An investigation of the equations of state of the isoelectronic substances CsI–Xe and RbBr–Kr. Phase transitions in CsI and RbI

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Results are given of an experimental investigation of the equations of state of two pairs of isoelectronic materials: cesium iodide (CsI)–xenon (Xe) and rubidium bromide (RbBr)–krypton (Kr), at pressures up to 55 GPa. It was established that within the limits of experimental error, the compression isotherms of CsI–Xe and of RbBr–Kr become indistinguishable at pressures above 15 and 20 GPa, respectively. The existence of a tetragonal phase in rubidium bromide at pressures above 45 GPa was established, similar to the tetragonal phase of CsI. The question is discussed of the redistribution of electron density in alkali-halide crystals at high pressures and the influence of this effect on the equation of state and the stability of the crystal lattice.

Studies of the physical properties of alkali-halide and van der Waals crystals have played an important part in the establishment of solid state physics and in the development of the theory of intermolecular interaction. However, as it turned out, the role of these materials is far from being exhausted. The progress in high-pressure technique has made it possible to use these materials effectively again as model substances in solving both old classical and new problems in the physics of the condensed state of matter.

Among these problems are the metallization of close-packed substances, the stability of the crystal lattice, intermolecular interaction, and the equation of state.

The results of the present work bear directly on all three problems mentioned, and although we will not discuss the first of them, we will show that a successful solution of the problem of metallization is impossible without detailed information on the crystal structure and equation of state of the material.

We present here the results of an investigation of the equations of state of the isoelectronic pairs of substances CsI–Xe and RbBr–Kr at pressures up to 55 GPa and at room temperature. In the course of these studies the existence of a phase transition in CsI was confirmed, associated with a tetragonal distortion of the initial cubic phase with the CsCl type structure, and a similar transition in RbBr was found for the first time. Extremely interesting results were obtained from a comparative analysis of the equations of state of CsI-Xe and RbBr–Kr. It turned out that the compression isotherms of the corresponding pairs merge at sufficiently high pressure and become indistinguishable on raising the pressure further. The results of the present work which concern the equations of state of CsI and Xe have been published in part before.[1,2] Other groups of authors have also carried out similar investigations. The corresponding results have been published: the equation of state of Xe,[3,5] the equation of state and phase transitions in CsI,[6–10] and phase transitions in CsBr and CsCl.[11–13]

We note that, unlike other work, in our experiments the isoelectronic materials were studied simultaneously in a single high-pressure cell and were under identical conditions, which in spite of possible systematic errors enabled the coincidence of the equations of state of the isoelectronic substances to be observed.

EXPERIMENTAL TECHNIQUE

The CsI and RbBr specimens and a ruby microcrystal were housed in the aperture of a metallic gasket fixed to one of the diamonds of a high-pressure cell. By means of a special device[14] the cell was then filled with xenon or krypton at temperatures of ≈ 270 and ≈ 145 K and pressures of ≈ 60 and 5 bar, respectively. The pressure in the cell was measured with the help of the ruby gauge, using the scale proposed by Mao *et al.*[15] All the experiments were carried out at room temperature. The initial thickness of the metal gasket made from the alloy "Inconel" was 40–100 μm and the diameter of the opening was 150–250 μ. Both powder and single-crystal specimens were used in the experiment.

X-ray photography of the powdered CsI specimens was carried out with filtered MoK_α radiation ($60 \text{ kV} \times 80 \text{ mA}$). The exposure time was 8–70 hours, depending on the volume of the specimen. The distance from the film to the specimen was determined by using a standard material deposited on the bearing surface of the diamond. For this purpose aluminum or gold of thickness 10 and 0.5 μm, respectively were used. The cell geometry enabled the (110), (200), and (211) reflections of CsI and the (111), (200), (220), and (311) of Xe to be recorded at low pressures. It should be pointed out that the reflections belonging to Xe were recorded in the form of small fragments of the rings. The (211) reflection of CsI became unobservable at pressures of ≈ 20 GPa, due to the geometry of the cell, as were the (311) and (220) reflections of Xe at pressures of ≈ 15 and ≈ 25 GPa, respectively.

In the case of the single-crystal photography the CsI specimen with dimensions $\approx 50 \times 50 \mu$m and thickness ≈ 15 μm showed up outside the previously prepared plate oriented perpendicular to the [001] axis (see Fig. 1). After the cell was filled with xenon and its crystallization we were always able to find a sufficiently large single-crystal xenon block, suitable for single-crystal measurements. The single-crystal photography was carried out with a standard "DRON-2.0" diffractometer, using MoK_{α_1} radiation with a germanium monochromator. Thanks to the use of monochromatic radiation and to the perfection of the initial micro-single crystals of CsI, the accuracy of a single-crystal picture was appreciably higher than for powder photography and was ≈ 0.002 Å,
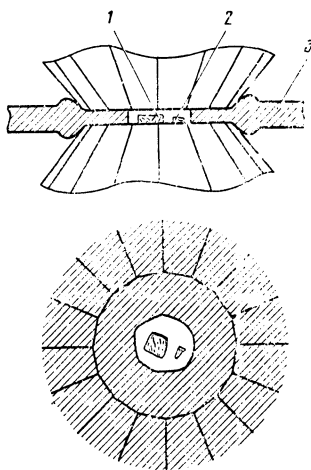
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FIG. 1. The positioning of a CsI single-crystal and the ruby manometer in the high-pressure cell: 1) CsI crystal, 2) ruby chip, 3) metal gasket of "Inconel" alloy.

FIG. 3. The difference in pressures $[\Delta(V) \equiv P_1(V) - P_2(V)]$, corresponding to one and the same value of the volume of an alkali-halide crystal and the isoelectronic noble gas, as a function of the specific volume V/V_0; $V_{0\,CsI} = 46.7$ Å^3/at, $V_{0\,RbBr} = 32.7$ Å^3/at, obtained by extrapolating the compression isotherm of RbBr in the CsCl structure to zero pressure; 1) (CsI–Xe), 2) (RbBr–Kr).

while the accuracy of powder photography was not more than 0.01 Å. Unfortunately, the width of the diffraction lines increased with increasing pressure and their intensity fell, which is evidently associated with the nonuniformity in pressure over the volume of the cell and with the accumulation of plastic deformations in the specimen. For example, at pressures above 30 GPa the accuracy of the single-crystal photography was about 0.01 Å, which leads to an error of the order of 1% in calculations of the values of the CsI and Xe volume. The weakening of the diffraction maxima on increasing the pressure meant that we could not use the standard scintillation counter at high pressures, and used a linear position-sensitive detector for single-crystal photography.

Experiments with RbBr were only carried out on powder specimens, since at atmospheric pressure RbBr has the NaCl type of structure and makes a transition to the CsCl structure at pressures $P \approx 5$ kbar. This phase transition is characterized by a relatively large ($\approx 10\%$) volume jump and is accompanied by a destruction of single-crystal specimens. Since the characteristic radiation of Rb, Br, and Kr
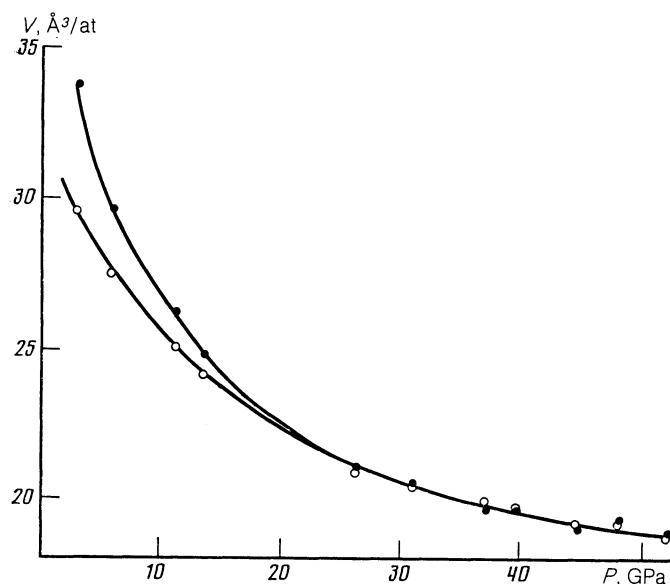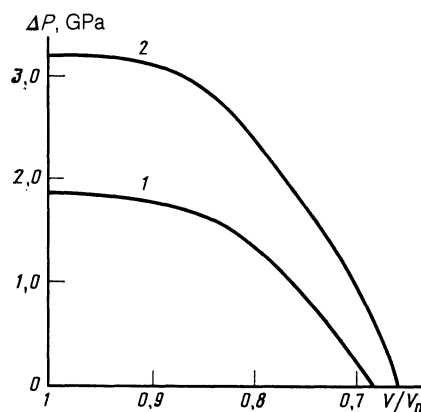
has an energy of ≈ 13 keV, obtaining a powder diagram by using MoK_α radiation (≈ 17 keV) is made difficult by the strong luminescence. In studying RbBr and Kr we therefore used an energy-dispersive technique, which had a somewhat lower accuracy in determining the interplanar space (≈ 0.02 Å). The (110) reflection of RbBr and the (111) reflection of Kr were observed in this way. In this case the accuracy in determining the volume was 2–3%.

RESULTS OF THE EXPERIMENT

The compression isotherms of RbBr and Kr are shown in Fig. 2. The compression isotherms of Kr and RbBr merge at a pressure of ≈ 20 GPa, in the same way as for the case of CsI and Xe,[9,10] and remain indistinguishable up to pressures of ≈ 55 GPa. The difference between the equations of state of CsI–Xe and RbBr–Kr is shown in Fig. 3 as a function of the relative compression. In Fig. 4 are shown our results and
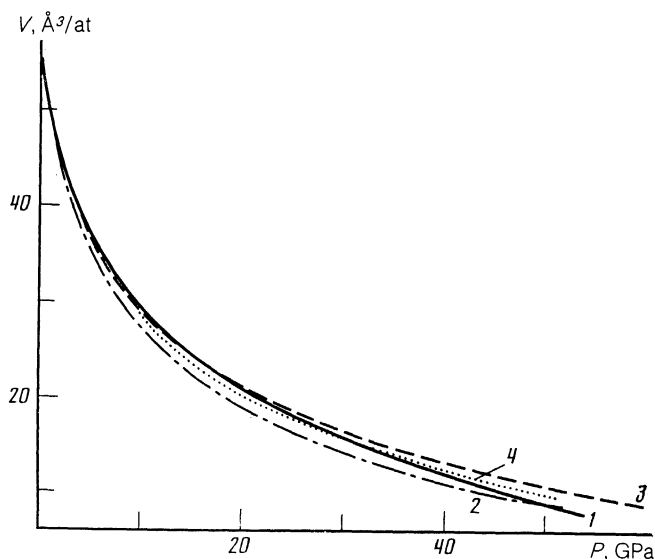

FIG. 2. Compression isotherms of (○) RbBr and (●) Kr.

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FIG. 4. Results on the equation of state of CsI. Curve 1) our results, 2) Ref. 7, 3) Refs. 9 and 10, 4) results of a microscopic calculation.[16]

FIG. 6. The diffraction picture given by a RbBr–Kr mixture at pressures of: a) 5.8 GPa (exposure time 16 hours) and b) 47.9 GPa (exposure time 50 hours); obtained with the help of an energy dispersion detector.

literature data on the equation of state of CsI, and also the results of a numerical calculation of the equation of state.

We remark that the absolute accuracy of experiments to investigate the equation of state in diamond anvils is clearly insufficient to establish the fact of coincidence of the equations of state on the basis of results obtained in separate experiments. As can be seen from Fig. 4, curves 2 and 3 obtained at different times by one and the same group of authors,[7,9,10] have a divergence appreciably greater than the stated experimental accuracy, which is evidence of the existence of unrecognized systematic errors, the influence of which on the difference in the equations of state was appreciably reduced in our work, since the materials investigated were under identical conditions.

The (110) reflection belonging to CsI was split into two (Fig. 5) at a pressure of 35–40 GPa, and this is associated with a tetragonal distortion of the initial structure.[1,2,6–10] A similar splitting was observed in RbBr at a pressure above 45 GPa (Fig. 6). The ratio of the cell parameters c/a after the transition was ≈ 1.05–1.1. We note that the transition takes place at different pressures in different series of experiments (with different rates of loading) (see Figs. 7 and 8), which is evidently related to the difference in the distribution of pressure inside the cell which arises for different rates of loading (see also Ref. 6). However, since this transition is not ac-

companied by any significant density change, the different position of the transition point does not show up in the equation of state in any way.

DISCUSSION OF THE RESULTS

The coincidence of the compression isotherms of two different pairs of isoelectronic materials CsI–Xe and RbBr–Kr over a wide pressure range must be attributed to sufficiently universal causes. In our opinion such a universal cause could be a redistribution of electron density in RbBr and CsI for high compression.

As is well known, the electron clouds of the ions Cs^+, I^-, and Rb^+, Br^- are identical with the electron clouds of the corresponding noble gases Xe and Kr. Assuming that the Cs^+–I^- and Rb^+–Br^- interaction potentials also coincide with the interaction potentials of Xe–Xe and Kr–Kr, respectively (apart from the Coulomb attraction of the ions), we can express the specific energy in our materials in the form

$$\varepsilon_1 = N_1 \varphi(r), \tag{1}$$

$$\varepsilon_2 = N_2 \varphi(r) - \alpha e^{*2}(r)/r, \tag{2}$$

where r is the nearest neighbor distance, ε_1 and ε_2 are respectively the energies of the free gas and of the alkali-halide crystal, $\varphi(r)$ is the pair interaction potential of atoms of the free gas, N_1 and N_2 are the effective number of nearest neighbors, determined by the geometry of the corresponding lattice in the form of the potential $\varphi(r)$ [for the case of $\varphi(r) = r^{-n}$, $n \to \infty$, $N_1 = 12$, $N_2 = 8$]. The second term in Eq. 2 describes the Coulomb attraction in the ionic crystal, α is the Madelung constant and $e^*(r)$ is the effective ionic charge.

Substituting $r = 2^{1/2}V^{1/3}/2^{1/3} \approx 1.12V^{1/3}$ and $r = 3^{1/2}V^{1/3}/4^{1/3} \approx 1.09V^{1/3}$ for a fcc lattice and for a lattice of the CsCl type into Eqs. (1) and (2), respectively, and differentiating with respect to the volume, we obtain the equation of state for the $T = 0$ K isotherm in the form

$$P_1 = -0.37V^{-\frac{1}{3}}N_1\varphi'(1.12V^{\frac{1}{3}}), \tag{3}$$

$$P_2 = -0.36V^{-\frac{1}{3}}[N\varphi_2'(1.09V^{\frac{1}{3}}) - V^{-\frac{1}{3}}\alpha e^{*2}(1.09V^{\frac{1}{3}})/1.19 \\ + 2\alpha e^* e^{*'}(1.09V^{-\frac{1}{3}})/1.09V^{\frac{1}{3}}] \tag{4}$$

(the prime denotes differentiation). The last term in Eq. (4) arises because of our assumption that the effective ionic charge e^* is volume dependent. In the absence of this term, i.e., for the condition $e^*(V) = $ const, the coincidence of the isotherms of Eqs. (3) and (4) over a wide pressure range is only possible under the condition that the potential $\varphi(r)$ is of the form $\varphi(r) = C/r^4 - D/r$ ($A \approx 11$). However, the existence of a Coulomb term D/r in the interaction potential of atoms of a noble gas is implausible and renders the rigid ion
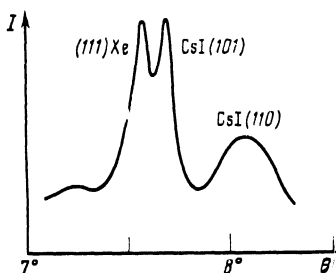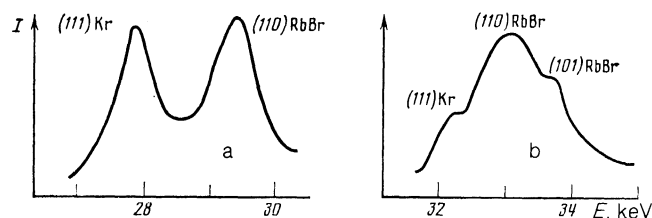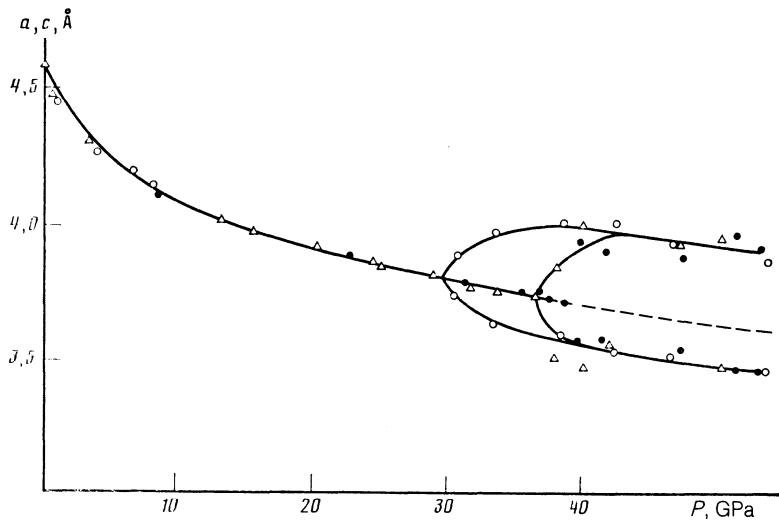

FIG. 5. The diffraction pattern given by a CsI–Xe mixture at a pressure of 37 GPa (obtained with the help of a linear position-sensitive detector).

FIG. 7. The cell parameters of CsI as a function of pressure: ●) obtained at a loading rate of ≈ 1 GPa/day, △) the region 32–38 GPa traversed at a single loading, ○) the region 10–30 GPa traversed in a single loading.

model inapplicable.[1] Within the framework of the assumptions made, therefore, we must regard the effective ionic charge as volume dependent. We can try to establish this dependence within the framework of the model proposed. If, in fact, we consider $P_1(V)$ and the first term in $P_2(V)$ [see Eqs. (3) and (4)] to coincide roughly [or $N_1 = 12$, $N_2 = 8$, this condition is satisfied exactly for a potential $\varphi(r) \sim r^{-15}$][2] it is easy to obtain an expression for the effective charge $e^*(V)$ as a function of volume:

$$e^{*2}(V) = \frac{1,09}{\alpha} V^{\prime\prime}$$

$$\times \int_V^{V_0} \Delta P(V)\,dV + CV^{\prime\prime}. \tag{5}$$

Here $\Delta P(V) = (P_1 - P_2)$ is the difference between the compression isotherms of the noble gas and the alkali-halide crystal. The results of a calculation, using Eq. (5), of the effective charge in CsI and RbBr from our results on the equation of state are shown in Fig. 9. As can be seen, the behavior of the effective charge and its value for densities corresponding to the point where the isotherms come together, is the same for both materials. On the same figure are shown the results of a microscopic model calculation,[16]
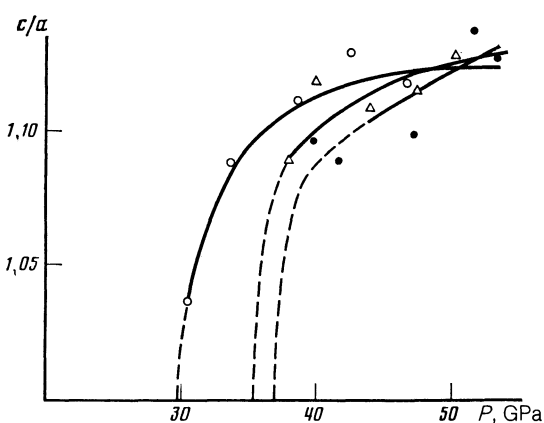
which agrees well with our estimates in the high pressure region. We may note that the results of a calculation[16] of the equation of state of CsI also agrees well with our results (see Fig. 4).

We turn now to the phase transition which takes place in CsI and RbBr. As is known,[17] a body centered cubic lattice[3] formed of atoms with a short-range repulsive potential is unstable with respect to a shift in directions equivalent to [110]. Within the framework of the nearest neighbor approximation, the shear modulus $\mu = (C_{11} - C_{12})/2$ in the [110] direction can be written in the form[17]

$$\mu = {}^8\!/_3\varphi'(r)r/V_z + 2{,}4e^{*2}/rV_z, \tag{6}$$

where V_z is the volume of the elementary cell. Since the first term in Eq. (6) is always negative, it is clear that the condition $\mu > 0$ for stability of the lattie is only satisfied because of the second term in Eq. (6) determined by the long-range Coulomb forces. Since the absolute value of $\varphi'(r)$ increases more rapidly with decreasing r than $1/r$, it is clear that for sufficiently large compression the expression of Eq. (6) goes to zero, the lattice becomes unstable with respect to shifts in
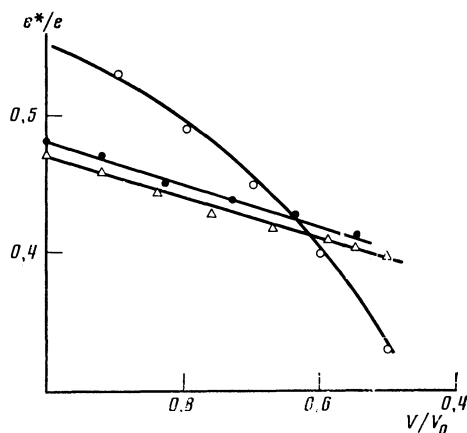

FIG. 8. The ratio c/a of the parameters of the CsI cell in the tetragonal phase as a function of pressure for different rates of loading (the symbols are the same as in Fig. 7).

FIG. 9. The dependence of the effective charge e^* on the specific compression V/V_0; $V_{0\,CsI} = 46.7$ Å³/at, $V_{0\,RbBr} = 32.7$ Å³/at, obtained by extrapolating the compression isotherm of RbBr in the CsCl structure to zero pressure: △) CsI, ●) RbBr, ○) the result of a microscopic calculation for CsI.[16]

[110] directions and as a result, a tetragonal distortion will occur, equivalent to a combination of two appropriate shifts along different diagonals (for example, [110] and [101]).

Calculations[8] showed that for the same degree of compression as is reached in CsI ($V/V_0 \approx 0.52$), the shear modulus should remain positive. This fact and also the existence of a similar tetragonal distortion in other cesium salts (CsBr and CsCl)[11-13] provided the basis for associating the existence of this phase transition with an electronic transition in cesium.[8] However, the possibility of a reduction in the effective ionic charge was not taken into account there. The existence also of a tetragonal distortion in RbBr (see Fig. 6) for the same relative compression ($V/V_0 \approx 0.52$) compels us to consider that the reason for this phases transformation is, nevertheless, the relative reduction in the contribution of the Coulomb forces associated with the reduction in the effective charge. This seems all the more valid since the change in the effective charge in CsI and RbBr at the moment of transition is practically identical (Fig. 9).

We note that distortions corresponding to the ratio of the cell parameters $c/a > 1$ and $c/a < 1$ correspond to essentially different physical situations, since the first of them leads to a denser packing and in the limit $c/a = 2^{1/2}$ corresponds to a face-centered cubic lattice (for indistinguishable positive and negative ions). In view of this, the expansion of the thermodynamic potential in terms of the order parameter, $\eta = (c/a - 1)$, should contain cubic terms, while the transition itself should be first order, although volume effects observed experimentally are vanishingly small. We remember that since the jump in the order parameter is not more than 5–10%, the volume jump should be not more than 1%, which corresponds to the limits of experimental accuracy.

We turn to another experimental fact which requires at least a qualitative explanation. As can be seen from Fig. 5, the widths of the (110) and (101) reflections in the tetragonal phase of CsI differ by about 4–5 fold. It is natural to suppose that the broadening of the reflections is associated in the first place with nonuniform conditions in the high-pressure cell and, as a consequence, with non-uniformity in η. Taking the volume of the elementary cell to be constant to a first approximation, it is not difficult to obtain for the parameters of the elementary cell a and c:

$$a = (2V_z)^{1/3}(1+\eta)^{-1/3}, \quad c = (2V_z)^{1/3}(1+\eta)^{2/3}.$$

Using the expressions for the interplanar spacings d, corresponding to the (101) and (110) reflections:

$$d_{101} = ac/(a^2+c^2)^{1/2}, \quad d_{110} = a/2^{1/2},$$

we obtain the increases in d for change in the order parameter:

$$\delta(d_{101}) = \frac{(2V)^{1/3}(K^4-2)}{3(K^2+1)^2}K^{-4/3}[(K^2+1)K^{-2}]^{1/2}\delta\eta,$$

$$\delta(d_{110}) = \frac{(2V)^{1/3}}{3\cdot2^{1/2}}K^{-4/3}\delta\eta, \quad K=c/a.$$

From this we obtain the ratio $\gamma = \delta(d_{110})/\delta(d_{101})$ corresponding to the ratio of the widths of the reflections for $K \approx 1.1$, equal to $\gamma \approx 5$, which agrees well with our results.

In conclusion the authors consider it essential to point out that the transition observed in the halides of heavy alkali metals is not quite usual. The dependence of the transition pressure on the rate of loading (see Figs. 7 and 8 and Ref. 6) makes us think that a pressure gradient provides a stimulus here, and it is possible that under purely hydrostatic conditions the corresponding phase transition would take place at appreciably higher pressures and would be accompanied by a significant jump in the order parameter. This question can, evidently, be solved in further experiments by using a more plastic medium than xenon as the transmitting medium (hydrogen, helium).

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Note added in proof (December 26, 1986): Experiments recently carried out using helium as the pressure transmitting medium show that, evidently, in an ideal hydrostatic medium the initial cubic CsI structure would transform directly into an orthorhombic structure.

[1)]The neglect of thermal vibrations plays no appreciable part in the present case, since at pressures above 10 GPa the Xe isotherms obtained at different temperature are practically indistinguishable.[14]

[2)]An estimate of this difference, using the potential obtained from the equation of state of Xe, gives a value ≈ 6–9 kbar.

[3)]Considering the ions to be identical, the CsCl type of structure can be regarded as a body centered cubic lattice.

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