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POLYMORPHIC TRANSITION IN SODIUM CHLORIDE UNDER PRESSURE

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With the aid of x-ray analysis performed under pressures up to 18000 kg/cm^2, a polymorphic transition in sodium chloride has been discovered in which the cubic face-centered structure changes into the cubic CsCl type. The lattice parameter of the new phase at atmospheric pressure is $a_0 = 3.36 \pm 0.04$ Å, and the density $\rho = 2.535$ g/cc.

INTRODUCTION

UNDER normal conditions the halides of the alkali metals have a cubic face-centered structure of the NaCl type. Three salts are exceptions: the chloride, bromide, and iodide of cesium; all these have the cubic structure of the CsCl type. The experiments of Bridgman showed [1-4] that the compressibilities of the salts of rubidium and potassium change discontinuously under increasing pressure. Bridgman associated this phenomenon with the occurrence of polymorphic transformations. The correctness of his hypothesis was proved by x-ray analyses performed under pressures greater than at the transition point by Jacobs [5] for RbI, by Vereshchagin and Kabalkina [6] for RbCl, and by Jamieson [7] for KI. It was found that the cubic face-centered structure changed in these cases into the primitive cubic structure of the CsCl type. Reduction of temperature causes an analogous transition in rubidium salts [8], and in the cesium salts the primitive structure changes into the face-centered on increasing the temperature.[9]

We have assembled in Table I published data on the conditions for polymorphic transitions in the alkali-halide compounds. It is seen that the transition pressure increases in going from cesium salts to lithium salts, and from iodides to fluorides.

Since the NaCl and CsCl structures are two of the simplest and most highly symmetrical, they repeatedly serve as the objects of theoretical studies. In a series of papers, tentative values for the transition pressures in the alkali-halides have been calculated on the basis of the classical semi-empirical Born-Mayer theory. [10-12] These values reproduce well the general character of the transition pressure changes in going from left to right and down the columns in the table. Unfortunately, a large quantitative discrepancy is observed in the values for the transition pressures, and for the cesium halides the theoretical calculations predict stability of the NaCl type structure rather than the cubic CsCl type.

In the halides of sodium and lithium Bridgman did not discover transitions under pressures up to 100,000 kg/cm^2, which also corresponds in general with the theoretical estimates. However, x-ray analysis enabled us to discover in NaCl a transformation in which the structure changed into the CsCl type.

Table I. The pressures and temperatures of polymorphic transitions in the halides of the alkali metals

	Li, 0.68		Na, 0.98		K, 1.33		Rb, 1.49		Cs, 1.65	
	Theory [5,10—12]	Experiment —	Theory [5,10—12]	Experiment —	Theory [5,10—12]	Experiment [1—4]	Theory [5,10—12]	Experiment [1—4,8]	теория [5,10—12]	Experiment [9]
F, 1.33	310 000	—	200 000	—	88 000	—	68 000	—	35 000	—
Cl, 1.81	240 000	—	74 000	—	36 000	20 060	31 000	5 000 (—190 °C)	—	— (445 °C)
Br, 1.96	105 000	—	53 000	—	29 000	18 430	25 000	4 600	—	—
I, 2.20	68 000	—	39 000	—	21 000	18 200	15 000	4 050	—	—

Note: The ionic radii for sixfold coordination are given to the right of the symbols for the elements.

EXPERIMENT

We took x-ray photographs of powdered specimens of sodium chloride under various pressures. At our disposal was "Ékstra" table salt and powder made from a single crystal. Semi-qualitative spectrographic analysis showed the presence of the following impurities:

"Ékstra"	Fe < 0.003%,	Cu < 0.0003%
Single crystal	Fe < 0.002%,	Cu < 0.0001%

No traces of Co, Mn, Ni, Rb were found. The small difference in composition did not affect the results, and we shall not, therefore, distinguish in what follows between the specimens.

The pressure chamber which we used has been previously described.[13] Its basic part is a tapered beryllium piston, which moves along a bore of the same form in the chamber to increase the pressure of the petroleum. The pressure was measured with a manganin manometer with an error of ± 100 kg/cm^2. The specimen was placed in a bore drilled out of the body of the beryllium cone. The chamber was used with a cassette allowing several photographs on the same film.

The effect of pressure on the specimen is to displace the lines due to the specimen towards larger angles on the x-ray photograph. This enabled us to calculate the change of volume of the cell compared with its original volume. The curve showing the change of volume with pressure is given in Fig. 1. Its coefficients are: $a = 36 \times 10^{-7}$, $b = -22 \times 10^{-12}$. As in the case of barium and strontium, the curves of change of volume with pressure found by the x-ray method lie below the curves obtained by Bridgman[2] using the method of linear compressibility; this is additional confirmation of the conclusions we previously reached.[13] The mean departure of the experimental points from the smooth curve amounted to 0.20%.

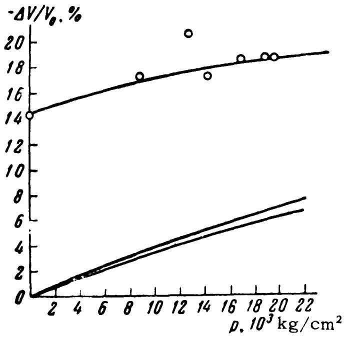

FIG. 1. Curves showing the changes of volume in sodium chloride under pressure. Of the two lower curves, the bottom one is constructed from our data, the upper one from Bridgman's data for the original phase. The topmost curve is for the high pressure phase.

Our pressure chamber had one feature which, in fact, assured success in the study of sodium chloride; namely, the beryllium piston is squeezed during its forward motion by the walls of the chamber with ever increasing force. Thus, contraction and filling-in of the bore containing the specimen sometimes occurs. As a result, significant shear forces arise in the specimen, and the quasi-hydrostatic pressure in the bore becomes greater than the hydrostatic pressure of the petroleum, which we measured with the manganin manometer. We observed similar phenomena frequently. We were always able to note this, since the displacement of the lines under pressure considerably exceeded the expected amount in these cases.

In eight cases we did, in fact, find on such films lines belonging to the high-pressure phase of NaCl. One of the typical x-ray photographs is shown in Fig. 2. The pressure acting on the specimen at the time of the photograph was determined from the displacement of the lines of the original phase. Taking into account the errors of measurement, we found that the new phase occurs at pressures greater than 17700 kg/cm^2. It should, however, be noted that this value does not correspond to the pressure of total transformation, because we usually dealt only with very small quantities of the transformed phase, i.e., with the start of the transition.

The scattering angles of the new phase were calculated by photographing alongside a standard. The untransformed NaCl phase provided the standard here. However, we did not succeed in attaining great accuracy in determining the parameter, since the photographs were made with molybdenum radiation, and the maximum angle of scattering did not exceed $\theta = 21°$. Also the error in determining the distance between the lines of the new phase and the standard was 0.05–0.15 mm.

In Table II are collected data on the eight lines observed. Here, I is the intensity of the line; h, k, l are the Miller indices; θ is the Bragg scattering angle; d is the distance between the planes;

FIG. 2. Reproduction of one of the typical x-ray photographs. The topmost photograph was obtained before pressure was applied; the middle one while pressure was acting on the specimen; the lowest after taking off the pressure. The third bright line on the middle photograph belongs to the new phase; other weaker lines are not visible on the photograph.

Table II

Intensity of line I	*hkl*	θ	$\sin^2\theta$	*d*, Å	*a*, Å
Medium	110	8°38′	0.0225	2.37	3.35±0.05
Weak	200	12°20′	0.0457	1.66	3.33±0.03
»	210	13°37′	0.0554	1.51	3.38±0.04
»	211	15°02′	0.0673	1.37	3.35±0.05
»	220	17°28′	0.0901	1.18	3.35±0.03
Extremely weak	300 221	18°45′	0.1033	1.107	3.32±0.02
» » »	311	20°24′	0.1214	1.021	3.38±0.03
Very weak	222	21°16′	0.1316	0.981	3.39±0.03
				Mean value	3.36±0.04

Table III

Compound	*b*, Å (NaCl type)	*a*, Å (CsCl type)	Limits of possible value
RbCl	6.56	3.82	$3.70 < a < 4.12$
RbI	7.32	4.34	$4.23 < a < 4.60$
KI	6.06	4.13	$3.51 < a < 3.81$
CsCl	7.10	4.20	$4.10 < a < 4.46$
NH_4Cl	6.53	3.86	$3.77 < a < 4.11$
NH_4Br	6.90	4.05	$3.99 < a < 4.33$
NH_4I	7.24	4.37	$4.18 < a < 4.55$

a is the lattice parameter of the new phase at atmospheric pressure.

The indexing showed that the high-pressure phase has a structure of the CsCl type. The average lattice parameter is $a_0 = 3.36 \pm 0.04$ Å; the density of the new phase is $\rho = 2.535$ g/cc; the density of the original phase is, according to the x-ray data, $\rho_0 = 2.165$ g/cc. The change of volume occurring during this transformation is $\Delta V = 14.2\%$ per mole.

If we follow the conclusions of Goldschmidt[14] that a transition accompanied by a change of coordination number from 6 to 8 leads to an increase of 3% in the distance between the differing ions, the predicted lattice parameter of the new phase of NaCl is 3.35 Å. This value is in good agreement with that found. A possible value for the lattice parameter of the new phase can also be obtained from the more general consideration that in a similar transformation the distance between nearest neighbors and the density of the substance both increase. If a is the lattice parameter of the transformed phase, and b that of the original, then from the first condition after the transformation we have $a > b \cdot 3^{-1/2}$ and from the second $a < b \cdot 2^{-2/3}$. It can be assumed, then, that the parameter a can be confined between the close limits

$$0.58\,b < a < 0.63\,b.$$

For b = 5.64009 Å, as in NaCl, the parameter a for the CsCl type structure should, under normal conditions, obey the relation $3.26 < a < 3.55$.

In Table III are assembled data for a series of salts which are transformed under pressure or temperature from the NaCl type structure to the CsCl type. For all salts except KI (a = 4.13 Å), the lattice parameters for the CsCl type structure satisfy well the inequality given above. More plausibly, in the case of KI the results given in the literature[7] are too high.

We also determined the variation of volume with pressure for the new phase. This variation is described by the equation (see Fig. 1)

$$-\Delta V/V_0 = 14.30 \cdot 10^{-2} + 36.0 \cdot 10^{-7}\,p - 60.0 \cdot 10^{-12}\,p^2,$$

where V_0 is the volume occupied by one molecule in the NaCl structure.

We also noted traces of the new phase after removing the pressure from the specimen. It might have been supposed that the preservation of the new phase after removing the pressure in the camera was aided by some pressure "locked" in the bore of the cone; however, an estimate of such residual pressure from the displacement of the lines of the original phase gives a value not greater than 600 atm.

A quantitative phase analysis which we made enabled us to evaluate the approximate proportion of the new phase in the specimens. It is known that the intensity of the diffraction rings for NaCl varies linearly with the volume of the substance participating in the scattering. Therefore the intensities of the lines in the x-ray photographs from the mixed specimens were compared with the intensities of the lines from specimens with 100% of the original phase.

The phase analysis showed that the specimen contained on average 2% of the new phase after the pressure was removed.

DISCUSSION OF RESULTS

It can now be affirmed that in table salt pressure causes a polymorphic transition with a change of structure into the CsCl type. A characteristic feature of this transformation is its exceptional sluggishness. The stability of the new phase at pressures close to atmospheric testifies to this, as does the fact that after a long time under pressure (an exposure lasted 10—20 hours) not more than 8% of the substance was transformed.

Shear forces occurring in our specimens also play a large part in the transition process. It is known that Jacobs[5] could not obtain transformation in an RbI specimen free from deformation by impressing a purely hydrostatic pressure of gas on it.

It is also possible that the further application of pressure leads to retardation of the transformation, and that it never proceeds throughout the entire mass of the specimen. The presence of a new phase in such a small volume specimen can be detected only with the aid of x-ray photographs, whereas the use of other methods for detecting a polymorphic transition necessitates establishment of a step change in some measured parameter—the magnitude of the step being usually related to the percentage of the transformed phase in the specimen.

As is well known, in Bridgman's experiment[1-4] the change in volume of a bulk specimen under hydrostatic pressure of liquid was measured while shear forces were insignificant. The experiment was performed rapidly compared with our prolonged exposures.

All that has been said above serves to explain why Bridgman did not detect a transformation in NaCl.

In the light of the new data, it is of interest to check the possibility of transitions in the lithium halides, since only in them has a transformation with a structure change into the CsCl type still not been discovered.

In conclusion we wish to draw attention to the fact that for all the cases studied in ionic crystals the face-centered cubic lattice structure changes into a CsCl type structure. It is, however, still difficult to say at present whether this is a general law.

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