

Effect of Pressure on the Crystal Structure of CsMnCl₃ and RbMnCl₃*

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Received January 21, 1971

The hexagonal 9R structure of CsMnCl₃ has been found to transform at ~10 kbar to the 6H polytype structure ($a = 7.268 \text{ \AA}$, $c = 17.85 \text{ \AA}$) and further transform above ~25 kbar to the 3C polytype structure ($a = 5.111 \text{ \AA}$). A pressure-temperature phase diagram is presented. At pressures greater than 7 kbar the 6H polytype structure of RbMnCl₃ transforms to the 3C polytype structure ($a = 5.058 \text{ \AA}$). The quenched high pressure phases of Cs and Rb are stable at atmospheric pressure to 300 and 400°C, respectively. These polytype transformations are related to similar ones found for ABX₃ compounds where X is fluorine or oxygen.

Introduction

There is a large class of structurally related compounds that have the general composition ABX₃, where A is a large cation, B is a smaller cation able to accept octahedral coordination, and X is an anion such as O, S, F or Cl. The structures of this class all contain close-packed AX₃ layers having cubic (*c*) or hexagonal (*h*) stacking of successive layers, the B cations occupying the all-anion octahedra. If all layers are hexagonal close-packed, the octahedra form isolated chains of face-shared octahedra as shown in Fig. 1a. This structure is designated (2H), in accordance with polytype notation, which indicates two formula units per hexagonal primitive cell. If two-thirds of the layers are hexagonal close packed in the sequence *hhc*, the octahedra form face-shared triples joined by common corners. This arrangement is shown in Fig. 1b and is designated 9R. For one-third hexagonal close packing in the sequence *chcch*, the octahedra form face-shared pairs connected by intermediary octahedra that share only corners. Figure 1c shows this arrangement, which is designated 6H. When all layers are cubic close packed, the octahedra share only corners. This gives the perovskite structure represented by Fig. 1d and designated 3C. These four polytypes (2H, 9R, 6H and 3C) are the only ones found for stoichiometric ABX₃ compounds when X is F, Cl

or Br. Katz and Ward discuss these and other related structures in greater detail in Ref. (1).

It has been shown that high pressure always favors a polytype structure with more cubic close packing

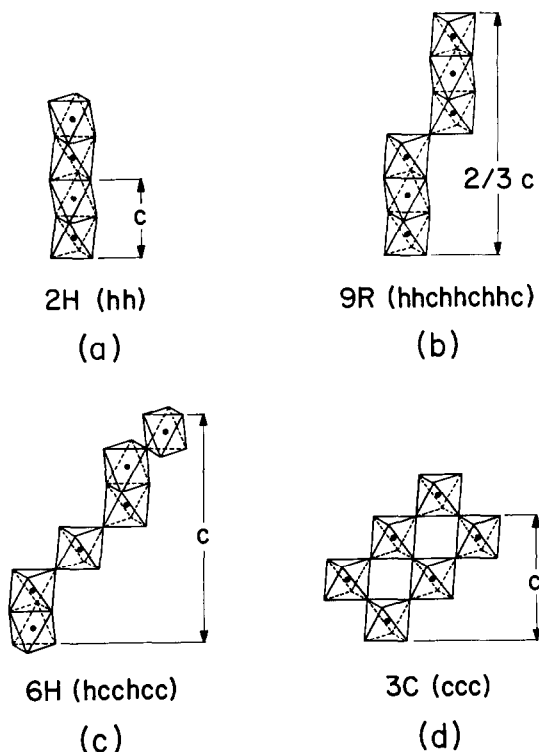


FIG. 1. Octahedral arrangement for ABX₃ polytypes.

* This work was sponsored by the Department of the Air Force.

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if X is oxygen (2, 3, 4), fluorine (3, 5, 6, 7), or chlorine (8). We describe in this paper the effect of high pressure on the structures of CsMnCl_3 and RbMnCl_3 , which at atmospheric pressure have the 9R and 6H structures, respectively (9, 10, 11).

Experimental

The atmospheric-pressure forms of CsMnCl_3 and RbMnCl_3 were prepared by reacting stoichiometric amounts of the respective alkali chloride and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a flowing stream of dry HCl or N_2 gas. The samples, contained in silica boats, were first heated to 200°C and held for a few hours to allow all the water of hydration to be removed. The temperature was then raised to 500°C for a few more hours, followed by cooling in the furnace with the gas still flowing. The products were characterized by X-ray powder diffraction using a Norelco vertical diffractometer with graphite monochromated CuK_α radiation. Since both the atmospheric and high-pressure phases are hygroscopic, all X-ray diffraction was performed with the entire goniometer enclosed in a large glove bag filled with flowing dry nitrogen. The powder diffraction patterns obtained for atmospheric pressure samples of CsMnCl_3 and RbMnCl_3 are in good agreement with those published earlier (10, 11).

All high pressure runs were performed in a belt apparatus (12) capable of developing pressures to 90 kbar. In a typical run, a sample of the freshly prepared atmospheric-pressure phase was loaded, within a glove bag filled with dry nitrogen, into a cylindrical gold capsule having gold end plugs. The specimen was first subjected to the desired pressure, and then the temperature was raised rapidly with an internal tubular graphite heater. After a half-hour at temperature, the sample was quenched to room temperature by shutting off the power to the heater. Finally, the pressure was released, and the product was studied by powder X-ray diffraction as described above.

Results and Discussion

CsMnCl_3 with the 9R structure was found to transform to the 6H structure at 8 kbar and 700°C. It transforms to the cubic perovskite structure (3C) at 27 kbar and 700°C. Since the perovskite structure has only cubic close packing, no further transformations are expected. The same progression of transformations (9R \rightarrow 6H \rightarrow 3C) with high pressure is found for CsCoF_3 (13). Figure 2 summarizes these

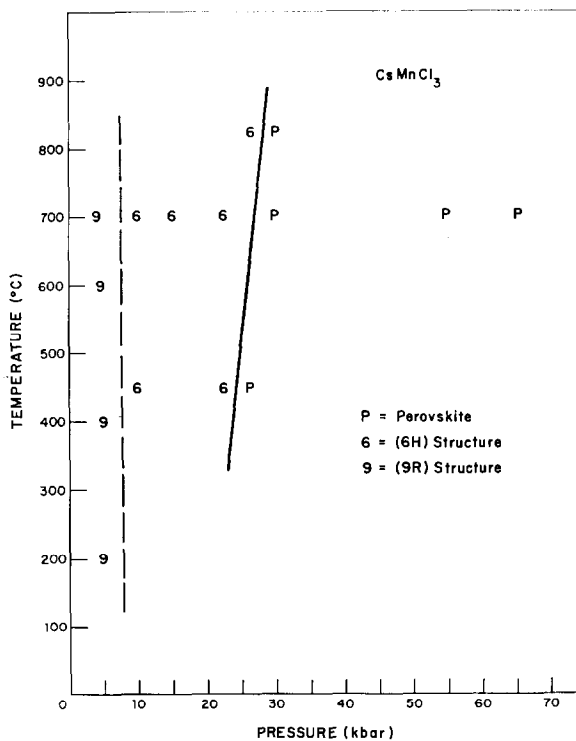


FIG. 2. Temperature vs. pressure phase diagram for CsMnCl_3 .

results in a pressure-temperature phase diagram and shows the general temperature insensitivity of these structural transformations. Phase diagrams for various fluorides (5, 6) having these structures show similar temperature dependence.

Table I lists our observed X-ray data for the 6H polytype and compares the observed intensities to intensities calculated for a model with ideal close-packed positions for all atoms and an overall temperature factor of 1.0. There are discrepancies between observed and calculated intensities that are outside of our experimental error and they indicate that some of the atoms which are allowed by the space group to vary, have moved from their ideal positions. This would be quite consistent with the refined 6H structures of RbNiF_3 (14, 15), CsCdCl_3 (16), and CsMnF_3 (17), where some atoms have moved significantly from their ideal close-packed positions.

Table II lists our observed X-ray data for the perovskite (3C) form of CsMnCl_3 and compares observed intensities to the intensities calculated for the ideal perovskite structure and an overall temperature factor of 1.5. The agreement between observed and calculated intensities is quite good and

TABLE I
X-RAY DATA FOR HIGH PRESSURE CsMnCl₃(6H)

$a = 7.268(5) \text{ \AA}$				$c = 17.85(5) \text{ \AA}$ (hexagonal)			
hkl	I_{calcd}^a	I_{obsd}	d_{obsd}	hkl	I_{calcd}	I_{obsd}	d_{obsd}
1 0 2	1.6	4	5.12	3 0 3	0.1	26	1.984
0 0 4	1.1	2	4.43	2 1 5	1.0		
1 0 3	30.8	33	4.30	2 0 7	25.0	8	1.898
1 1 0	100.0	175	3.48	3 0 4	1.2		
1 0 4	72.6			1 1 8	7.9		
1 1 2	2.3	—	—	2 2 0	54.1	75	1.819
2 0 1	14.4	17	3.10	2 0 8	17.0		
1 0 5	1.3			2 1 7	18.8	15	1.743
2 0 2	42.3	70	2.961	2 2 4	0.5		
0 0 6	27.2			3 1 3	5.0	15	1.679
1 1 4	3.9	—	—	2 0 9	10.4		
2 0 3	86.7	90	2.778	3 1 4	14.4	15	1.625
2 0 4	94.9	90	2.566	2 1 8	2.4		
2 1 1	0.3	32	2.360	4 0 1	1.6	6	1.569
2 0 5	12.5			3 1 5	0.4		
1 0 7	24.0	4	2.297	1 0 1 1	5.7	22	1.552
2 1 2	0.4			4 0 2	5.1		
1 1 6	1.2	—	—	2 2 6	19.5	5	1.527
0 0 8	1.4	—	—	2 0 1 0	8.2		
2 1 3	12.9	12	2.209	3 0 8	3.8	15	1.522
3 0 0	22.7	58	2.099	4 0 3	11.9		
2 1 4	31.1			2 1 9	1.0	18	1.487
1 0 8	3.1	4 0 4	15.3				
				0 0 1 2	5.4		

^a Based on ideal close-packed positions for all atoms.

confirms the perovskite structure for CsMnCl₃ above 27 kbar.

Both high pressure forms of CsMnCl₃ have moderate stability at atmospheric pressure. There was no sign of retransformation after treatment at 200°C in N₂ for 3 days, but there was complete retransformation to the 9R structure after heating a few hours at 300°C. All of the high pressure forms of CsBF₃ compounds transform to the atmospheric phase at 200–500°C, while many of the ABO₃ compounds have high pressure forms that only slowly retransform at 1100°C and atmospheric pressure. A summary of crystallographic data, including unit cell volumes for all forms of CsMnCl₃, are given in Table III.

The 6H atmospheric-pressure structure of RbMnCl₃ transforms to the cubic perovskite

TABLE II
X-RAY DATA FOR THE HIGH PRESSURE PEROVSKITE FORMS OF AMnCl₃

CsMnCl ₃ ($a = 5.111(3) \text{ \AA}$)			RbMnCl ₃ ($a = 5.058(3) \text{ \AA}$)			
d_{obsd}	I_{obsd}	I_{calcd}	hkl	I_{calcd}	I_{obsd}	d_{obsd}
5.11	8	6	1 0 0	1.4	1	5.05
3.62	100	100	1 1 0	84	85	3.57
2.95	61	65	1 1 1	66	70	2.915
2.55	82	81	2 0 0	100	100	2.526
2.285	4	4	2 1 0	0.4	0	—
2.087	44	44	2 1 1	37	40	2.067
1.805	47	51	2 2 0	62	55	1.791
1.705	2	{0.4 1.6}	{3 0 0 2 2 1}	{0.0 0.1}	0	—
1.616	19	18	3 1 0	15	16	1.595
1.541	22	22	3 1 1	21	16	1.520
1.475	16	16	2 2 2	19	16	1.457
—	0	0.9	3 2 0	0.0	0	—
1.366	18	20	3 2 1	16	14	1.350
1.278	8	7	4 0 0	8	9	1.262
—	0	{0.6 0.6}	{4 1 0 3 2 2}	{0.0 0.0}	0	—
1.205	9	{6 3}	{4 1 1 3 3 0}	{5 2}	8	1.193
1.172	8	8	3 3 1	8	7	1.159
1.143	16	18	4 2 0	21	16	1.131
1.117	1	0.9	4 2 1	0.0	0	—
1.090	4	4	3 3 2	3	2	1.079
1.044	10	13	4 2 2	16	10	1.032
—	0	{0.1 0.4}	{5 0 0 4 3 0}	{0.0 0.0}	0	—
1.003	9	{3 6}	{5 1 0 4 3 1}	{2 5}	5	0.992
0.983	5	{5 1}	{5 1 1 3 3 3}	{5 2}	2	0.974

structure (3C) above 7 kbar at 700°C. As with CsMnCl₃, this transformation is not very sensitive to temperature. Compounds, such as RbNiF₃, TiNiF₃, CsFeF₃ and CsMnF₃, all of which have the same 6H structure at atmospheric pressure, also transform to the perovskite structure at high pressure (3, 5, 7). Table II lists our observed X-ray data and compares it to intensities calculated for the ideal perovskite structure ($a = 5.058 \pm 0.003 \text{ \AA}$) and an overall temperature factor of 1.5. The table is also constructed to show the similarities of the highest-pressure forms of CsMnCl₃ and RbMnCl₃. In Table III, the crystallographic data, including unit-cell volumes, are given for all forms of CsMnCl₃ and RbMnCl₃. At atmospheric pressure, the perovskite

TABLE III
CRYSTALLOGRAPHIC DATA FOR $AMnCl_3$ ($A = Cs, Rb$)

Compound	Polytype structure	Synthesis pressure (kbar)	Cell dimensions (Å)	Volume formula unit (Å ³)
CsMnCl ₃	9R	Atm-10	7.288 × 27.44 ⁽¹¹⁾	137.9
	6H	10-25	7.268 × 17.85	136.1
	3C	Above 25	5.111	133.5
RbMnCl ₃	6H	Atm-7	7.165 × 17.815 ⁽¹⁰⁾	132.0
	3C	Above 7	5.058	129.4

form of RbMnCl₃ is stable in dry N₂ to 300°C, but transforms to the 6H form when heated for a few hours at 400°C.

It is interesting to note that, whether the starting materials are prepared in HCl or N₂ gas, there are no observable differences in the transition pressures or cell dimensions for CsMnCl₃ and RbMnCl₃. However, samples prepared in HCl gas are very hygroscopic while those prepared in N₂ gas are not affected by normal humidity at room temperature. One can speculate that the difference is due to the presence of small amounts of hydroxide that have remained after the calcining and reaction of MnCl₂·4H₂O. Once incorporated at low temperatures, the hydroxide is not removed by further heating in nitrogen but can be replaced by heating in hydrogen chloride gas. There also exists the possibility that very small amounts of nitride ions are replacing chloride ions when the starting materials are prepared in N₂ gas.

At atmospheric pressure, the series of alkali-metal manganese chlorides AMnCl₃ ($A = Cs, Rb, Tl, K$) shows the usual trend of more cubic close-packing of ACl₃ layers as the size of the A cation decreases. For $A = Cs$, the 9R structure is stable with 1/3 cubic close packing, for $A = Rb$ the 6H structure is stable with 2/3 cubic close-packing, and for $A = Tl$ and K the perovskite structure (3C) is stable with all cubic close packing of ACl₃ layers. The Na¹⁺ ion is too small to form any of the close-packed structures (20). The Cs and Rb compounds also transform at high pressure to all-cubic close packing, just as do all other oxide and fluoride hexagonal polytypes. The size of the Mn²⁺ ion appears to be unique for the chlorides, since it is the only B cation that allows a mixture of hexagonal and cubic close-packing. B cations larger than Mn²⁺ (Cd²⁺, Ca²⁺, Sr²⁺)

always form structures with all cubic close-packed layers, while for B cations smaller than Mn²⁺ (Fe²⁺, Co²⁺, Ni²⁺, Mg²⁺) structures having only hexagonal close-packed ACl₃ layers are formed. Attempts to prepare high-pressure polytypes of ACoCl₃, ANiCl₃, and CsFeCl₃, all of which have the 2H structure, were unsuccessful. Without the use of *in situ* X-ray diffraction, it is not possible to establish whether the polytypes are formed at high pressure, but are not retained at atmospheric pressure by quenching techniques, or whether insufficient pressure was used. We feel that at high pressure new polytypes are formed and that the thermal energy available at room temperature is sufficient to effect retransformations for these compounds. A similar situation was observed in our studies (21) of the 2H form of BaVS₃ and BaTaS₃. In those experiments, high pressure treatment to 90 kbar also did not result in new polytypes, but instead gave materials whose 2H structure was severely disordered. We believe that this disorder results when a high pressure phase slowly retransforms to its atmospheric pressure form during temperature quenching.

Acknowledgment

We gratefully acknowledge the many valuable discussions with J. B. Goodenough. Thanks are also due to D. A. Batson and D. M. Tracy for their technical assistance with many of the experimental aspects of this work.

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