$ were fitted to a linear function. The slope was then divided by the shock velocity to obtain the absorption coefficient. The statistical uncertainty in the slope of the absorbance increase, and thus in the absorption coefficient, was on the order of a few percent.