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High-pressure phase transition in CsBr

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Static-compression data have been collected on cesium bromide up to a pressure of 70 GPa ($V/V_0 = 0.500$) with use of x-ray diffraction through the diamond-anvil cell at room temperature. CsBr, which is in the CsCl ($B2$) structure at zero pressure, undergoes a second-order phase transition to the tetragonal CuAu I structure at 53 (± 2) GPa. Only one other alkali halide, CsI, has been shown to undergo a similar distortional transition at high pressures. With the extrapolation of the available data, both halides are expected to achieve the fcc lattice by about 130 GPa. Our new CsBr data are in good agreement with an Eulerian finite-strain equation of state derived from the ultrasonically measured elastic constants.

INTRODUCTION

Complete descriptions of the equations of state of the alkali halides necessitate an understanding of the properties of these compounds in the CsCl ($B2$) structure. Aside from CsCl, CsBr, and CsI, which exhibit this structure at room pressure and temperature, a number of the NaCl- ($B1$-) structure alkali halides transform to the $B2$-structure phase at high pressure.[1–6] Recently, CsI has been shown to undergo a second-order phase transformation to the CuAu I structure at 40 GPa.[7–10] This transition involves a continuous tetragonal distortion of the cubic $B2$ structure.

To determine if transformation beyond the $B2$ structure is characteristic of the cesium halides, we have carried out x-ray diffraction experiments on CsBr to ~70 GPa. Because of the high compressibility of CsBr, these measurements also provide an empirical test of equations of state based on ultrasonically measured elastic constants. Finally, we were able to compare the optical absorption edges of CsBr and CsI at similar compressions, although quantitative absorption spectra were not collected in the present experiments.

EXPERIMENTAL PROCEDURE

Polycrystalline cesium bromide of 99.9% purity (Alpha Ventron Corp.) was used in all the experiments. Samples were compressed in a Mao-Bell-type diamond cell[11] and the ruby fluorescence technique was used to measure the pressure for each run at 4–8 locations within the sample.[12,13] X-ray diffraction patterns were collected on film using a rotating-anode x-ray generator and Mo radiation.

Mineral oil was used as a pressure medium in some but not all runs; however, the degree of sample hydrostaticity was not improved by the pressure medium (details are provided in Table I). Most data were collected using Mo $K\alpha$ radiation only (Table I). Lattice parameters for the $B2$ structure were determined using one to five of the following diffraction lines: (100), (110), (200), (211), and (220). One lattice parameter for the tetragonal high-pressure structure was calculated using the (100) and (110) diffraction lines, and the (200) line when visible. The second lattice parameter was determined from the (101) = (011) line, and the (211) and (112) lines when visible.

RESULTS AND DISCUSSION

The static-compression data for CsBr are plotted in Fig. 1 and listed in Table I. The data are compared with Eulerian and Lagrangian finite-strain equations of state[14–16] extrapolated from ultrasonic values of the elastic constants of CsBr.[17] The Eulerian finite-strain formalism is in good agreement with the CsBr data to a volume compression of 50%. In contrast, the Lagrangian equation of state is considerably softer than the data at compressions beyond 30% of the zero pressure volume. Thus, the present results are in accord with the measurements on a number of materials that demonstrate the success of the Eulerian finite-strain form of equation of state.[7,8,14,16,18–20]

At 53 (± 2) GPa, the diffraction lines of CsBr gradually split, indicating that the $B2$ structure undergoes a phase transition to a CuAu I structure (equivalent to a body-centered tetragonal distortion in a monatomic lattice). The c/a ratios for the high-pressure structure are given in Table I and plotted as a function of pressure in Fig. 2. The gradual increase in c/a ratio and the apparent lack of volume change upon distortion (Fig. 1) indicate that the phase transition is of second order. The only other alkali halide that transforms beyond the $B2$ structure at high pressures is CsI, and it exhibits the identical second-order distortional transition.[7–10]

As noted previously,[8,9] the effect of the tetragonal distortion is to change the lattice towards the fcc type for which $c/a = \sqrt{2}$. Thus, beyond the pressure required for closure of the band gap, the cesium halides are expected to be fcc metals. Although the second-order transition sets in at a higher pressure for CsBr than CsI, the change in the c/a ratio with pressure is somewhat larger in the bromide. Consequently, CsBr is expected to achieve the fcc lattice at 136 (± 6) GPa, which is virtually the same as for CsI (129 ± 5 GPa, Refs. 8 and 9).

The phase transitions occur at different pressures in CsI and CsBr: 39 (± 1) and 53 (± 2) GPa, respectively. The volume compression at the transition, however, is the same: tetragonal distortion is definitely occurring at $V/V_0 = 0.54$ in both cases. Both in the present experiments on CsBr and in previous work on CsI (Refs. 7 and 8) broadening of diffraction lines without splitting could be observed in one run. At this point of incipient tetragonal distortion the observed volume compression is $V/V_0 = 0.546$ (± 0.003) for CsBr

TABLE I. Static compression data for CsBr.

Run number	Pressure (GPa)	V/V_0	c/a	Sample[a]
060584	0.56 (±0.03)	0.969 (±0.002)	1.000	*b*1*m*
100781	4.88 (±0.16)	0.857 (±0.002)	1.000	*a*6*y*
060684	6.18 (±0.21)	0.821 (±0.002)	1.000	*b*1*m*
100381	6.34 (±0.15)	0.830 (±0.003)	1.000	*a*6*y*
100581	11.93 (±0.71)	0.731 (±0.003)	1.000	*a*6*y*
060784	14.34 (±1.88)	0.706 (±0.003)	1.000	*b*1*m*
101281	23.39 (±1.49)	0.664 (±0.002)	1.000	*a*6*y*
101781	30.52 (±1.65)	0.635 (±0.002)	1.000	*a*6*y*
060984	34.46 (±1.23)	0.588 (±0.009)	1.000	*c*1*m*
061184	36.24 (±4.03)	0.581 (±0.005)	1.000	*c*1*m*
092081	42.58 (±3.77)	0.586 (±0.004)	1.000	*a*6*y*
102081	51.35 (±1.59)	0.562 (±0.003)	1.000	*a*6*y*
091581	52.43 (±3.78)	0.553 (±0.005)	1.000	*a*6*y*
061584	52.46 (±3.53)	0.542 (±0.002)	1.000	*c*1*m*
061884	54.84 (±2.49)	0.546 (±0.003)	(1.000)[b]	*c*1*m*
070484	60.75 (±1.79)	0.525 (±0.002)	1.083 (±0.022)	*c*1*m*
071084	61.68 (±2.04)	0.510 (±0.001)	1.095 (±0.011)	*c*1*m*
062984	66.22 (±2.35)	0.505 (±0.001)	1.113 (±0.007)	*c*1*m*
062084	66.33 (±2.97)	0.502 (±0.001)	1.085 (±0.014)	*c*1*m*
062284	69.79 (±2.58)	0.507 (±0.001)	1.136 (±0.004)	*c*1*m*
062584	69.89 (±4.08)	0.500 (±0.001)	1.121 (±0.011)	*c*1*m*

[a] *a*, *b*, and *c* refer to different samples. 1 and 6 label the two diamond cells used. *y* indicates that a pressure medium (mineral oil) was used. *m* indicates that a graphite monochromator was used to provide pure Mo $K\alpha$ radiation ($\lambda_{\bar{\alpha}}=71.073$ pm).

[b] Splitting is marginally observed but cannot be quantitatively resolved—pattern is interpreted as cubic.

and $V/V_0=0.544$ (±0.003) for CsI.

As with the pressures, the optical properties of CsI and CsBr differ at the phase transition. Upon compression, the band gap of CsI decreases from its zero-pressure value of 6.4 to 2.4 eV at the onset of the tetragonal distortion at 40 GPa.[7–9] The band gap of CsBr, which is 7.3 eV at zero pressure, only approaches a value of 2.5 eV at pressures above 70 GPa. As a result, there is a striking difference in the colors of CsI and CsBr at the phase transition: the former is bright orange whereas the latter is a pale yellow in transmitted light (samples are about 10 μm thick in both cases).

Recent lattice dynamical[21] and static-lattice[8] calculations demonstrate that the cubic structure becomes unstable, and a tetragonal distortion sets in, when the first-neighbor repulsive forces dominate sufficiently over the second-neighbor repulsion. Qualitatively, the high-pressure transition observed here is analogous to the well-known dynamical insta-

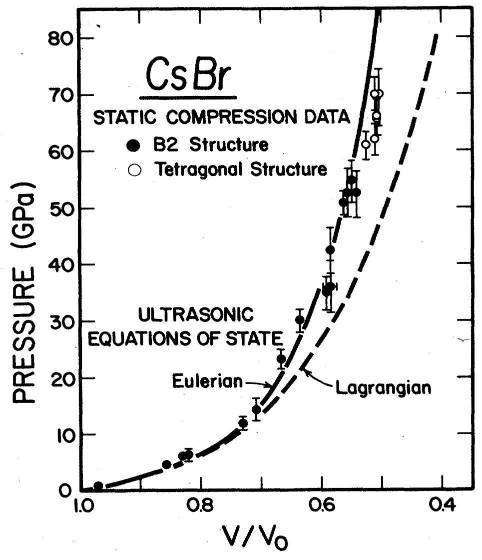

FIG. 1. Room-temperature equation of state for the *B*2 and tetragonal structures of CsBr as determined by x-ray diffraction. The data are compared with Eulerian and Lagrangian finite-strain equations of state computed using the ultrasonic data of Barsch and Chang (Ref. 17).

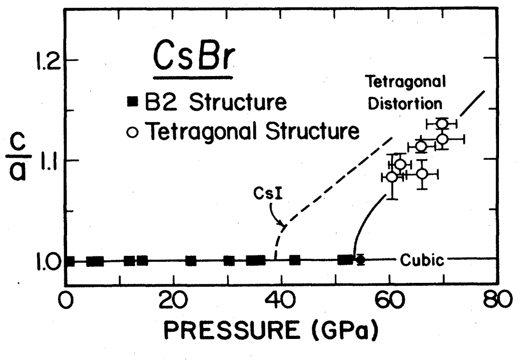

FIG. 2. Ratio of unit cell parameters c/a is plotted as a function of pressure for CsBr. The amount of distortion observed in the run at 54.8 GPa was too small to be resolved quantitatively. The continuous increase of the c/a ratio above 53 GPa is similar to that observed in CsI above 39 GPa (dashed line—no data shown) (Ref. 8).

bility of the bcc lattice.[21,22] What is notable, however, is that this tetragonal distortion towards the fcc lattice has only been observed in the cesium halides so far. For comparison, neither RbI nor KI, which have been compressed to $V/V_0 \lesssim 0.49$ in the $B2$ structure, exhibit this transition.[3] Apparently, the presence of the low-lying[23] Cs $5d$ states help to precipitate the tetragonal distortion of the $B2$ structure at high pressures.

Note added in proof. Huang, *et al.* have recently reported data showing the same transition in CsBr as described here [Phys. Rev. B **30**, 2968 (1984)].

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