New data on the equation of state for the phase transitions of cesium iodide (the role of hydrostatics)

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(Submitted 20 October 1989)
Zh. Eksp. Teor. Fiz. **97**, 1321–1325 (April 1990)

Results are presented on the experimental study of compression isotherms of CsI at pressures up to 52 GPa and room temperature, by using compressed helium as the pressure-transmitting medium. It is established that the CsI compression isotherm thus obtained differs from the results obtained in essentially nonhydrostatic conditions. It is demonstrated that the use of helium as the pressure-transmitting medium alters the character of the phase transformations in CsI at high pressures.

The present work reports on x-ray diffraction studies of compression isotherms of CsI single crystals performed by using diamond anvils. The novelty of the present study is the use of compressed helium as the pressure transmitting medium. This yielded a series of new results.

In order to obtain high pressures a diamond cell was used, which allowed us to record the x-ray spectrum over a wide range of diffraction angles. The single-crystal sample of CsI of dimensions $60 \times 40 \times 15\,\mu\text{m}^3$ was placed on one of the diamonds in front of a slit of 150 μm diameter, drilled in a metallic gasket (Inconel X 750). The cell was filled with helium using a special system consisting of a high pressure container provided with a power connection and a gas compressor.

The x-ray spectrum was recorded with a standard double-track DRON-2.0 diffractometer provided with a special set-up which allowed rotation of the chamber in two angular directions and centering of the chamber with respect to the axis of the beam. The (110) and (200) reflections were observed. The interplanar distances were determined to within ± 0.001 A.

The pressure was measured with a calibrated ruby manometer.[1] (To make comparison with the data from other experiments more convenient, we used the scale proposed in Ref. 1, instead of the "diamond" scale established in Ref. 2. We also note that the discrepancy between these calibration curves at 50 GPa is less than 10%). The pressure was determined with a precision of the order of 0.05 GPa.

The results obtained are as follows:

1. Equation of state. The available published data refer to the compression isotherms of CsI at room temperature up to pressures of 95 GPa, obtained in static conditions, without using any pressure-transmitting medium. All these data are in good agreement with each other and, surprisingly, are practically indistinguishable from the shock adiabat of Ref. 3. This last fact indicates either the presence of significant systematic errors in one of the methods, or negligibly small thermal pressures in shock compression, which is rather improbable. Another possible explanation of this result is related to the possible decomposition of CsI into its constituent elements under the action of the shock wave.[4] However, in what follows we provide a convincing argument in favor of the conclusion that nonhydrostatic conditions of the experiment can alter significantly the shape of the compression isotherm and of the phase diagram of materials.

Figure 1 shows a comparison of the first section of the compression curve of CsI obtained in this work with those of other authors (Refs. 5–11). It is to be noted that the results of the present experiment, which is truly hydrostatic up to pressures of about 12 GPa (the crystallization pressure of

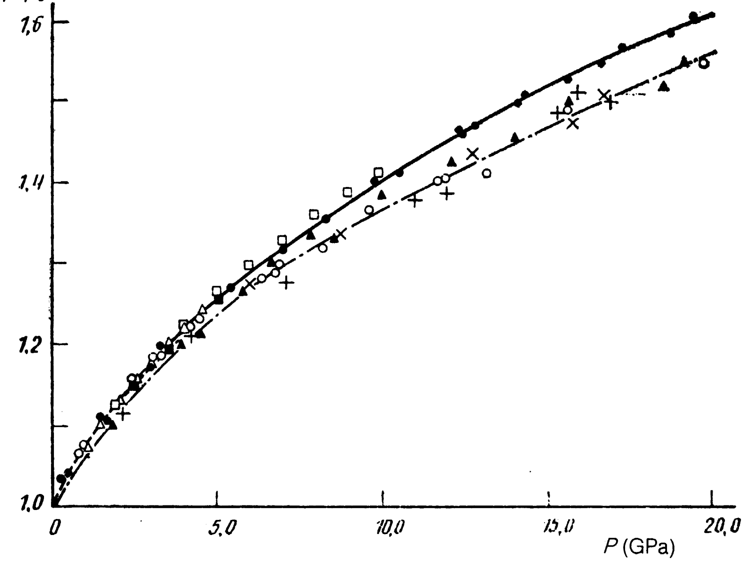

FIG. 1. The density of CsI as a function of pressure, for $P \leqslant 20$ GPa: ● present work; dashed line—Ref. 5; ○—Ref. 8; □,■—Ref. 6; △—Ref. 7; ▲—Ref. 9; +—Ref. 10; ×—Ref. 11.

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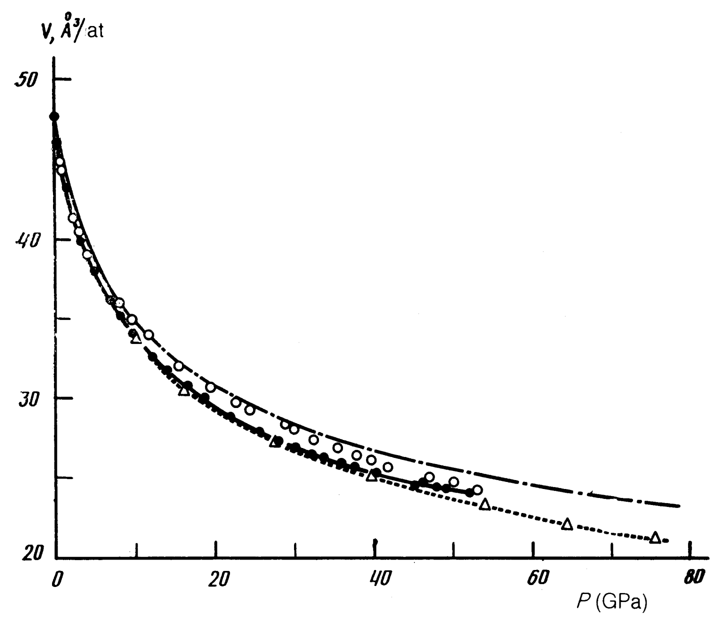

FIG. 2. Compression isotherms of CsI: ●—present work; ○—Ref. 8; dash-dotted line—Refs. 9–11; △—Ref. 12.

helium at room temperature is about 12 GPa), agree closely with the compression curve of CsI calculated from ultrasound experiments (Refs. 6 and 7); up to pressures of about 5 GPa (the crystallization pressure of xenon at room temperature is about 5 GPa), and also agree with the experiments that use xenon as the pressure-transmitting medium.[8] At the same time, the results obtained in Refs. 9–11 without using a pressure-transmitting medium differ from the "hydrostatic" data at various compressions, and result in a significantly larger bulk modulus of elasticity at $P = 0$.

Figure 2 shows the room-temperature compression isotherm of CsI based on the data of the present work. Included here are also the results of our previous studies performed by using Xe as the pressure-transmitting medium,[8] as well as the generalized CsI compression curve obtained without any pressure-transmitting medium (compiled from the data of Refs. 9–11). Moreover, Fig. 2 also shows the room-temperature CsI compression isotherm calculated by the method of superposition of plane waves with subsequent thermal corrections.[12] As seen in this figure, all three curves are distributed in the P–V space such that, for any given volume, the measured pressure increases as the hydrostatic character of the pressure-transmitting medium decreases. The physical reasons for this behavior are fully obvious and are related to the occurrence of stresses at the contact surfaces of a compressed mixture of solid materials that have different elasticity moduli (see, e.g., Ref. 13).

These data clearly demonstrate that the nonhydrostatic character of the pressure-transmitting medium can introduce significant errors in the determination of pressure, and should be taken into account in quantitative measurements. Related to this, we remark (see Fig. 2) that only the "hydrostatic" compression curve of CsI shows agreement with the equation of state calculated by using the method of superposition of plane waves.

2. Phase transition. A number of previous studies have demonstrated the existence of two phase transitions in CsI in the pressure range up to 70 GPa.[9–11] These results imply that at a pressure of 45 GPa the cubic phase of CsI is transformed into the tetragonal phase, which in turn is transformed into the rhombic phase at a pressure of 65 GPa.

Aleksandrov, Zisman, and Stishov,[14] using xenon as the pressure-transmitting medium, observed a peculiar property of the first of the these phase transitions, namely: the faster the cell was loaded, the lower was the transition pressure. This behavior led to the conclusion that the phase transition of CsI is extremely sensitive to the character of the stress distribution. Naturally, it was considered interesting to study the properties of the phase transition of CsI in conditions as close to hydrostatic as possible, which can be accomplished by using helium as the pressure-transmitting medium.

In our study of the phase transition of CsI, we observed the evolution of the (110) reflection with varying pressure. Let us recall that the initial sample was in single-crystal form. As one can see in Fig. 3, the initial reflection splits into three reflections, each of which is observed at slightly different angles of incidence of the primary x-ray beam on the sample material (the maximum angular difference is 3°). One thus got the impression that the original single crystal

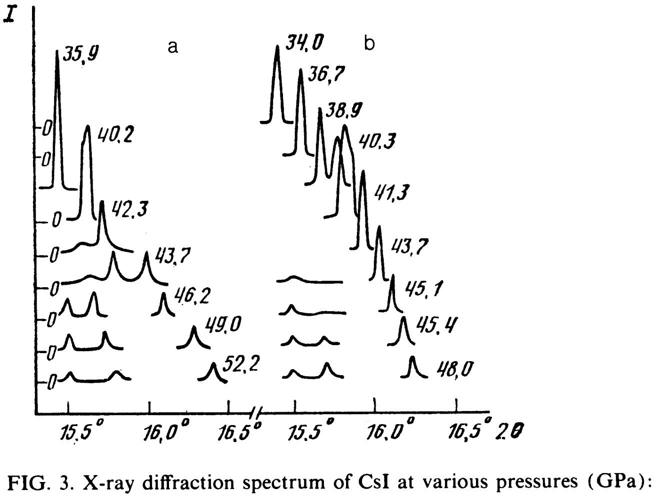

FIG. 3. X-ray diffraction spectrum of CsI at various pressures (GPa): (a)—increasing pressure; (b)—decreasing pressure.

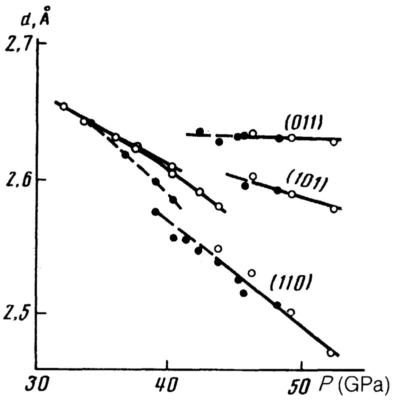

FIG. 4. Pressure dependence of the interatomic distance in CsI in the region of phase transitions: ○—increasing pressure; ●—decreasing pressure.

was divided into three domains, which in fact agrees with the idea of formation of the rhombic phase. In this case, the three reflections obtained can be indexed as (110), (101), and (011) (see Fig. 4). The calculated compression isotherm of CsI, based on these data, is a rather smooth extension of the compression isotherm of the cubic phase (see Fig. 2). In Figs. 3 and 4, one can also see a transition region characterized by a broadening of the initial (110) reflection of the cubic phase, the appearance of additional reflections, etc. These features of the phase transition can presumably be correlated with the occurrence of nonhydrostatic stresses at pressures above 30–35 GPa.[2] It is possible that these characteristic features may also be related to the difference in intensities of the reflections of the rhombic phase (the preponderence of one of the domains). In the ideal case, the intensities of all three reflections should be the same.

Thus, the crystal structure of CsI under uniform compression does not evolve towards a densely packed cubic, as was put forward earlier (Ref. 14). This conclusion is also supported by the work of Mao *et al.*,[15] which provides indications of the existence of a hexagonal close-packed structure at pressures above 150 GPa.

In conclusion, we would like to emphasize again that, if the nonhydrostatic experimental conditions are not taken into account, this may result in severe errors in the interpretation of experiments at superhigh pressures.

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Translated by Irina Nelson