

***P-T* PHASE RELATIONS OF METHYLAMMONIUM HALIDES ***

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ABSTRACT

Systematic phase relations of $\text{CH}_3\text{NH}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were studied as functions of pressure below 200 MPa and of temperature between 100 and 420 K by use of high-pressure DTA, and the enthalpy and entropy of transition were estimated by using DSC at atmospheric pressure. The undercooled metastable δ' phase in the chloride, and the stable β' phase in the iodide were newly discovered. This observation confirmed the common property among all the halides that the room-temperature tetragonal phases (α or α') transformed to the two kinds of low temperature phase through two distinct phase transitions; one was of the reconstructive first-order (to β or β') and the other of the higher order (to δ or δ'). The complicated phase relationship on halogen substitution was discussed in view of the non-spherical aspect of the methylammonium ion in contrast with the cases of alkali halides and ammonium halides.

INTRODUCTION

The systematic understanding on the phase transitions of a series of compounds with substituted halogens has been obtained for alkali halide and ammonium halide crystals [1,2]. For example, in the case of ammonium halides, the increase in pressure was found to be equivalent to the decrease in ionic size of the halogen, i.e., the phase relation of the chloride at atmospheric pressure was essentially the same as that of the bromide at some high pressure, etc. It is of interest to try a similar systematic study on the phase relation of methylammonium halides. This series of halides compounds is relatively simple with the formula type A^+X^- next to ammonium salts. Only one hydrogen atom in the NH_4^+ ion was replaced by a CH_3 group.

The crystals of methylammonium halides are known to have several modifications. They are β , γ , and α in $\text{CH}_3\text{NH}_3\text{Cl}$ [3], β , α , α' , and δ

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(metastable) in $\text{CH}_3\text{NH}_3\text{Br}$ [4,5], and δ , α' , and ϵ in $\text{CH}_3\text{NH}_3\text{I}$ [4,6], respectively. The crystal structures of α and α' phases were determined to be tetragonal, D_{4h}^7-P4/nmm [7–10]. However, the structures of each phase are not exactly the same as each other. The ϵ phase in $\text{CH}_3\text{NH}_3\text{I}$ is known to have the CsCl structure [6]. The structures of the low temperature phases β , γ , and δ are yet unknown. Numerous studies, mainly spectroscopic, have been performed with particular attention to the rotational motions of the CH_3NH_3^+ ion [4–6,11–13]. However, no systematic phase relations among the three halides with respect to both temperature and pressure have been obtained. The nature of the phase transition also remains unclear.

High pressure DTA was carried out in the temperature range 100–450 K and a pressure range up to 200 MPa for the purpose of investigating phase transitions as a function of two parameters, temperature and pressure. Furthermore DSC was carried out at atmospheric pressure to derive the entropies of the phase transitions.

EXPERIMENTAL

Methylammonium chloride was purchased from Wako Pure Chemical Ind. Ltd. Methylammonium bromide and iodide were prepared from aqueous solutions of methylamine by adding hydrobromic acid and hydroiodic acid, respectively. All the compounds were purified by repeated recrystallization from methanol solution. The crystallizations were forced to proceed rapidly in the dark with a rotary evaporator because $\text{CH}_3\text{NH}_3\text{Br}$ and especially $\text{CH}_3\text{NH}_3\text{I}$ decomposed readily in a solution with light. The crystals thus obtained were dried in vacuo at room temperature for more than 12 h and preserved under vacuum in the dark. Elemental analyses of the compounds are as follows. $\text{CH}_3\text{NH}_3\text{Cl}$: C, 17.89 (17.79); H, 8.91 (8.96); N, 20.72 (20.75); Cl, 52.77 (52.51)%. $\text{CH}_3\text{NH}_3\text{Br}$: C, 10.82 (10.73); H, 5.41 (5.40); N, 12.48 (12.51); Br, 71.43 (71.36)%. $\text{CH}_3\text{NH}_3\text{I}$: C, 7.73 (7.56); H, 3.81 (3.80); N, 8.78 (8.81); I, 79.76 (79.83)%. The values in parentheses are calculated ones.

All the phase transitions at high pressures were observed by means of a home-made high pressure DTA apparatus described elsewhere [14]. The samples were loaded into the cell in an atmosphere of dry nitrogen in the dark. The transition temperature was determined as the rising temperature of the peak for the first-order transitions and as the peak temperature for the higher order transition. The heating rate of DTA experiments was 1–1.5 K min^{-1} .

The enthalpy and entropy of transition were estimated by using a Perkin-Elmer DSC-II at atmospheric pressure. The inaccuracy of the measurement is expected to be smaller than 2%.

RESULTS AND DISCUSSIONS

 $\text{CH}_3\text{NH}_3\text{Cl}$

The phase transitions of the $\text{CH}_3\text{NH}_3\text{Cl}$ crystal at atmospheric pressure were reported by Aston and Ziemer [3]. Three (α , β , and γ) phases are known to exist below room temperature [3]. The α phase undercooled readily and transformed to the β phase irreversibly on cooling. The γ phase is realized by heating the β phase, and can exist between the α and β phases at low pressures. Both of the β - γ and γ - α transitions are of first order.

Figure 1 shows the DTA curves observed in the present measurements at 0.1 and 200 MPa. The phase relations as a whole are shown in Fig. 2 as a P - T diagram.

A new phase transition was found at 213.4 K on cooling (run 1) just before transition to the β phase took place. This transition was characterized by a long tail on the low temperature side. When the sample was heated from the temperature just above the transition to the β phase, as shown in run 2, this new transition appeared at the same temperature as on cooling in run 1. This transition was considered to be of higher order in view of the shape of the peak and the non-existence of any hysteresis phenomenon. The

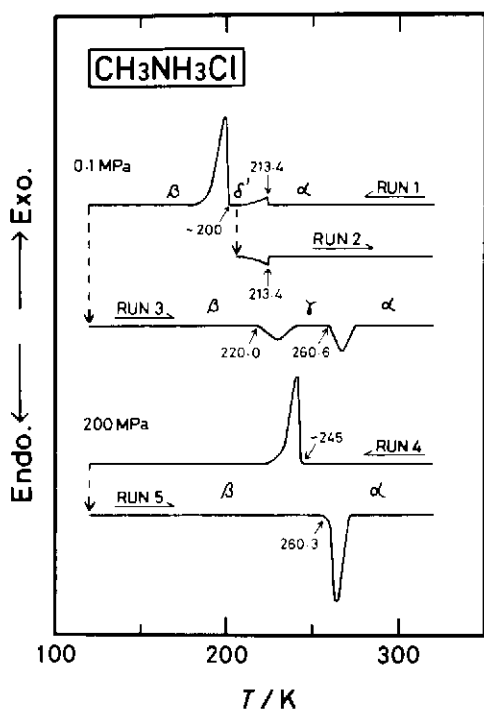


Fig. 1. DTA curves of $\text{CH}_3\text{NH}_3\text{Cl}$ crystal at 0.1 MPa and 200 MPa.

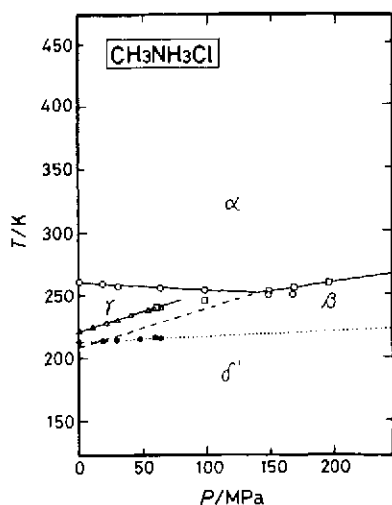


Fig. 2. Phase diagram of CH₃NH₃Cl crystal. (···) Phase transition line between metastable δ' and α phases.

shape and the heat effect of this transition were quite similar to those of the α'-δ transition in CH₃NH₃Br and CH₃NH₃I crystals as will be described later, while the pressure dependence of the transition temperature differed by a factor of 2. Therefore, we designate this new metastable phase δ' after the δ in the bromide or iodide. The δ'-α transition could not be observed above 60 MPa because the α phase transformed into the stable β phase on cooling before reaching the δ' phase region.

On heating the β phase from liquid N₂ temperature, two endothermic anomalies appeared at 220.0 and 260.6 K (run 3). These peaks were attributed to the β-γ and γ-α transitions, respectively. The transition temperatures almost exactly agreed with the results of 220.4 and 264.5 K obtained by Aston and Ziemer [3]. Peaks of the β-γ and γ-α transitions, especially the former, were not so sharp in spite of the fact that the transitions were of first order. This indicates that these transitions proceed slowly compared with other transitions of methylammonium halides, as will be shown below.

Runs 4 and 5 were taken at 200 MPa on cooling and heating, respectively. Only one peak due to the β-α transition appeared in each curve. The transition temperatures were found to be 245 and 260.3 K, respectively. The latter temperature is shown in Fig. 2 (□). This large hysteresis phenomenon indicated that the β-α phase transition was of first order.

The β-γ transition became harder to observe with increasing pressure because of its slowness. The plot (Δ) of the β-γ transition temperature was obliged to end at 70 MPa in Fig. 2 for this reason. The γ-α transition temperatures (○) above 70 MPa were measured by previously taking round-about but clever measures on the P-T surface; the β phase was transformed into the γ phase completely at atmospheric pressure and then the pressure was increased to the desired value.

In view of the above situation some ambiguity was probably involved in the determination of the β - γ transition temperature. A triple point among α , β , and γ phases was therefore assumed to be given as the intersection of the two (γ - α and β - α) transition lines as shown in Fig. 2. Then it is located at 139 MPa and 252 K. The β - γ transition line observed does not pass through the triple point. This will be interpreted as due to a superheating phenomenon of the β - γ transition which arises for a kinetic reason. The transition line in equilibrium would be like the dashed line drawn in Fig. 2 parallel with the measurement from the triple point.

CH_3NH_3Br

Figure 3 shows DTA curves of the CH_3NH_3Br crystal taken at 0.1 and 50 MPa. Phase transitions at atmospheric pressure (run 1–run 3) were observed to be almost coincident with the result of Ishida et al. [5]. The metastable δ

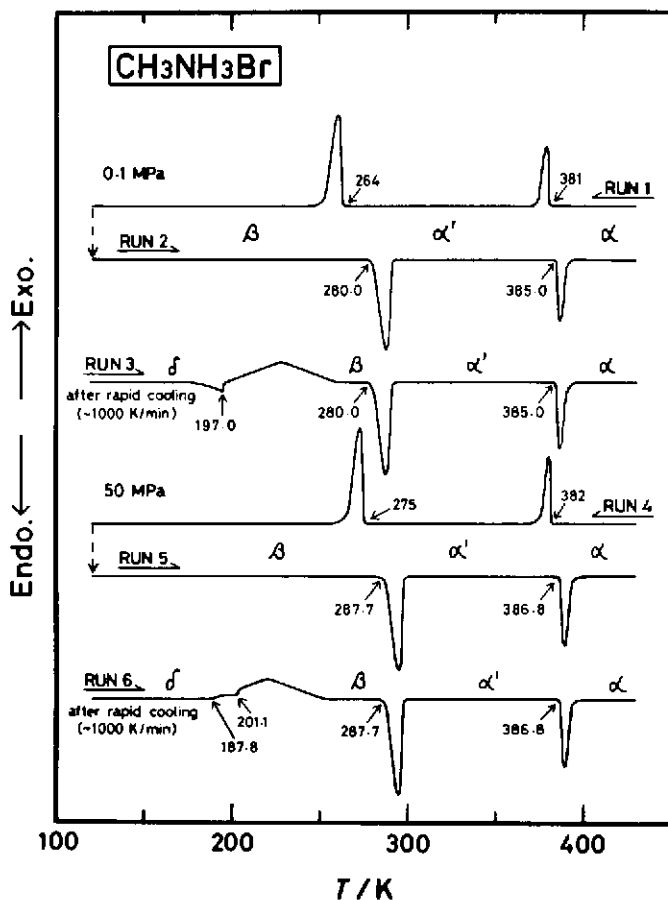


Fig. 3. DTA curves of CH_3NH_3Br crystal at 0.1 MPa and 50 MPa.

phase, however, could not be obtained by the usual rapid cooling (ca. 15–20 K min⁻¹), as pointed out by them. The α' phase transformed into the stable β phase before transforming into the δ phase at such cooling rates. The δ phase was obtained only by directly immersing the sample-loaded cell in liquid N₂. The cooling rate was estimated to be ca. 1000 K min⁻¹.

Runs 4 to 6 are the curves obtained at 50 MPa. The β - α' and α' - α transition points shifted towards higher temperature with pressure. The irreversible α' - β transition at high pressure occurred at a lower temperature than that at atmospheric pressure (run 3) and its thermal effect overlapped with that of the δ - α' transition. Above 50 MPa the δ - α' transition could not be observed because the δ - β transition took place before the δ - α' transition.

Figure 4 is the phase diagram of CH₃NH₃Br. The γ phase observed in the chloride disappeared and the α' phase interposed between the α and β phases. Every transition line has positive slope. A triple point among the α , α' and β phases, if any, is expected to exist at ca. 830 MPa and 410 K.

It is known from NMR [5], IR [4], and X-ray [10] studies that the methylammonium ion is orientationally disordered with its three-fold axis located on the four-fold crystallographic axis in the tetragonal α or α' phases, while from the calorimetric study on the chloride [3], it is ordered in the β phase. This orientational degree of freedom would contribute to the entropy of transition from β to α or α' phases by the value of $R \ln 4$ (≈ 11.5 J K⁻¹ mol⁻¹). The entropies of β - α' and α' - α phase transitions were measured by using DSC in the present study to be 16.3 and 3.84 J K⁻¹ mol⁻¹, respectively. It is reasonable that the former is over 11.5 J K⁻¹ mol⁻¹ and that the sum of the entropies of β - α' and α' - α transitions in the

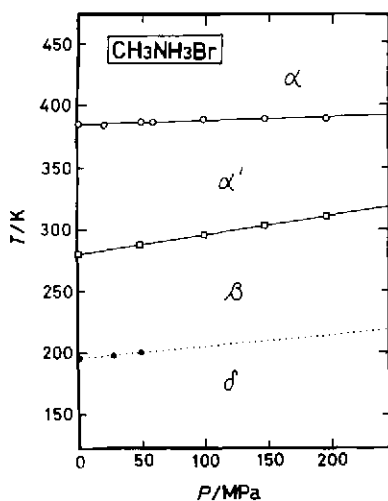


Fig. 4. Phase diagram of CH₃NH₃Br crystal. (· · ·) Phase transition line between metastable δ and α' phases.

bromide, $20.1 \text{ J K}^{-1} \text{ mol}^{-1}$, is close to the sum of those of β - γ and γ - α transitions in the chloride, $18.7 \text{ J K}^{-1} \text{ mol}^{-1}$. What makes the large difference between the entropies of α and α' phases $3.84 \text{ J K}^{-1} \text{ mol}^{-1}$ is of interest and to be explained in future.

$\text{CH}_3\text{NH}_3\text{I}$

Runs 1 and 2 in Fig. 5 show the DTA curve of the $\text{CH}_3\text{NH}_3\text{I}$ crystal taken at atmospheric pressure. The cooling curve exhibiting two exothermic peaks was almost the same as that observed by Ishida et al. [6]. The heating curve, on the other hand, exhibited a new anomaly which had not been reported so far. A small, broad exothermic peak and a small endothermic one appeared around 190 and at 246.1 K, respectively, after the endothermic effect due to the δ - α' transition finished. Run 3 is the similar heating curve

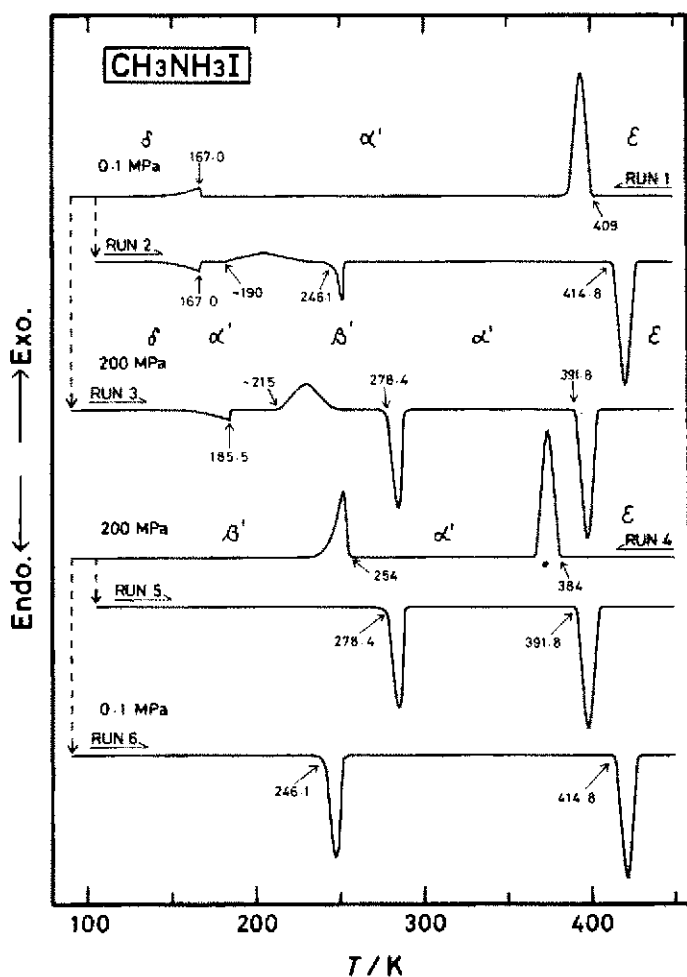


Fig. 5. DTA curves of $\text{CH}_3\text{NH}_3\text{I}$ crystal at 0.1 MPa and 200 MPa.

taken at 200 MPa on the sample which was cooled down to liquid N₂ temperature at atmospheric pressure in run 1 and then pressurized at that temperature to 200 MPa. The exothermic peak at ca. 215 K and endothermic one at 278.4 K are clearly larger in these areas than those in run 2.

Runs 4 and 5 are the sequences of cooling and heating at 200 MPa, respectively. A large exothermic anomaly appeared at 254 K in the former run and the corresponding endothermic one appeared at 278.4 K in the latter, while the δ - α' transition observed at 185.5 K in run 3 disappeared completely in both cooling and heating directions. Run 6 shows the heating curve for the sample released to a pressure to 0.1 MPa after completion of run 4. The phase transition took place at 246.1 K, the same temperature as that in run 2.

These observations indicate the existence of a new stable low temperature phase. The transition of the new phase to the α' phase takes place at 246.1 K under atmospheric pressure. This phase has not been found out probably because the α' phase undercools readily and hardly transforms into the stable phase during the first cooling to liquid N₂ temperature. Transition from the undercooled α' phase to this new phase seems to occur appreciably only on heating at atmospheric pressure and proceeds more easily under high pressure than at atmospheric one. The δ phase which had been considered as the stable phase in the low temperature region, was found to be really a metastable phase.

The lowest temperature phases in CH₃NH₃Cl and CH₃NH₃Br crystals are well known to be the β phase. Analogical reasoning suggests the new stable phase to be the β phase as well. In fact the pressure dependence of the transition temperature from the relevant phase to the α' phase is the same as that of the β - α' phase transitions in CH₃NH₃Br (see Table 1). The entropy of transition is, however, not exactly the same as that of CH₃NH₃Br. The former was obtained from the calorimetric measurement to be 13.5 J K⁻¹ mol⁻¹ as will be described elsewhere [15], and the latter from DSC to be 16.3 J K⁻¹ mol⁻¹. At present it cannot be stated in a decisive way whether the stable phase is the β phase or not. The new phase was tentatively designated β' for this reason. The β' - α' phase transition at each pressure was measured on heating after transformation into the β' phase completely at about 200 MPa.

The α' - ϵ phase transition at atmospheric pressure was observed at almost the same temperature as that by Ishida et al. [6]. According to their report, the ϵ phase has the CsCl structure and the CH₃NH₃⁺ ion performs isotropic reorientational motion rapidly around its center of mass. The entropy of transition was obtained by the present DSC measurement to be 14.8 J K⁻¹ mol⁻¹ (= $R \ln 5.9$). This might suggest that the CH₃NH₃⁺ ion is randomly distributed among six equivalent orientations of the C-N axis which, in view of the spatial symmetry, correspond to the six face centers of the cubic lattice.

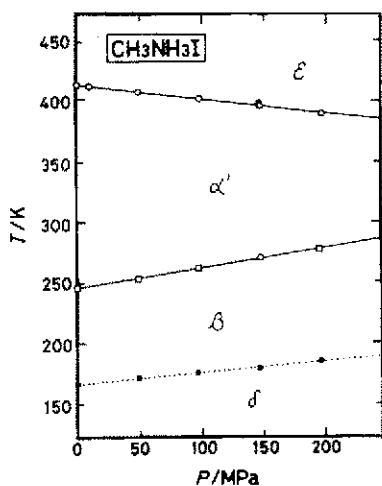


Fig. 6. Phase diagram of $\text{CH}_3\text{NH}_3\text{I}$ crystal. (···) Phase transition line between metastable δ and α' phases.

Figure 6 shows the phase diagram of $\text{CH}_3\text{NH}_3\text{I}$. With the replacement of β by β' , it is very similar to the phase diagram of $\text{CH}_3\text{NH}_3\text{Br}$ (Fig. 4) in the low temperature region. In the high temperature region, however, the cubic ϵ phase appears in the iodide instead of the tetragonal α phase. It should be noted that the temperature of α' - ϵ transition has a negative pressure dependence (-0.11 K MPa^{-1}) in spite of the accompanied large increase in entropy. It follows that reorientation of the C-N axis of the CH_3NH_3^+ ion does not require an increase in volume but rather brings about a decrease in it.

Unified phase relation of the three halides

Table 1 shows the thermodynamic quantities of all the phase transitions. The value of $\Delta_{\text{trs}}V$, except for the β' - α transition in $\text{CH}_3\text{NH}_3\text{I}$, was calculated by using the Clausius-Clapeyron's equation

$$\frac{dT_{\text{trs}}}{dP} = \frac{\Delta_{\text{trs}}V}{\Delta_{\text{trs}}S}$$

In the present work, two new phases were found. One is the metastable δ' phase which is realized by undercooling the α phase in $\text{CH}_3\text{NH}_3\text{Cl}$, and the other is the β' phase which is the low temperature stable phase in $\text{CH}_3\text{NH}_3\text{I}$. These findings lead to the unified understanding of the phase relations of methylammonium halides that the room-temperature tetragonal phases (α or α') transform into the low temperature phases through two quite different transitions. One is first-order to the β or β' phase and the other is second-order to the δ or δ' phase in the undercooled metastable state. Figure 7 shows the phase relationship of the three halides at atmospheric pressure.

TABLE 1

The thermodynamic quantities associated with phase transitions of methylammonium halides

Sample	Phases	T_{trs} (K)	dT_{trs}/dp (K MPa ⁻¹)	$\Delta_{\text{trs}}H$ (kJ mol ⁻¹)	$\Delta_{\text{trs}}S$ (J K ⁻¹ mol ⁻¹)	$\Delta_{\text{trs}}V$ (cm ³ mol ⁻¹)
CH ₃ NH ₃ Cl	$\beta \rightarrow \gamma$	220.0	0.31	1.779 ^a	8.071 ^a	2.5
	$\gamma \rightarrow \alpha$	260.6	-0.058	2.818 ^a	10.66 ^a	-0.62
	$\beta \rightarrow \alpha$	232 ^b	0.148			
	$\delta' \rightarrow \alpha$	213.4	0.045			
CH ₃ NH ₃ Br	$\beta \rightarrow \alpha'$	280.0	0.16	4.57	16.3	2.6
	$\alpha' \rightarrow \alpha$	385.0	0.033	1.48	3.84	0.12
	$\delta \rightarrow \alpha'$	197.0	0.092			
CH ₃ NH ₃ I	$\beta' \rightarrow \alpha'$	220	0.17	2.97 ^c	13.5 ^c	2.98 ^c
	$\alpha' \rightarrow \epsilon$	414.8	-0.11	6.13	14.8	-1.7
	$\delta \rightarrow \alpha'$	166.1	0.094			

^a Reference 3.^b Transition temperature at atmospheric pressure extrapolated from the data at high pressures.^c Reference 15.

Details of phase relations among the three halides are, however, rather complicated with the appearance and/or disappearance of phases through each halogen substitution so that each phase diagram cannot be obtained by a simple shift in pressure of the others as in the cases of ammonium halides. Figure 8 shows schematically the Gibbs energy relations among the β , α' , α and ϵ phases at atmospheric pressure, assuming that the phases are stable in the order β , α' , α and ϵ at the lowest temperature and oppositely ϵ , α , α'

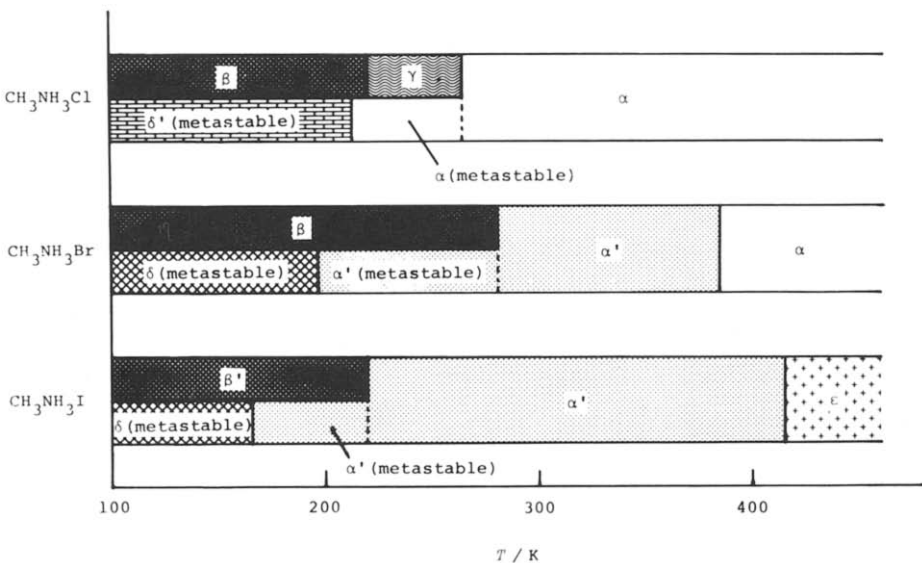


Fig. 7. Phase relationship of methylammonium halides at atmospheric pressure.

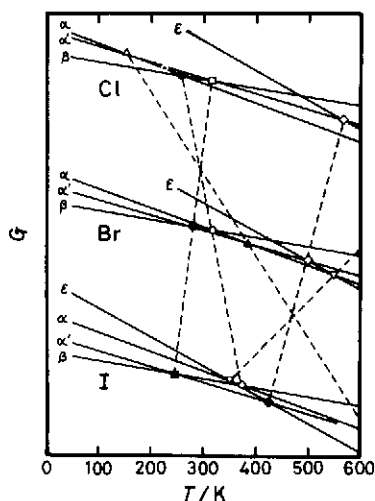


Fig. 8. Schematic Gibbs energy relations among the β , α' , α , and ϵ phases of methylammonium halides. Solid and open symbols represent observed and hypothetical phase transition points, respectively.

and β at the other ultimate high temperature. In this figure the difference between the β and β' phases, if any, was neglected. Solid symbols represent the temperature observed experimentally. Corresponding to the points of metastable (except for the α - ϵ phase transition in the bromide) and, therefore, usually unobservable transitions, open symbols should not mean the exact values of temperature but the relative positions referred to the observed values. By way of an example, both the β - α and β - α' transitions increase in temperature with increasing pressure, while the former increases and the latter decreases in temperature through the substitutions of Cl by Br and further by I. That is to say, the substitution corresponds, apparently, to increasing pressure for the former and decreasing for the latter. The α - ϵ and α' - ϵ transitions also belong to the former class (because they decrease in temperature with increasing pressure), while δ - α' (not shown in the figure) belongs to the latter.

Such complication should be attributed to deviation from the ideal spherical methylammonium ion with respect to its shape and the manner of its interaction with others. The size of the ion is ~ 0.49 nm long in the C-N axis and $0.3 \sim 0.4$ nm in diameter in its perpendicular direction. The methyl group favors neither ionic nor hydrogen bonding, while the ammonium group does. The length of the hydrocarbon (i.e., methyl) group is, besides, not long enough to separate the group from the $-\text{NH}_3^+\text{X}^-$ ionic region with the resulting formation of a bilayer structure in the crystalline state. The stability of the phases must involve, as an important factor, the energy for accommodation of a methyl group in the three-dimensional ionic and/or hydrogen bondings. (If the hydrocarbon group is long enough, part of a

phase relation might be clearly correlated between change in pressure and substitution of halogens on account of the relatively clear separation of two groups in the crystal structure.)

A close examination of P - T phase diagrams of A^+X^- ionic compounds (A = alkali metal, ammonium ion; X = halogen) suggests some phenomenological tendency that pressurization brings the phase relation of some compounds closer and closer to that of the compound whose ionic-radii ratio is around unity. In this respect it is noted that the ϵ phase of the present compounds has the CsCl structure. Being in the disordered state with respect to orientation of the C-N axis itself, the methylammonium ion would behave like a sphere with effective diameter ~ 0.49 nm compared to that for I^- of ~ 0.22 nm. For this highly disordered cubic phase, reasoning deduced from simple A^+X^- compounds would be suitably applied. The anionic replacement of Cl by Br and further by I corresponds to approaching an ionic-radii ratio of unity and, therefore, the pressurization effect. Considering the reverse situation, the α - ϵ transition temperature observed in iodide will be raised with substitution of I by Br and further by Cl. It is not unnatural to expect the α - ϵ transition in bromide and chloride to occur at temperatures higher than 420 K, which is the maximum temperature accessible by the present apparatus. This reasoning will be reserved for future study.

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