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Polymorphic Transitions in Metallic Halides

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An x-ray powder analysis of RbI made at 4500 kg/cm^2 pressure and room temperature shows the crystal form of RbI to be body-centered cubic under these conditions. The lattice constant is 4.33_5A. The volume change from the face-centered lattice which is stable below 4000 atmospheres is 0.037 cm^3 per gram. This is about 0.009 cm^3 per gram greater than Bridgman's piston displacement value and the difference may be significant.

With the exception of the fluorides, all of the rubidium and potassium halides undergo polymorphic transformations under pressure, which in the light of the present knowledge of RbI are assumed to be of the face-centered to body-centered type. The method of Born and Mayer is used to calculate the lattice constants for both face- and body-centered types of each halide at the experimentally known temperature and pressure of equilibrium. From these the volume changes of the transformation are computed. They are found to agree quantitatively with the experimental values. Theoretical values for the transition pressure are also given. These are confirmed by experiment only in a qualitative manner, but the method may be used to explain, for instance, the nonoccurrence of transitions in the sodium halides up to 50,000 atmospheres. Similar calculations are made for AgI, the crystal form of which has been previously shown by the author to be face-centered cubic at pressures beyond 3000 kg/cm^2.

INTRODUCTION

THE alkali halides are known experimentally to exist in two cubic crystal forms (NaCl and CsCl types). The rubidium and the potassium halides (with the exception of the fluorine salts) have been found by Slater[1] and Bridgman[2, 3] to exhibit crystal polymorphism under pressure. These salts are of the NaCl type under atmospheric conditions. Intuitively, it is to be expected that the high pressure forms are of the CsCl type, and a supposition to that effect has generally been made. The present work includes an x-ray analysis of one of these halides (RbI) at a pressure considerably beyond the equilibrium pressure. The x-ray diffraction lines thus obtained show definitely that RbI at 4500 kg/cm^2 pressure is body-centered cubic (CsCl type). This would indicate a high probability that the other transitions are of the same type, i.e., face-centered to body-centered cubic.

The equilibrium lattice constants for the alkali halides may be determined theoretically by the method due to Born and Mayer.[4] With the various parameters empirically adjusted at one atmosphere the agreement between theoretical and experimental lattice values is excellent.[5] The parameters thus determined (on the basis of the known interatomic distances in the crystal forms, stable under atmospheric conditions) are used in the present case to determine the lattice distances for both crystal forms of each alkali halide, under conditions of temperature and pressure at which the two forms are known to be in equilibrium. This calculation involves an extension of the usual procedure to include the effect of pressure. The necessary additions to the theory will be described in a later part of this paper. From the lattice constants so determined one can readily deduce the change in volume which occurs when a given salt is transformed from the one crystal form to the other. These values may be compared with the experimentally determined values. For the rubidium halides the agreement is excellent. For the potassium salts the agreement is not so good, but is, nevertheless, quite satisfactory. Bridgman has failed to find transitions in the sodium halides up to pressures of 50,000 kg/cm^2. The present calculations show (in the case of NaI) that at 49,000 kg/cm^2 the volume change which would take place if a transition were to occur is already too small for a certain and accurate detection. If

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[1] J. C. Slater, Phys. Rev. **23**, 488 (1924).
[2] P. W. Bridgman, Zeits. f. Krist. **67**, 363 (1928).
[3] P. W. Bridgman, Phys. Rev. **48**, 893 (1935).
[4] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).
[5] M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

the transition were to take place at a slightly higher pressure, there would be no volume change at all. At still higher pressures the volume change is in such a direction as to favor the stability of the face-centered type of lattice. Since considerations of the energy involved in this transition indicate that the transition would not take place at a pressure lower than this (50,000 kg/cm^2), it may be logically predicted that the transition under hydrostatic pressure will not be found.

For the transformations which do occur, it should be possible to predict theoretically the equilibrium pressures. However, it is actually found that the uncertainties in the energy terms are usually too large to allow an accurate determination of these pressures. This is to be expected since the calculation of the pressure involves the difference in two energy terms, each of which is about a hundred times as large as the difference term. Nevertheless, the agreement with the experimental pressures is in all cases qualitatively satisfactory insofar as the pressure sequence for the six transitions involved is in perfect agreement with experiment. Numerically, the calculated pressures are found to be from $2\frac{1}{2}$ to 7 times greater than the experimental.

AgI has been previously shown by the author to exist under pressure in the face-centered cubic form.[6] AgCl and AgBr are known to be stable at atmospheric pressure in this crystal form, but have been found by Bridgman[7] to transform to another crystal form under pressure (presumably body-centered cubic). A similar transition from the face-centered form of AgI might reasonably be expected. Yet, efforts to detect the same have been unsuccessful up to pressures of 50,000 atmospheres. One may calculate the various factors involved in such a transition by using the same method as for the alkalis. The parameters computed by Mayer[8] are employed for this purpose. These calculations indicate that the transition will probably take place at a pressure beyond 50,000 atmospheres. The volume change to be expected is small, but increases with increasing pressure (in contrast to NaI). This excludes the chance of its changing sign, thus making the occurrence of the transition an impossibility.

THE TRANSFORMATION: RbI(I) INTO RbI(II)

The transition pressure for RbI(I) and RbI(II) is given by Bridgman[2] as 3,900 kg/cm^2 at 25°C. There is a certain region of "indifference" (region of possible metastable equilibrium) which amounts to something like 200 kg/cm^2 on either side of the equilibrium curve. By use of the pressure camera described by the author in a previous publication,[6] an attempt was made first to obtain a diffraction pattern from RbI(II) at 4700 kg/cm^2, which is 800 kg/cm^2 beyond the equilibrium pressure, and 600 kg/cm^2 beyond the region of indifference as found by Bridgman. The diffraction lines so obtained indicated that the salt remained completely in the form of RbI(I). Several attempts were then made on pretreated specimens (specimens previously subjected to high pressures) since it is sometimes found that the transitions take place more readily for these. The results of these experiments were likewise negative, as were attempts to transform the salt through heating by mounting it on a resistance wire in the camera and passing a current through the same after the application of pressure. The material used in these experiments was Eimer and Amend's C.P. (presumably of about the same purity as the stock used by Bridgman). Through the generosity of Professor Archibald of the University of British Columbia, the author obtained some rubidium salt of "atomic weight" purity. Professor Baxter of Harvard University kindly converted the same into RbI, by utilizing "atomic weight" iodine for this purpose. Several runs were made with this salt, and it was found to transform readily at pressures as low as 4000 kg/cm^2.

A certain significance is attached to these experiments. In the x-ray pressure camera used in the present case, the *pressure is perfectly hydrostatic*, since the individual crystal grains are acted upon only by helium gas. In the case of Bridgman's experiments the pressure is only approximately hydrostatic, since he employed a free-piston type of piezometer. The salt was placed under kerosene in an accurately machined

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[6] R. B. Jacobs, Phys. Rev. **54**, 325 (1938).
[7] P. W. Bridgman, Proc. Am. Acad. **72**, 63 (1937).
[8] J. E. Mayer, J. Chem. Phys. **1**, 327 (1933).

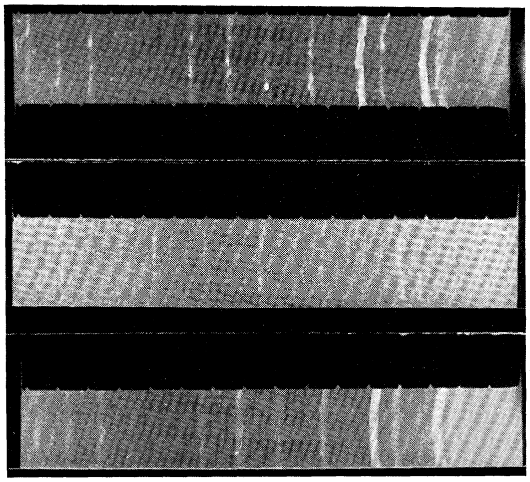

FIG. 1. Above: RbI(I) before transformation. Center: RbI(II) at 4500 atmospheres. Below: RbI(I) after transformation.

cylinder and was separated from the external hydrostatic compressive medium by means of an accurately fitted, freely-moving piston. In this case the pressure was partially transmitted from grain to grain as a mechanical force, which certainly cannot be regarded as hydrostatic as far as single grains are concerned. Shearing forces are unquestionably present. The effect of large shearing forces on polymorphic transitions has been demonstrated by Bridgman,[9] but the role played by small accidental shearing forces in the usual "hydrostatic" pressure experiment has not been previously recognized. In the present case the lack of these in the pressure camera undoubtedly is a large factor in accounting for the inability to transform the commercially obtainable C.P. salt.

The actual mechanism of a polymorphic crystal transformation has not been well explained. The role of an impurity is not known. The large effect produced by the impurities present in the "C.P." RbI in the present investigation is not a common experience. In the first place a foreign atom is generally regarded as a favorable site for the nucleus of a new crystal, and hence as a catalyst rather than as an inhibitor of a transition. The instantaneous crystallization of an undercooled liquid upon the introduction of foreign particles is a familiar example of this action. The role of the impurities in the RbI appears to be of a different nature. It is possible that they are segregated to a certain extent and localized on the intercrystalline boundaries of the mosaic crystals. Here it is possible that their action might be such as to prevent cooperative action from one mosaic to the next. It would not be difficult to explain the action of shearing forces in overcoming the effect of such impurities.

The question also arises as to the role of the individual crystal grain in a polymorphic transition, i.e., does it transform as a unit, or does it break up into smaller parts? In the case of transitions induced by temperature, the grain size is generally reduced materially. Here thermal agitation may be an important factor in breaking up the crystal grains. This is a factor which is eliminated in a pressure transition, and hence it becomes of interest to study the grain size with the pressure camera. In the case of $CsClO_4$, it has already been observed[6] where two crystal forms were simultaneously present, that the new phase was composed of the larger crystal grains, and showed in this case that a transformation is more likely to occur in a large grain than in a small one. Fig. 1 shows the effect of a transformation on the grain size of RbI. The three diffraction diagrams represent the condition of the same sample before, during, and after the application of pressure. The upper diagram is "splotchy" and indicates a large grain size. The lower diagram is uniform and the lines broadened which indicates a considerable "breaking up" of individual grains. The x-ray evidence would then unmistakably show first, that the larger crystals are the more likely to transform,

TABLE I. *Diffraction data for* RbI(II). *Temp.* 25°C. *Pressure* 4500 kg/cm^2.

BRAGG ANGLE (×2) 2θ (DEGREES)	MILLER INDICES h, k, l	INTERPLANAR DISTANCE $d_{h,k,l}$ (A)	LATTICE CONSTANT d (A)
28.88	110	3.08_6	4.36_3
41.46	100(2)	2.17_4	4.34_8
51.43	121	1.77_5	4.34_8
60.15	110(2)	1.53_7	4.34_7
68.16	130	1.37_2	4.33_9
82.94	123	1.15_9	4.33_6
97.97	101(3)	1.02_1	4.33_0
105.13	120(2)	0.968_1	4.33_0
129.60	431	0.850_3	4.33_6
	Lattice constant $= 4.33_5$A		

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[9] P. W. Bridgman, Proc. Am. Acad. **71**, 387 (1937).

and second, that there is an appreciable subdivision of grains in a pressure transition.

The data for the crystal structure of RbI(II) are given in Table I, in which the measured values from the more intense lines of the diffraction pattern are used.

From the lattice constant thus found one may compute the volume change from RbI(I) to RbI(II). This gives a value of 0.037 cm^3/gram at 4500 kg/cm^2 which is about 0.009 cm^3/g greater than Bridgman's piston displacement value. The scattering of Bridgman's experimental points would indicate a maximum allowable error of 0.005 cm^3/gram in his measurements. The uncertainties in the lattice constants should not introduce more than 0.003 cm^3/g error. In the most unfavorable case, the difference between the piston-displacement and the x-ray values could then possibly be attributed to experimental uncertainties. In the case of AgI the author found a similar situation, which could not be attributed reasonably to experimental error. In that case it was pointed out that an incomplete transition will result in too low a measured volume change for the piston-displacement method. Definite evidence was also given for the existence of a partial transition. It is possible that the present investigation affords another example of this phenomenon.*

CALCULATIONS

It is desirable to calculate the lattice constants of the various halides at the pressures at which the two crystal forms are known to exist in equilibrium. Since it is the usual procedure to make such calculations at zero pressure, some small alterations in the method are necessary. We use the thermodynamic potential Φ, defined as follows:

$$\Phi = U - TS + PV. \qquad (1)$$

For equilibrium of a single phase,

$$(\partial\Phi/\partial V)_{T,P} = 0 = \partial U/\partial V - T(\partial S/\partial V) + P,$$

or
$$\partial U/\partial V = T(\partial S/\partial V) - P. \qquad (2)$$

The "temperature term," $T(\partial S/\partial V)$, may be further reduced, since

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V = -(\partial V/\partial T)_P/(\partial V/\partial P)_T = \alpha_T/\beta. \qquad (3)$$

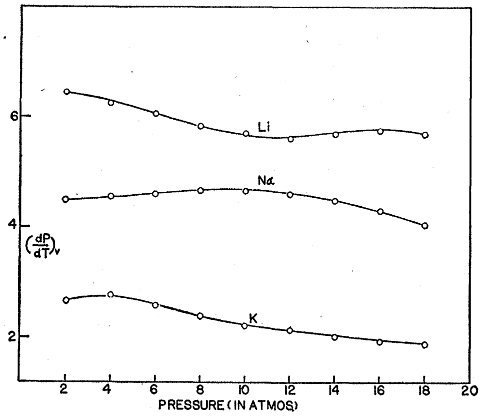

FIG. 2. $(\partial P/\partial T)_V$ as a function of pressure for the alkali metals. (Data from Bridgman.)

At atmospheric pressure the values of α_T and β (thermal expansion and compressibility, respectively) are known and may be used to compute $(\partial P/\partial T)_V$. On the other hand, at high pressures the values for α_T are not known in the case of the alkali halides, and one cannot compute $(\partial P/\partial T)_V$ directly at any optional pressure. However, it seems reasonable that the quantity is invariant with pressure. In the case of the alkali metals Bridgman[10] has given sufficient data for the evaluation of $(\partial P/\partial T)_V$ over a considerable range of pressures. The values thus obtained are shown plotted in Fig. 2. Here no significant variation of the quantity with the pressure is in evidence. In the following calculations on the metallic halides, the assumption is made that $(\partial P/\partial T)_V$ is constant with respect to pressure. This assumption is not too hazardous, since even a considerable variation in the value of this quantity would affect the lattice constants only slightly. Physically, this

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* Professor Bridgman has informed the author that he has recently repeated his experiments on AgI, using a somewhat modified procedure. He now subjects the salt to a pressure far in excess of the equilibrium pressure. The volume change is then measured as the pressure is reduced below its equilibrium value, and again when the pressure is raised a second time. He now obtains a volume change of about 0.0280 cc/g which is in agreement with the x-ray values. Apparently the treatment at very high pressures overcomes the inability of the salt to completely transform near equilibrium pressure.

[10] P. W. Bridgman, Proc. Am. Acad. **70**, 93 (1935).

TABLE II. *Calculations for transitions in rubidium halides.*

PRESSURE USED IN CALCULATIONS (kg/cm²)		RbCl f.c.	RbCl b.c.	RbBr f.c.	RbBr b.c.	RbI f.c.	RbI b.c.
		5,500		5,000		4,500	
r (obs.)	$\times 10^8$ cm	3.23_5		3.38		3.61_5	3.75
r (cal.)	"	3.24	3.39	3.38	3.54	3.61	3.78
C	$\times 10^{60}$ erg-cm^6	691	1,023	898	1,348	1,330	2,039
D	$\times 10^{76}$ erg-cm^8	96	147	134	209	224	367
$C/r^6+D/r^8$	$\times 10^{12}$ ergs	0.68	0.76	0.68	0.77	0.68	0.79
$\alpha l^2/r$	"	12.27	11.83	11.76	11.33	11.02	10.61
$(3T/NB)(dV/dT)$*	"	0.90	0.79	0.91	0.81	1.06	0.94
$(3V/N)P$	"	1.10	0.98	1.14	1.01	1.24	1.10
$B(r)$	"	1.72	1.67	1.65	1.56	1.45	1.39
E	"	11.23	10.92	10.80	10.54	10.25	10.41
Vol. (cal.)	$\times 10^{24}$ cm^3	$68._0$	$60._0$	$77._2$	$68._3$	$94._1$	$83._2$
ΔV (cal.)	"		$8._0$		$8._9$		$10._9$
ΔV (obs.)	"		$9._7$		$8._7$		$(9._6, 12._9)$†
P (cal.)	kg/cm^2		39,000		30,000		22,000
P (obs.)	"		5,500		5,000		4,000

* α/B—taken as same for both body-centered and face-centered types.
† —piston displacement and x-ray values, respectively.
NOTE.—For a summary of values used for compressions, thermal expansions, etc., see reference 5.

TABLE III. *Calculations for transitions in potassium halides.*

PRESSURE USED IN CALCULATIONS (kg/cm²)		KCl f.c.	KCl b.c.	KBr f.c	KBr b.c.	KI f.c.	KI b.c.
		19,000		17,000		17,000	
r (obs.)	$\times 10^8$ cm	3.05		3.19_5		3.40_5	
r (cal.)	"	3.04	3.21	3.19	3.37	3.40	3.60
C	$\times 10^{60}$ erg-cm^6	452	682	605	930	924	1,472
D	$\times 10^{76}$ erg-cm^8	560	893	800	1,343	1,420	2,521
$C/r^6+D/r^8$	$\times 10^{12}$ ergs	0.65	0.70	0.65	0.72	0.68	0.77
$\alpha l^2/r$	"	13.08	12.49	12.47	11.90	11.70	11.14
$(3T/NB)(dV/dT)$	"	0.91	0.82	0.95	0.87	1.02	0.94
$(3V/N)P$	"	3.14	2.85	3.35	3.04	3.92	3.60
$B(r)$	"	2.12	1.96	1.98	1.82	1.86	1.72
E	"	11.61	11.24	11.14	10.80	10.51	10.19
Vol. (cal.)	$\times 10^{24}$ cm^3	$56._2$	$51._0$	$64._9$	$59._0$	$78._6$	$71._9$
ΔV (cal.)	"		$5._2$		$5._9$		$6._7$
ΔV (obs.)	"		$6._7$		$6._4$		$7._2$
P (cal.)	kg/cm^2		74,000		59,000		49,000
P (obs.)	"		20,000		19,000		18,000

quantity gives the difference between the lattice constants at absolute zero and at the temperature at which the calculation is made.

The internal crystal energy may be subdivided, i.e.

$$U=U(T)+E(r)+h\nu_0/2. \tag{4}$$

$U(T)$ represents the thermal energy and $E(r)$ the lattice energy proper. The latter quantity is given by the expression:

$$E(r)=-\alpha e^2/r-C/r^6-D/r^8+B(r). \tag{5}$$

These terms represent the electrostatic, the dipole-dipole, the dipole-quadrupole, and the repulsion energies, respectively. Eq. (5) substituted into Eq. (2) gives the equation:

$$3TV\alpha_T/N\beta+3PV/N=\alpha e^2/r+6C/r^6+8D/r^8+\partial B(r)/\partial r. \tag{6}$$

This expression may be solved for r, the distance between nearest neighbors in the crystal. The values for the van der Waals coefficients C and D, and for the repulsion coefficients in $B(r)$ are taken from papers by Huggins and Mayer[5] and by Mayer.[11]

Equation (5) serves for the evaluations of $E(r)$ after the values for (r) are obtained. Equilibrium between the two phases of the crystals (b.c. and f.c.) requires that their thermodynamic potentials be equal, or that:

$$\Phi_1=\Phi_2,$$

or $$U_1-TS_1+PV_1=U_2-TS_2+PV_2. \tag{7}$$

For the alkali halides it is known from experiment that the equilibrium curves in the $P-T$ plane run almost parallel to the temperature axis. This indicates that the temperature terms are very nearly the same for each phase, and hence they can be neglected in comparison with the pressure terms. With this simplification, Eq. (7) becomes

$$E_1(r)+PV_1\simeq E_2(r)+PV_2$$

or $$P\simeq\frac{E_2(r)-E_1(r)}{V_1-V_2} \tag{8}$$

from which one may solve for P, the equilibrium pressure. Not much accuracy can be expected here because P will be a small difference between two large terms.

In the calculations given below, the interatomic radii are solved for at the experimental equilibrium pressures and at room temperature. These radii are substituted into Eq. (8) for the solution for P. This is a first approximation for P. More accurately, one would take this value of P, and again solve for the equilibrium radii, and use these in turn for a better approximation of P. Actually, this is not done, since the very approximate nature of the P's obtained does not warrant the effort involved in carrying out the second approximation.

The results of these calculations for the rubidium and potassium halides are given in Tables II and III. Sodium iodide is given in Table IV.

DISCUSSION OF RESULTS

A comparison of the calculated and experimental interatomic distances for the face-

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[11] J. E. Mayer, J. Chem. Phys. 1, 270 (1933).

TABLE IV. *Calculations for transitions in* NaI.

PRESSURE USED IN CALCULATIONS (kg/cm²)		f.c. 0	b.c. 0	f.c. 49,000	b.c. 49,000
r (obs.)	$\times 10^8$ cm	3.23		3.03_5	
r (cal.)	"	3.23	3.50	3.04	3.31
C	$\times 10^{60}$ erg-cm^6	482	864	482	864
D	$\times 10^{76}$ erg-cm^8	630	1,436	630	1,436
$C/r^6+D/r^8$	$\times 10^{12}$ ergs	0.48	0.53	0.70	0.76
$\alpha l^2/r$	"	12.31	11.46	13.08	12.12
$(3T/NB)(dV/dT)$	"	1.16	1.13	0.97	0.96
$(3V/N)P$	"	0	0	8.10	8.05
$B(r)$	"	1.40	1.28	2.54	2.30
E	"	11.39	10.72	11.24	10.57
Vol. (cal.)	$\times 10^{24}$ cm^3	$67._4$	$66._1$	$56._2$	$55._9$
ΔV (cal.)	"		$1._3$		$0._3$
ΔV (obs.)	"		—		—
P (cal.)	kg/cm²				No trans.
P (obs.)	"	—	None to 50,000		—

centered lattices shows good agreement in all cases over a wide pressure range. This is particularly significant in the case of sodium iodide in which the over-all volume change is almost 20 percent in 50,000 atmospheres and where the final compressibility is roughly one-fourth the original.[12] This agreement would indicate that the van der Waals coefficients were of about the correct magnitude, and that the exponential form of the repulsion coefficient gives a fairly good representation of experimental fact. Rubidium iodide furnishes the only experimental observation of a body-centered halide in this group. The agreement here is not quite as good as for the face-centered types.

The volume changes provide the most interesting part of the calculations. They, of course, involve the lattice constants of both the face-centered and the body-centered structures (assumed, except RbI). It will be observed that in every case the experimental and theoretical volume changes check within the limits of accuracy to be expected. The method can therefore be regarded as entirely satisfactory for such calculations.

Enough has been said about pressure calculations to indicate that no especial agreement can be expected here. However, it may be pointed out that for the six salts which are known to have high pressure modifications, the pressure sequence as given by the theory is confirmed by experiment.

It has been suggested in the literature[13] that better energy relations may be obtained in the case of NH_4Cl and CsCl by multiplying the van der Waals coefficients by some arbitrary factor, which, in turn, involves a recalculation of the repulsion coefficients. Since the energy difference between a body-centered and a face-centered lattice is not very sensitive to variations in the van der Waals forces, an appreciable energy change can result only from a large variation in the forces. This, of course, results in a new calculated compressibility. In view of the apparent validity of the present theoretical compressibilities, one could not justify a serious alteration of the van der Waals constants as used. It is possible that the energy discrepancies may be traced to some nonionic force. It is pointed out, however, that the pressure calculations can be expected to be more accurate for very high pressure transitions, since the energy deviations are approximately constant for any halide series. Thus if the values 19, 20, and 26×10^{-14} erg/molecule are subtracted from the calculated energy differences of the iodides, the bromides, and the chlorides, respectively, the calculated pressures will in all cases agree with the experimental to better than 1000 kg/cm². Hence, if the sodium halides were to exhibit polymorphism under pressure, one would expect the calculated pressures to approximate more closely the experimental values than they did in the case of rubidium or potassium.

No pressure transformations have been observed in the sodium halides up to 50,000 kg/cm². By analogy we would expect NaI to transform first in the sodium series. It is worth while to consider the theoretical predictions for this salt. The calculations (Table IV) are made for atmospheric and for 49,000 kg/cm² pressure. For the latter pressure the calculated volume change is very small (of the order of magnitude of a probable deviation of an experimental point). At still higher pressures the volume change will reverse its algebraic sign. The energy difference between the two crystal phases at 49,000 kg/cm² and below is sufficiently large to indicate with some certainty that the face-centered lattice is always stable in this region. Above 49,000 kg/cm², the reversal of sign in the volume term will preclude the possibility of building a sufficiently high external work term ($p\Delta v$) to equal the internal energy difference. In view of these

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[12] P. W. Bridgman, not yet published.

[13] A. May, Phys. Rev. **52**, 339 (1937).

considerations, it is fairly safe to predict that NaI will not experience a face-centered to body-centered transformation under hydrostatic pressure alone.

SILVER IODIDE

Mayer[8] has evaluated the van der Waals and the repulsion coefficients for AgI, and has pointed out that a NaCl type of lattice is theoretically more stable than the ZnS type *unless* homopolar energy is associated with the latter type of lattice. The experimental values for the lattice constant which he derived for the ZnS type of lattice were too large. This was likewise explained by the presence of homopolar binding. At the present time it is possible through the knowledge of the existence of AgI in the NaCl type lattice at high pressures to test further the validity of Mayer's assumptions. The calculations for AgI are summarized in Table V. The agreement between theory and experiment for the lattice constant of the face-centered lattice at 3750 kg/cm² is here regarded as a check on the correctness of the van der Waals and repulsion terms used. This would remove doubt as to a possible explanation of Mayer's results through his use of incorrect values in these quantities rather than in the existence of the homopolar energy assumed. The calculated energy difference between the face-centered lattice and the ZnS type amounts to 55×10^{-14} erg per molecule at 3,750 kg/cm², where the two forms are now known to exist simultaneously. The external work and temperature terms can account only for a few percent of this energy. The conclusion that the ZnS lattice is not purely ionic, appears inescapable at this point.

TABLE V. *Calculations for transitions in* AgI.

PRESSURE USED IN CALCULATIONS (kg/cm²)		(ZnS)	f.c.	b.c.	f.c.	b.c.
		3,750	3,750	3,750	145,000	
r (obs.)	$\times10^8$ cm	2.80	3.03_5		—	
r (cal.)	"	(~2.95)	3.05	3.30	2.85	3.07
C	$\times10^{60}$ erg-cm^6	850	1,450	2,209	1,450	2,209
D	$\times10^{76}$ erg-cm^8	1,467	2,460	4,000	2,460	4,000
$C/r^6+D/r^8$	$\times10^{12}$ ergs	2.15	2.14	2.00	3.27	3.14
$\alpha l^2/r$	"	13.34	13.04	12.15	13.95	13.06
$(3T/NB)(dV/dT)$	"	1.47	.62	.61	.51	.49
$(3V/N)P$	"	.74	.63	.61	19.72	19.00
$B(r)$	"	3.05	2.19	2.10	4.79	4.74
E	"	12.43	12.98	12.05	12.43	11.47
Vol. (cal.)	$\times10^{24}$ cm^3	—	$56._7$	$55._5$	$46._3$	$44._6$
ΔV (cal.)	"		$10._7$	$1._2$		$1._7$
ΔV (obs.)	"		*(9_2), (11_5)	—		—
P (cal.)	kg/cm²			$\sim8\times10^5$		$\sim6\times10^5$
P (obs.)	"			None to 5×10^4		None to 5×10^4

* Piston displacement and x-ray values, respectively.

AgBr and AgCl at atmospheric pressure crystallize into the face-centered cubic form. Bridgman[7] has found each of these to have polymorphic transitions at pressures around 13,000 kg/cm² (presumably from f.c. to b.c.). It appeared probable that AgI could be further transformed; i.e., from its high pressure face-centered lattice to a body-centered crystal. Professor Bridgman[14] tried the experiment up to 50,000 atmospheres without success. It is possible that the transition will take place at a higher pressure. Two approximations are shown in Table V for the theoretical pressures. Because of the small volume change to be expected the uncertainties in pressures are large. They do, however, agree with the experiment insofar as no face-centered to body-centered transition is predicted below 50,000 atmospheres. It is pointed out that here the face-centered lattice is the least compressible. The calculated volume change *increases* with pressure, and makes the eventual occurrence of the transition highly probable.

In conclusion the author wishes to express his gratitude to Professor Bridgman for many discussions on this subject and for the extensive use of his experimental material.

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[14] Not yet published.

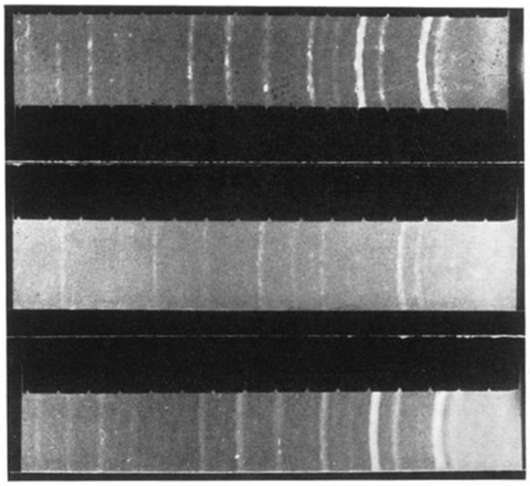

FIG. 1. Above: RbI(I) before transformation. Center: RbI(II) at 4500 atmospheres. Below: RbI(I) after transformation.