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

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The equations of state of the isoelectronic substances Xe and CsI have been studied in diamond anvils at pressures up to 55 GPa at room temperature. Above 15 GPa the compression isotherms of Xe and CsI become indistinguishable.

The physical properties of the isoelectronic substances Xe and CsI at extremely high pressures have recently attracted considerable research interest.[1–10] The primary reason for this interest is that it may be possible to directly observe metal-insulator transitions in Xe and CsI by means of advanced high-pressure techniques.[11]

In this letter we discuss another intriguing aspect of the physics of isoelectronic Xe and CsI: a comparative study of their equations of state.

The ions Cs^+ and I^- have filled xenon-like electron shells, so that the short-range forces acting in the ion pair Cs^+-I^- should be essentially identical to those acting in the atom pair Xe-Xe. Nevertheless, according to the classical model of rigid ions, the compression isotherms of CsI and Xe are always separated by an interval $\Delta P \sim \alpha V^{-4/3}$, where P is the pressure, V is the volume, and α is the Madelung constant.

The actual situation is apparently quite different because of the continuity of the distribution of the electron density in the crystals and possible changes in the density upon compression. We would expect that the interval ΔP separating the Xe and CsI compression isotherms would be at least significantly smaller than predicted by the simple model of rigid ions.

The microscopic calculations in Refs. 12 and 13 generally support this interpretation, but they are not accurate enough to tell us exactly how the Xe and CsI compression isotherms interact with each other.

The results of the present study reveal a surprisingly simple situation, which would have been extremely difficult to predict. It turns out that the Xe and CsI *compression isotherms merge at* ~15 GPa *and then remain indistinguishable up to* 55 GPa.

The experiments on the equations of state of Xe and CsI were carried out by means of x-ray diffraction in a high-pressure diamond cell at room temperature. The pressure is measured with a ruby pressure gauge with the help of the scale of Ref. 14. The equation of state of CsI has been studied previously[6–8,15,16] at pressures up to 60 GPa. In equation of state of Xe has been studied[5,10,17] at pressures up to(1), 35 GPa.

A distinctive feature of these experiments is that the CsI and Xe are in the same cell, and the x rays are diffracted simultaneously by the Xe and CsI, adding substantially to the reliability of this comparative analysis. Furthermore, in addition to studying powdered samples we were able to carry out a diffraction study of Xe and CsI single crystals, improving the accuracy with which the properties of the unit cell can be determined.

In the experiments, the CsI samples, in the form of a powder or a microscopic single crystal, and a small piece of ruby are positioned in an aperture in a metal spacer which is mounted on one of the diamonds of the high-pressure cell. The cell is then filled with Xe to a pressure ~60 bar and a temperature ~270 K by a special apparatus.[3] The initial thickness of the metal (Inconel) interlayer is 40–100 μm, and the aperture is 150-250 μm in diameter.

The x-ray diffraction studies of the powdered samples are carried out by a photographic method with filtered Mo $K\alpha$ radiation (60 kV, 80 mA). The exposure time is varied from 8 to 70 h, depending on the volume of the sample. The distance from the film to the sample is determined with the help of a calibration film on the diamond support: an aluminum or gold film 10 or 0.5 μm, respectively, thick.

At pressures above 10 GPa we observe only the (110) reflection of CsI. In the interval 35–40 GPa, the (110) reflection splits in two. Adopting the simplest assump-

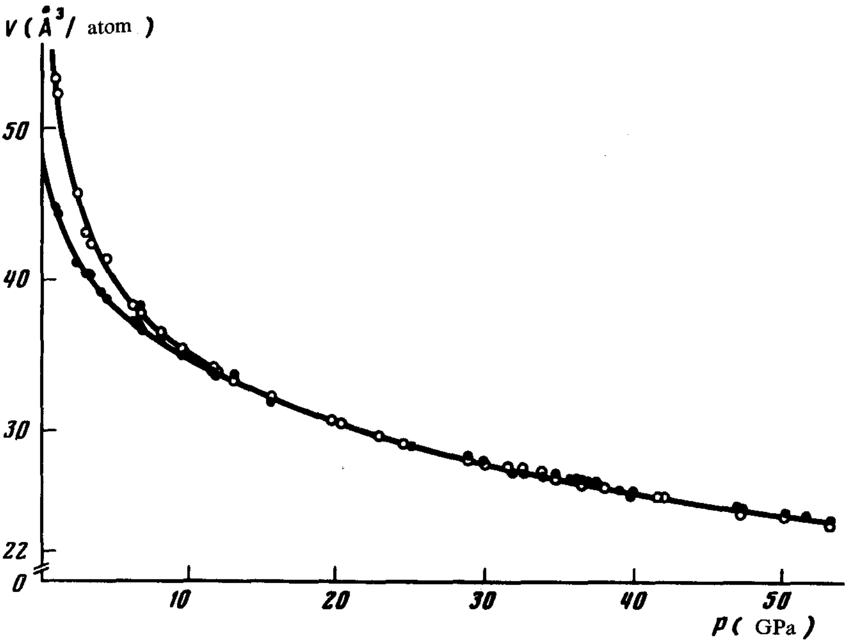

FIG. 1. Pressure dependence of the volume of CsI (●) and Xe (○) at room temperature according to the results of the present experiments.

tion, of a tetragonal distortion of the original structure, we indexed these reflections as (110) and (101). We found that the structural conversion in CsI is not accompanied by any significant change in density (see also Refs. 6–8).

In the experiments on the x-ray diffraction of a single crystal, a CsI single-crystal wafer 15 μm thick with other dimensions of 50×50 μm is placed in the pressure cell, which is then filled with xenon. In all cases it was possible to find a Xe grain large enough for the single-crystal measurements. These measurements were carried out on a standard single-circle diffractometer.

The single-crystal measurements were carried out at pressures up to 35 GPa, so that all the results for pressures above 35 GPa refer exclusively to the powder measurements.

The accuracy with which the dimensions of the unit cells of Xe and CsI were measured can be estimated to be on the order of 0.01 Å and 0.001–0.002 Å for the powder and single-crystal cases, respectively. The pressure was determined within ± 0.05 GPa from the shift of a ruby luminescence line. These estimates lead to an accuracy on the order of 1% for the calculated volumes of Xe and CsI.

It can be seen from Fig. 1 that the volumes per atom of the Xe and CsI crystals become equal at a pressure on the order of 15 GPa, above which the equations of state of Xe and CsI (per atom) are identical.

It thus seems obvious that the Coulomb contribution to the CsI pressure becomes negligibly small when the compression is large. This result means that at high pressures the electron density in the CsI crystal becomes redistributed, ultimately leading to decreases in the effective charges of the ions. A further study of this question would be of considerable interest.

We wish to emphasize that this experimental result apparently could not be achieved in independent studies of the equations of state of Xe and CsI, according to the data in Refs. 5–8, 10, and 15–17. It can be seen that the overall scatter in the experimental results obtained by different investigators is on the order of 5% in terms of the volume. The problem is undoubtedly that each specific experiment has been afflicted by systematic errors substantially larger than the declared errors of the measurements. It is clear that the simultaneous study of the compression of Xe and CsI in the present experiments has played a decisive role in establishing the merging of the Xe and CsI compression isotherms at high pressures.

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[1] For brevity, we will not cite or discuss studies on the shock compression of Xe and CsI.

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[1] K. Asaumi and Y. Kondo, Solid State Commun. **40**, 715 (1981).
[2] K. Syassen, Phys. Rev. B **25**, 6548 (1982).
[3] I. Makarenko, G. Weill, I. P. Itie, and J. M. Besson, Phys. Rev. B **26**, 7113 (1982).
[4] K. Asaumi, T. Mori, and Y. Kondo, Phys. Rev. Lett. **49**, 837 (1982).
[5] D. Schiferl, R. L. Mills, and L. E. Trimmer, Solid State Commun. **40**, 783 (1983).
[6] E. Knittle and R. Jeanloz, Science **223**, 53 (1984).
[7] K. Asaumi, Phys. Rev. B **29**, 1118 (1984).
[8] T. L. Huang and A. Ruoff, Phys. Rev. B **29**, 1112 (1984).
[9] I. N. Makarenko, A. F. Goncharov, and S. M. Stishov, Phys. Rev. B **29**, 6018 (1984).
[10] K. Asaumi, Phys. Rev. B **29**, 7026 (1984).
[11] M. Ross and A. K. McMahan, in: Physics of Solids Under High Pressure (ed. J. S. Schilling and R. N. Shelton), North-Holland, Amsterdam, 1981, p. 161.
[12] M. Ross and A. K. McMahan, Phys. Rev. B **21**, 1658 (1980).
[13] J. Aidun, M. S. T. Bukowinski, and M. Ross, Phys. Rev. B **29**, 2611 (1984).
[14] M. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).
[15] P. W. Bridqman, Proc. Am. Acad. Arts. Sci. **76**, 1 (1945).
[16] D. E. Hammond, in: Adv. High-Pressure Research (ed. R. H. Wentorf, Jr.), Academic Press, New York, Vol. 4, 1974, p. 161.
[17] K. Syassen and W. B. Holzapfel, Phys. Rev. B **18**, 5826 (1978).

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