X-ray study of equations of state of solid xenon and cesium iodide at pressures up to 55 GPa

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An experimental study of the equations of state of Xe and CsI has been carried out at pressures up to 55 GPa and at room temperature. It is shown that the compression isotherms of Xe and CsI coincide at pressures above 15 GPa.

Recently there has been considerable interest in the physical properties of the isoelectronic substances Xe and CsI at very high pressures.[1-10] The reason that so much attention is being paid to these substances is the possibility of directly observing a metal-insulator transition in Xe and CsI using modern high-pressure technology.[11] The present paper is devoted to another very intriguing side of the physics of Xe and CsI, namely, a comparative study of their equations of state. The point is that Cs^+ and I^- ions have closed xenon-like electronic shells, and the short-range interaction between Cs^+ and I^- ions and two Xe atoms is expected to be essentially identical. The main difference between Xe and CsI is the powerful Coulomb interaction in CsI. The role of the latter decreased on compression. However, in the framework of the classical rigid-ion model, the compression isotherms of Xe and CsI are always separated by the interval

$$P \sim \alpha V^{-4/3} ,$$

where P is the pressure, V the volume, and α the Madelung constant.

The real situation is probably different. At the very least, one may expect that the pressure interval between the Xe and CsI compression curves is considerably smaller than that which would follow from the classical model, due to a possible variation of the electron-charge-density distribution with pressure.

The theoretical calculations carried out in Refs. 12 and 13 confirm this conclusion in general, but the accuracy of the calculations is not high enough to describe in detail the relationship between the Xe and CsI compression isotherms. The results of the present study reveal a surprisingly simple picture which could hardly be predicted *a priori*. It turns out that CsI and Xe compression isotherms come together at a pressure of about 15 GPa, and do not split within experimental uncertainty up to 55 GPa.

The experimental study of the Xe and CsI equations of state was carried out using x-ray diffraction techniques, using a diamond-anvil–gasketed cell. The pressure was measured by the ruby-fluorescence method,[14] with a precision of ± 0.05 GPa. Previously, the Xe and CsI EOS were studied in Refs. 5, 10, 15 and 6–8, 16, 17, respectively. A remarkable feature of the present experiments is that, in the course of the experimental study Xe and CsI were placed in the same cell and diffracted simultaneously. The latter strongly increases the reliability of the comparative analysis. Moreover, we have succeeded in carrying out an x-ray diffraction

TABLE I. Experimental P-V data for CsI and solid Xe.

No.	P (GPa)	V_{CsI} (Å^3/atom)	V_{Xe} (Å^3/atom)
1	0.00	47.66	
2	0.80	44.72	53.33
3	0.95	44.38	52.38
4	2.39	41.13	45.70
5	3.02	40.42	43.15
6	3.32	40.32	42.51
7	4.07	39.06	41.75
8	4.43	38.74	41.30
9	6.31	37.21	38.40
10	6.73	36.98	37.89
11	6.80	36.61	37.77
12	8.14	36.01	36.54
13	9.49	34.87	35.61
14	11.65	33.93	34.23
15	11.83	33.88	34.05
16	13.10	33.74	33.45
17	15.55	31.94	
18	19.68	30.66	30.56
19	20.31	30.47	30.58
20	22.81	29.82	29.83
21	24.45	29.22	29.22
22	25.01	28.99	
23	28.90	28.32	28.23
24	30.02	27.97	27.88
25	31.54	27.71	
26	31.80	27.30	27.56
27	32.51	27.20	27.40
28	33.80	27.11	27.16
29	34.72	27.19	27.05
30	35.71	26.91	
31	36.18	26.97	
32	36.50	26.83	26.63
33	36.80	26.73	
34	37.42	26.71	
35	37.50	26.53	
36	38.04	26.33	26.28
37	38.87	26.17	
38	39.70	25.85	
39	39.90	26.10	
40	41.60	25.60	
41	41.97	25.55	25.60
42	47.37	24.89	24.54
43	47.33	24.99	
44	50.27	24.62	24.41
45	51.60	24.46	
46	53.20	24.12	23.78

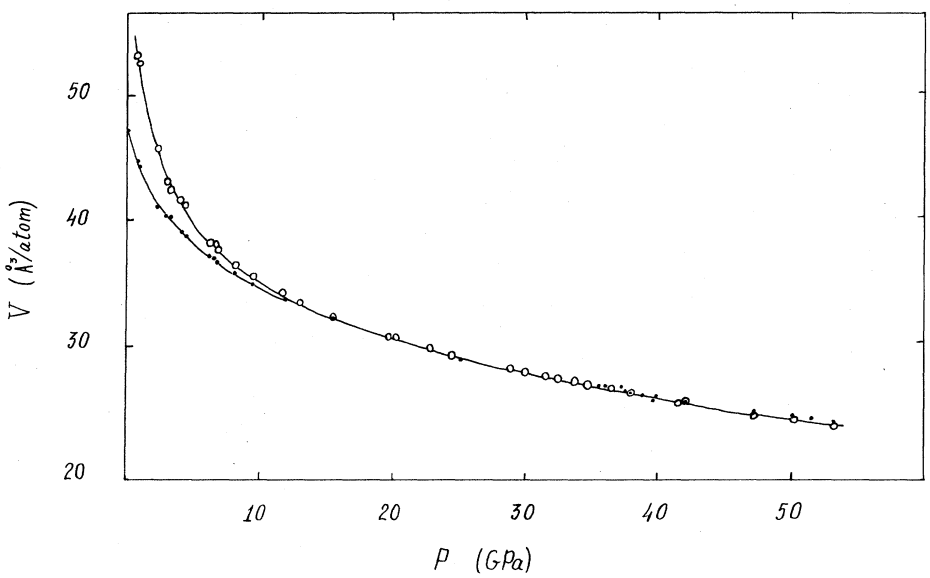

FIG. 1. Pressure dependence of Xe and CsI volumes at room temperature according to the present experimental results. Open and solid circles represent the data on Xe and CsI, respectively.

study of Xe and CsI monocrystalline samples, which provided us with high-precision lattice constants.

The experimental procedure can be briefly described as follows. Powder, or a small CsI monocrystal, was placed into the hole of the gasket attached to one of the diamonds. Then the cell was filled with xenon under a pressure of 60 bars, and a temperature of about 270 K. The initial thickness of the Inconel gasket was 40–100 μm, and the diameter of the hole was 150–200 μm. The x-ray diffraction study of the powder samples was carried out with the film technique using filtered Mo $K\alpha$ radiation (60 kV at 80 mA). Exposure time, depending on the volume of the samples, varied from 8 to 70 h. The film-to-sample distance was determined with the help of standard substances attached to the outer surface of one of the diamonds. Aluminum and gold in the form of thin films were used as standard substances.

The x-ray Debye-Scherrer pattern of CsI recorded at low pressures contained rings corresponding to the (110), (200), and (211) reflections. At pressures of more than 10 GPa, the (200) reflection disappeared for unknown reasons, and the (211) reflection could not be recorded due to geometry limitations. At pressures of 35–40 GPa we observed, as did the authors in Refs. 6–8, the splitting of the original (110) reflection into two. Using a simple hypothesis for the tetragonal distortion of the original CsI structure, these reflections were indexed as (110) and (101). In this case, the structural transformation in CsI occurred without any noticeable volume change (see also Refs. 6–8).

The Xe reflections [we observed (111), (200), (220), and (311) among them], as a rule, were presented as the fragments of rings that indicated the preferable orientation of

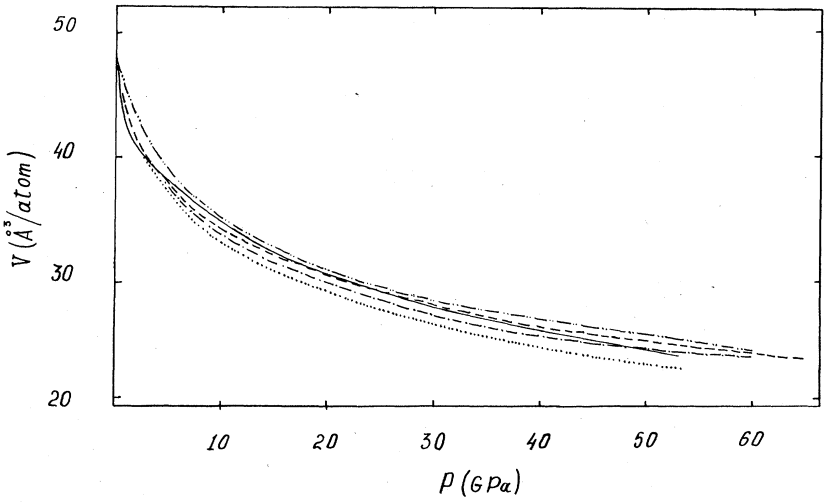

FIG. 2. Comparison of various P-V data for CsI. All data represent room temperature isotherms. Solid line, present data; dashed line, Ref. 7; dot-dashed line, Ref. 8; two dots-dashed line, Ref. 6; dotted line, Ref. 13.

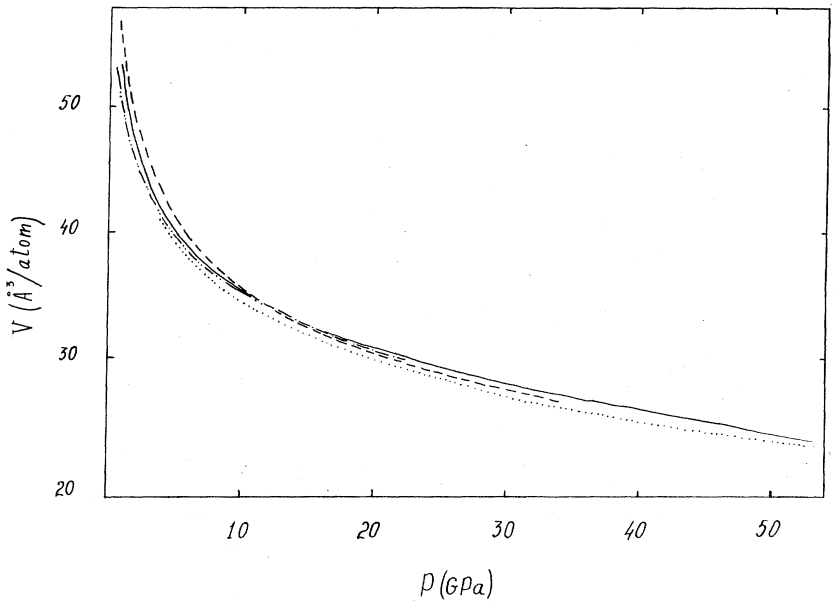

FIG. 3. Comparison of various P-V data for Xe. Most of the data represent room-temperature isotherms. Exceptions are indicated. Solid line, present data; dashed line, Ref. 10; dot-dashed line, Ref. 5; two dots-dashed line, Ref. 15 (85 K); dotted line, Ref. 12 (theory, 0 K).

Xe microcrystals, or rather the existence of a few relatively large Xe crystals.

An x-ray study was carried out on a monocrystalline CsI platelet, with dimensions $50\times 50\times 15\ \mu m^3$, placed in solid polycrystalline Xe, some grains of which were large enough to fit into a monocrystalline x-ray study.

A standard two-circle x-ray diffractometer with a scintillation detector and monochromatized Mo $K\alpha_1$ radiation were used to record monocrystalline reflections. In several trails the scintillation detector was replaced by a position-sensitive detector. On the whole, monocrystalline experiments had an advantage over powder film techniques owing to a greater sample-to-detector distance, and sharper reflections as a result of better monochromatization.

The recorded monocrystalline reflections were (110) and (220) for CsI, and (200) and (111) for Xe. Monocrystalline x-ray studies of Xe and CsI were performed at pressures up to 35 GPa and, consequently, all data obtained at pressures in excess of 35 GPa are based on powder x-ray measurements.

The precision of the Xe and CsI lattice constants, which were obtained from the experiments, is estimated to be about 0.01 Å, and 0.001–0.002 Å for the powder and monocrystalline x-ray measurements, respectively.

The pressure was measured from the shift of the R_1 luminescence line of ruby, with a precision of ± 0.05 GPa. These estimates yield a precision of about 1% for the calculated values of the volume of Xe and CsI at high pressure.

The experimental P-V data are presented in Table I.

The results of our measurements are illustrated in Fig. 1, and in Figs. 2 and 3 our results are compared with some other experimental and theoretical data. As can be seen in Fig. 1, the volume per atom in Xe and CsI crystals became equal at a pressure of about 15 GPa, and at higher pressure the Xe and CsI compression curves coincide within the experimental resolution.

In this connection one may conclude that the Coulomb contribution to the pressure of CsI becomes negligibly small at high compression. This means in turn, that redistribution of electronic density occurs in CsI at high pressure, which results in a decrease of the effective ionic charges. Further investigation of this problem would be of much interest.

It has to be emphasized that the experimental result discussed could hardly be obtained from independent studies of the Xe and CsI EOS, as follows from Figs. 2 and 3. One can see in Figs. 2 and 3 that the total scattering of the experimental data makes up about 5% of the volume. It undoubtedly proves the existence of unaccounted-for systematic errors in each experiment which essentially exceed the precision claimed in Refs. 5–8, 10, and 15–17. Obviously, the study of Xe and CsI which were placed into the same cell, as was done in our work, has played a crucial role in discovering the fact of the confluence of Xe and CsI compression isotherms.

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