

## 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<sup>2</sup>, 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  $a_0 = 3.36 \pm 0.04 \text{ \AA}$ , and the density  $\rho = 2.535 \text{ g/cc}$ .

## 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<sup>[1-4]</sup> 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<sup>[5]</sup> for RbI, by Vereshchagin and Kabalkina<sup>[6]</sup> for RbCl, and by Jamieson<sup>[7]</sup> 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<sup>[8]</sup>, and in the cesium salts the primitive structure changes into the face-centered on increasing the temperature.<sup>[9]</sup>

We have assembled in Table I published data on the conditions for polymorphic transitions in the alkali-halide compounds. It is seen that the tran-

sition 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.<sup>[10-12]</sup> 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<sup>2</sup>, 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.