

## Structural Study on Cubic-Tetragonal Transition of $\text{CH}_3\text{NH}_3\text{PbI}_3$

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The cubic-tetragonal phase transition of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  was investigated by single crystal X-Ray diffractometry. The crystal structure was refined at five temperatures in the tetragonal phase. The  $\text{PbI}_6$  octahedron rotates around the  $c$ -axis alternatively to construct the  $\text{SrTiO}_3$ -type tetragonal structure. A methylammonium ion is partially ordered; 24 disordered states in the cubic phase are reduced to 8. With decreasing temperature, the rotation angle of the octahedron increases monotonically, which indicates it is an order parameter of the cubic-tetragonal transition.

KEYWORDS: X-ray diffraction, structure analysis, order parameter, tetragonal phase, methylammonium triiodideplumbate

### 1. Introduction

Methylammonium triiodideplumbate,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  takes a cubic perovskite structure (space group  $Pm\bar{3}m$ ,  $Z=1$ ) at high temperature.<sup>1)</sup> Since the methylammonium ion,  $\text{CH}_3\text{NH}_3^+$  (hereafter abbreviated as  $\text{MA}^+$ ) has a lower symmetry of  $C_{3v}$ , the orientation of the  $\text{MA}^+$  ion should be disordered to satisfy the  $O_h$  symmetry. The same type cubic crystals can be realized with replacing I by Cl or Br; on decreasing temperature, all three compounds perform the cubic-tetragonal transition.<sup>1,2)</sup> In  $\text{MAPbI}_3$ , the transition temperature is 327.4K. The tetragonal crystal system (space group  $I4/mcm$ ,  $Z=4$ ) becomes orthorhombic below 162.2K.<sup>2,3)</sup>

In the cubic phase, a  $\text{MA}^+$  ion is in a cage made by four  $\text{PbI}_6$  octahedra. Because the octahedron is rather large compared with the general perovskite-type crystal such as  $\text{BaTiO}_3$ , it is considered that  $\text{MA}^+$  ions can move freely inside the cage at high temperatures.<sup>2)</sup>

The specific heat of  $\text{MAPbX}_3$  ( $X=\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ) was measured with high accuracy, and the transition entropy was estimated from the specific heat and the latent heat.<sup>3)</sup> The entropy of the cubic phase was estimated to be  $R\log 24$ . In order to explain the entropy change with accompanying the successive transitions, the following three models have been proposed.

Model A: The C-N axis of a  $\text{MA}^+$  ion aligns along  $\langle 100 \rangle$ , six directions. Since the  $\langle 100 \rangle$  axis has a 4-fold symmetry, the  $\text{MA}^+$  ion rotates around the axis to occupy 4-sites equivalently. The total degree of freedom is 6 times 4, i.e. 24.

Model B: The C-N axis aligns along  $\langle 110 \rangle$ , twelve directions. Since the  $\langle 110 \rangle$  axis has a 2-fold symmetry, the  $\text{MA}^+$  ion rotates around the axis to occupy 2-sites equivalently. The

total degree of freedom is 12 times 2, i.e. 24.

Model C: The C-N axis aligns along  $\langle 111 \rangle$ , eight directions. Since the  $\langle 111 \rangle$  axis has a 3-fold symmetry, the  $MA^+$  ion rotates around the axis to occupy 3-sites equivalently. The total degree of freedom is 8 times 3, i.e. 24.

It was demonstrated that each three models explained the observed type of successive transitions: cubic phase - tetragonal phase - orthorhombic phase.<sup>3)</sup>

We have analyzed the cubic structure by the use of X-ray diffraction data.<sup>4)</sup> Although the  $R$ -factor (the residue of the least-squares calculations) for each model gave almost the same goodness, the bond length of C-N was most plausible for the model B. The differential Fourier synthesis suggested that the halogen atoms were disordered to occupy four equivalent sites randomly.

On the other hand, more than 2 decades ago, the cubic structures of  $CsPbCl_3$  and  $CsPbBr_3$  were analyzed. The halogen atoms were assumed to vibrate within an anharmonic potential and the picture of disordered halogen atoms was abandoned.<sup>5)</sup>

Another way to clarify the disordered structure is to determine the tetragonal structure, which is considered to display the ordered configuration. In this report we collect intensity data of X-ray diffraction in the tetragonal phase of  $MAPbI_3$ . Usually even a small piece of crystal consists of many tetragonal domains. However, we succeeded to find a single crystal sample after a number of trials. The single crystal analysis has been performed successfully. It is found the rotation angle of the  $PbI_6$  octahedron increases with decreasing temperature in the tetragonal phase, which demonstrates the displacive character of the octahedron at the cubic-tetragonal transition.

## 2. Experimental

Single crystals prepared as described previously<sup>6)</sup> were kindly supplied by Prof. Gesi. Spherical samples were cut and polished into 0.3mm in diameter, among which a single crystal was selected and was mounted on an off-centered 4-circle diffractometer (HUBER 424) controlled by MXC (Mac Science). Cold nitrogen gas flow (Oxford Crysteram) was employed to keep the temperature of the sample within  $\pm 0.5K$ . Graphite-monochromated Mo  $K\alpha$  radiation was used from a rotating anode generator with 50kV-250mA.

The space group of the tetragonal phase ( $165K < T < 328K$ ) was confirmed to be  $I4/mcm$  ( $Z=4$ ), which is the same space group with the tetragonal phase of  $SrTiO_3$ . The intensity data were collected at 323K, 310K, 280K, 250K, 220K and 180K.

Lorentz and polarization corrections were made automatically by MXC. Absorption correction for spherical sample was made by numerical integration. Starting from the  $SrTiO_3$ -type parameters, structure parameters for Pb and I were refined by least-squares calculations (BDLS of AXS98 program<sup>7)</sup>). Atomic scattering factors were taken from *International Table*.<sup>8)</sup> The  $R$ -factor converged at  $R=0.151$  with the use of isotropic thermal parameters. Then

differential Fourier synthesis was made to find the positions of C and N of  $\text{MA}^+$  ion. The hydrogen atoms are neglected because of their poor contribution in scattering. The difference of C and N is little in comparison to Pb and I. Since  $\text{NH}_3$  of  $\text{MA}^+$  is considered to be positively charged, the closer positions to I are assigned to N. At the final stage of calculations, anisotropic thermal parameters were introduced for Pb and I, and the calculations converged at  $R=0.060$ . Crystal data at 220K are summarized in Table I.

### 3. Results

#### 3.1 Lattice constants

Firstly, the temperature dependence of lattice constants  $a$  and  $c$  is shown in Fig. 1; where  $\tilde{a} = a/\sqrt{2}$  and  $\tilde{c} = c/2$  are plotted for the tetragonal phase in order to compare with the cubic phase. With decreasing temperature, the parameter  $\tilde{a}$  decreases monotonically. On the other hand, the parameter  $\tilde{c}$  increases when the crystal transforms into the tetragonal phase. Since the unit cell volume  $\tilde{V}$  or the equivalent lattice parameter  $\tilde{d} = \tilde{V}^{1/3}$  depends linearly on temperature, the differences of  $\tilde{a}$  and  $\tilde{c}$  from  $\tilde{d}$  are considered to be the anomalous parts,  $\delta\tilde{a}$  and  $\delta\tilde{c}$ , of the lattice parameters, and are plotted in Fig. 2. Although the cubic-tetragonal transition accompanies latent heat and the character is a first order transition,<sup>3)</sup> the lattice parameters seem to change continuously with the following relations:

$$\delta\tilde{a} \text{ or } \delta\tilde{c} \propto (T_c - T)^{\tilde{\beta}}, \quad (1)$$

where the fitted transition temperature was  $T_c = 331\text{K}$ . The exponent is estimated as  $\tilde{\beta}=0.42(2)$  both for  $\delta\tilde{a}$  and  $\delta\tilde{c}$ .

#### 3.2 Superlattice reflections

With accompanying the cubic-tetragonal transition, superlattice reflections appear in the low temperature phase. The temperature dependences of two reflections 125 and 411 are plotted in Fig. 3. As if a second-order transition, the structure factor can be written in a power law relation:

$$F(hkl) = F_0(1 - T/T_c)^{\beta'}. \quad (2)$$

In the whole temperature range of the tetragonal phase, the exponent  $\beta'$  is fitted as 0.22(3).

#### 3.3 Tetragonal structure

The unit cell structure at 220K is shown in Fig. 4. The atomic parameters are listed in Table II. The  $\text{MA}^+$  ions align along the  $[101]_c$ ,  $[\bar{1}01]_c$ ,  $[0\bar{1}\bar{1}]_c$  and  $[01\bar{1}]_c$  direction of the cubic structure. Therefore the model B of the cubic structure is appropriate. However, the  $\text{MA}^+$  ions align not within (001) plane as expected previously, but they point  $\langle 111 \rangle$  direction of the tetragonal phase. In this configuration,  $\text{NH}_3^+$  is closer to  $\text{I}^-$  and the electrostatic energy

will be lower, here the charge is just nominal. Furthermore, the atomic spacing within  $x$ - $y$  plane will shrink and the spacing along the  $c$ -direction will expand; the probability to align  $\text{MA}^+$  within  $x$ - $y$  plane disappears.

The iodine atom deviates from the line connecting Pb atoms in the  $x$ - $y$  plane. As in the case of  $\text{SrTiO}_3$ , this deviation is considered to be induced by a rotation of the  $\text{PbI}_6$  octahedron around the  $c$ -axis. At 220K (110K below the transition temperature), this rotation angle  $\phi$  is  $10.5^\circ$ , which is larger than the angle  $1.4^\circ$  in  $\text{SrTiO}_3$  at 77K<sup>9)</sup> (28K below the transition temperature; the reduced temperature  $t = (105 - 77)/77 = 0.36$  is comparable to 220K of  $\text{MAPbI}_3$ ).

The increase of the superlattice reflection in the tetragonal phase shown in Fig. 3 can be explained either by the gradual increasing of the rotation angle, or by the gradual ordering of the disordered iodine atoms and  $\text{MA}^+$  ions. The former model is a displacive model with respect to iodine, and the latter one is the partially ordered model. These two models were analyzed at every temperature. It was found that the occupation probability of the splitted iodine converged to almost 1.0 if the anisotropic thermal parameters were adopted. Therefore we conclude that the displacive model is appropriate to the tetragonal structure.

The rotation angle  $\phi$  is plotted in Fig. 5. The temperature dependence is also fitted to the relation

$$\phi \propto (T_c - T)^\beta. \quad (3)$$

Since the number of data is a few, the transition temperature was fixed at 331K. The exponent was estimated as  $\beta=0.25(6)$ .

#### 4. Discussion

In the foregoing section, we described three kinds of temperature dependence: the deviation of lattice parameters, the intensity of superlattice reflections and the rotation angle  $\phi$  of  $\text{PbI}_6$  octahedron. Firstly we note a relation between  $\delta\tilde{a}$  and  $\phi$ . If the octahedron rotates around the axis parallel to the  $c$  axis by  $\phi$ , then the spacing between the neighboring Pb's decreases by  $a_0(1 - \cos \phi)$ , where  $a_0$  is the lattice parameter of the cubic phase. Therefore  $\delta\tilde{a}$  is proportional to  $\phi^2$  for small  $\phi$ . This is the reason why the exponent  $\tilde{\beta}$  for  $\delta\tilde{a}$  ( $\tilde{\beta}=0.42$ ) is twice of  $\beta$  for  $\phi$  ( $\beta=0.25$ ).

The  $\text{PbI}_6$  octahedron has large thermal vibration in cubic phase.<sup>4)</sup> The root mean squared displacement  $\sqrt{u_\perp^2}$  is about  $0.4\text{\AA}$  perpendicular to the Pb-I-Pb bond, but  $\sqrt{u_\parallel^2} \simeq 0.14\text{\AA}$  parallel to the bond. After the cubic-tetragonal phase transition  $\sqrt{u_\perp^2}$  decreases to  $2/3$ , which makes the bond to elongate along the tetragonal  $c$ -axis. This is schematically drawn in Fig. 6 to explain the expansion of the  $c$ -axis.

The observed exponent  $\beta'$  for superlattice reflections  $F(125)$  and  $F(411)$  coincides with

each other. The structure factor  $F(\mathbf{k})$  is given by the summation of the atomic position  $\mathbf{r}_j$  as

$$F(\mathbf{k}) \simeq \sum_j f_j e^{i\mathbf{k}\cdot\mathbf{r}_j^0} + i \sum_j f_j \Delta\mathbf{r}_j \cdot \mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}_j^0}, \quad (4)$$

where  $\Delta\mathbf{r}_j$  is a small deviation from the cubic phase position  $\mathbf{r}_j^0$ . The first term of the right hand side of eq. (4) is zero for a superlattice reflection. In our crystal the deviation of iodine is dominant in  $F$ . Since iodine I(1) rotates by  $\phi$ , its displacement is  $\Delta r = a_0 \sin\phi \propto \phi$ .

Therefore the exponent for structure factor  $F(hkl)$  of superlattice reflections coincides to that of the rotation angle  $\phi$ . The order parameter of the tetragonal phase is considered to be the rotation angle of the  $\text{PbI}_6$  octahedron, just as same as in  $\text{SrTiO}_3$ , though the magnitude of the angle is quite large in  $\text{MAPbI}_3$ .

In the early studies on  $\text{MAPbX}_3$ , the ordering of the orientation of the  $\text{MA}^+$  ion has been attributed to the trigger of the transition.<sup>2-4)</sup> The previous structure analysis of the cubic phase also suggested the disordered  $\text{PbX}_6$  octahedron in  $\text{MAPbCl}_3$ ,  $\text{MAPbBr}_3$  and  $\text{MAPbI}_3$ .<sup>4)</sup> However, the anharmonic thermal vibration has been introduced to analyze the cubic structure of  $\text{CsPbCl}_3$  and  $\text{CsPbBr}_3$ ,<sup>5)</sup> where the lattice parameters are almost the same as  $\text{MAPbCl}_3$  and  $\text{MAPbBr}_3$ . Since the residual electron density was at most  $1.0 \text{ e}/\text{\AA}^3$  as shown in the differential Fourier map (Fig. 1 of our previous report<sup>4)</sup>), the cubic structure may be analyzed well by the use of anharmonic thermal vibration model.

In summary, the tetragonal structure of  $\text{MAPbI}_3$  was determined successfully with the displacive model for iodine atoms by means of single crystal diffractometry. The  $\text{MA}^+$  ions still retain disordered in their orientations. Protons are considered to be motionally disordered around the C-N axis. The rotation of the  $\text{PbI}_6$  octahedron is considered to be the order parameter of the cubic-tetragonal transition.

Finally, the reason why the value of the exponent  $\beta$  is not 1/2 but about 0.25 can be explained in three ways.

- (1) The critical behavior appears as similar to  $\text{SrTiO}_3$ , where the exponent is about 1/3.<sup>9)</sup>
- (2) The transition takes place accidentally near the tricritical point. Then the classical value of the exponent is 1/4.
- (3) Since the transition is a first order one, a small discontinuity effectively suppresses the exponent if it is estimated by the continuous function of eq. (3).

Two of these reasons may cooperate to decrease the exponent from the classical value of 1/2.

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Table I. Crystal data of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  at 220K.

Phase	II
Space group	$I4/mcm$
$Z$	4
$a(\text{\AA})$	8.800(9)
$c(\text{\AA})$	12.685(7)
Index range	$0 \leq h \leq 12$ $0 \leq k \leq 12$ $0 \leq l \leq 16$
Number of independent reflections ( $F_o > 5\sigma F_o$ )	360
Radius of the sample (mm)	0.125
Absorption coefficient ( $\text{mm}^{-1}$ )	26.1
$R$ -factor	0.060
$\Delta/\sigma$	0.0387
$\Delta\rho[\text{e}/\text{\AA}^3]$	$-3.31 \leq \rho \leq 1.72$

Table II. Atomic parameters at 220K in the tetragonal phase of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . The e.s.d.'s are given in parentheses for independent parameters.

	$x$	$y$	$z$	$U_{eq} (\text{\AA}^2)$
Pb	0.0	0.0	0.0	0.0206(5)
I(1)	0.2039(8)	0.2961	0.0	0.05551(10)
I(2)	0.0	0.0	0.25	0.0521(18)
C	0.555(17)	-0.055	0.264(11)	0.0404(33)
N	0.459(20)	0.041	0.202(9)	0.0582(41)
	$U_{11}$	$U_{33}$	$U_{12}$	
Pb	0.0200(9)	0.0218(7)	0.0	
I(1)	0.0327(19)	0.0700(15)	0.0329(20)	
I(2)	0.0708(36)	0.0149(13)	0.0	

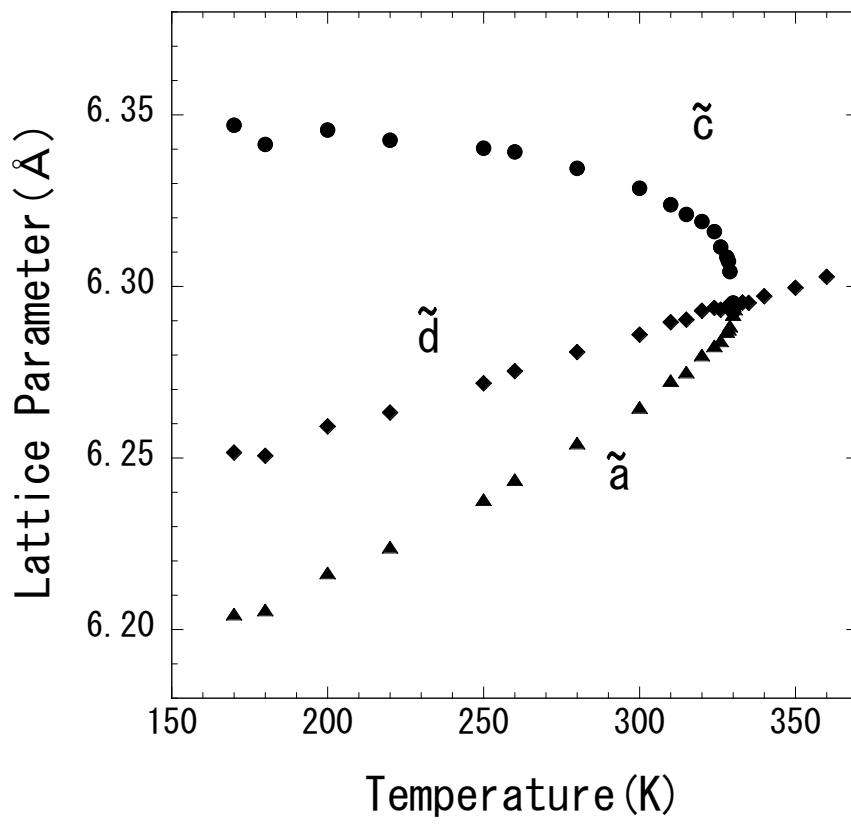


Fig. 1. The temperature dependence of lattice parameters in  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .



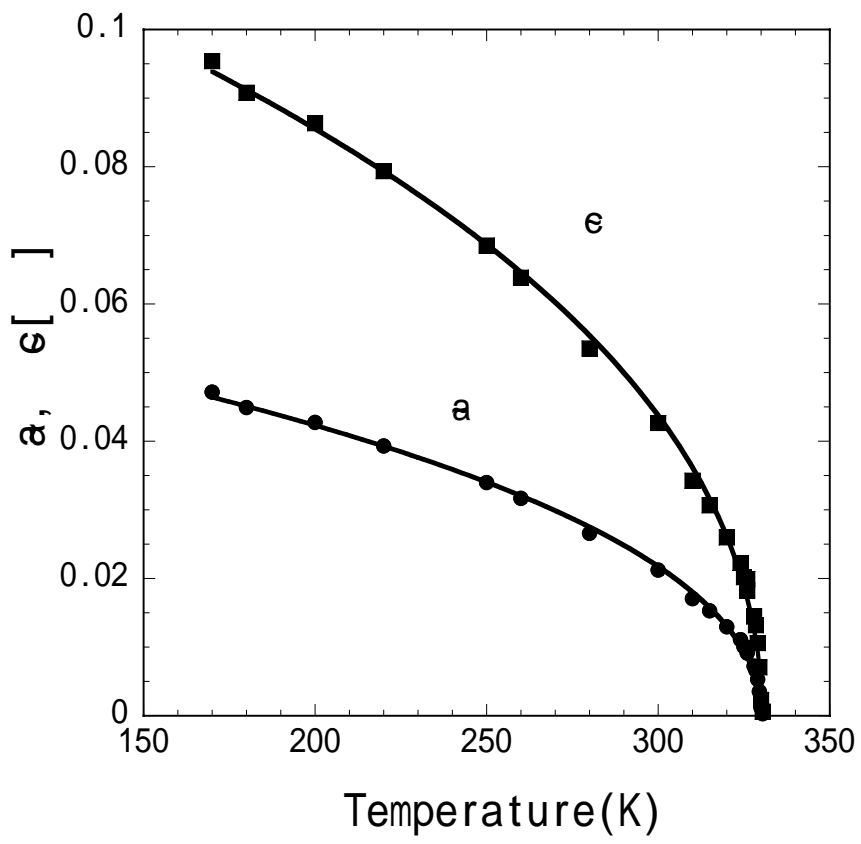


Fig. 2. The anomalous part of lattice constants in the tetragonal phase of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

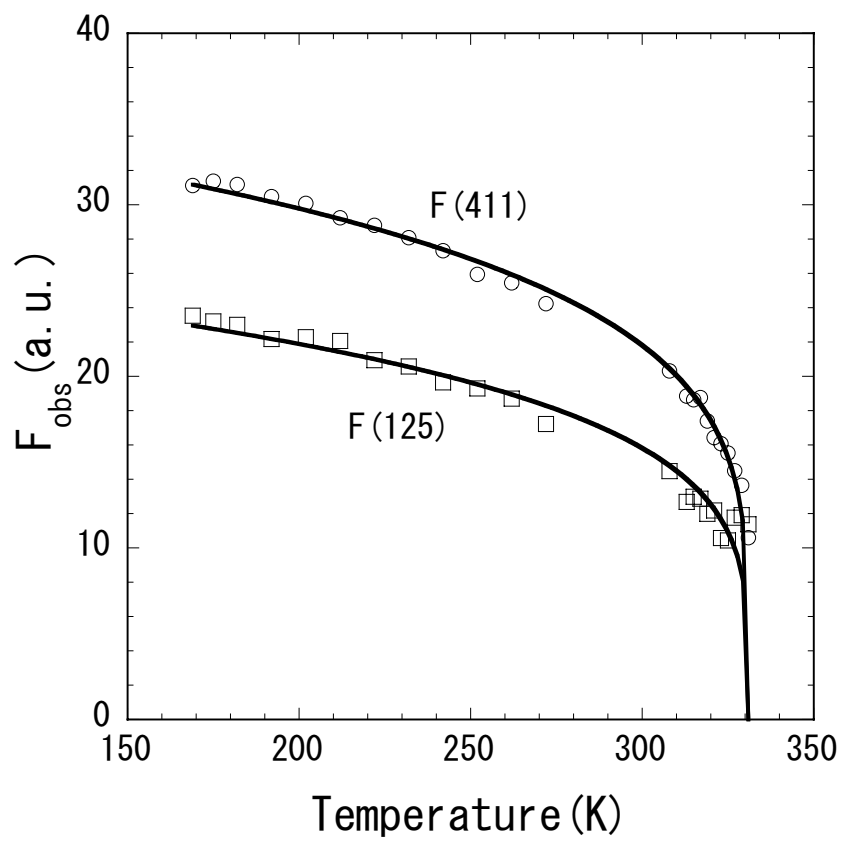


Fig. 3. The temperature dependence of structure factor for superlattice reflections in the tetragonal phase of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

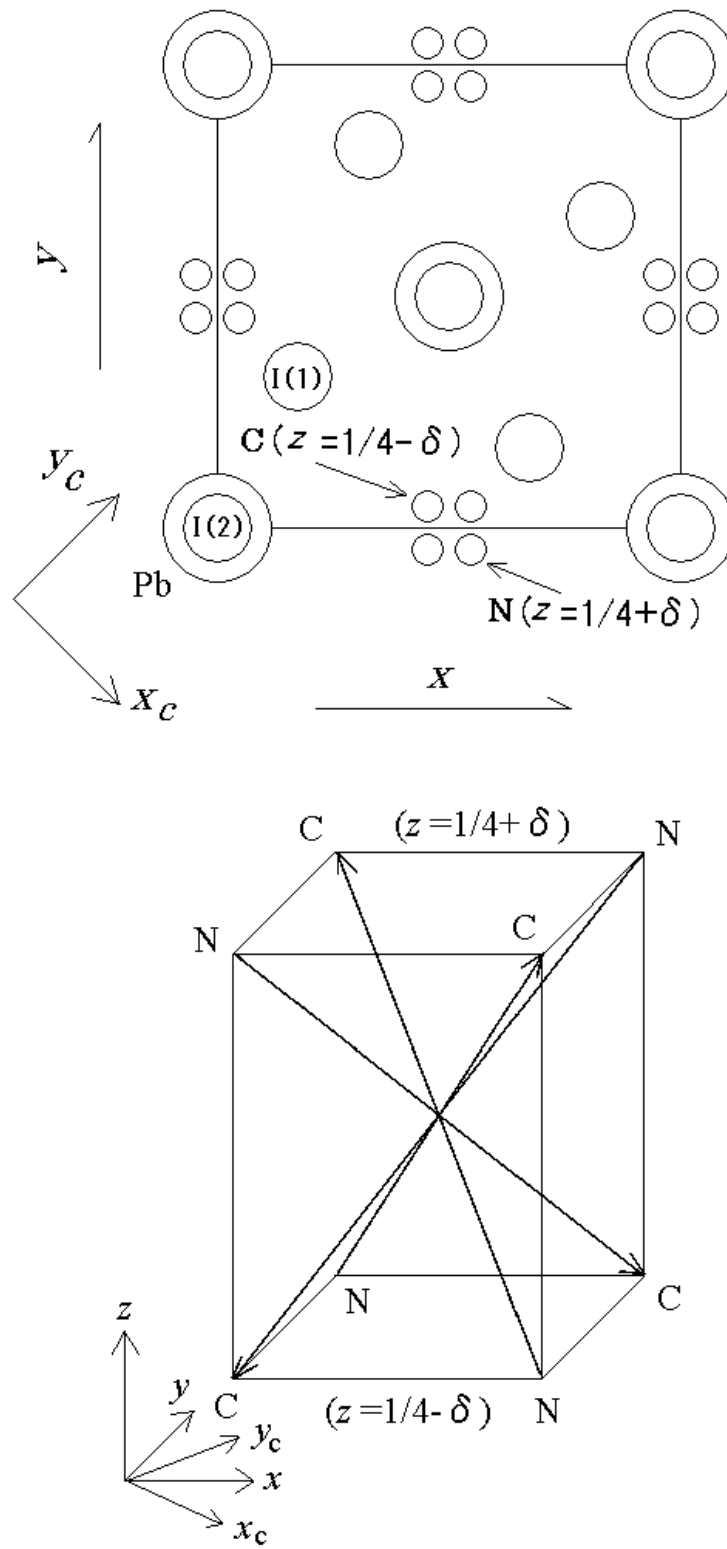


Fig. 4. The half of the tetragonal unit cell ( $0 < z < 1/2$ ) of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  projected on the  $x$ - $y$  plane (top). Directions of the methylammonium ion around  $(1/2, 0, 1/4)$  are indicated schematically in bottom.

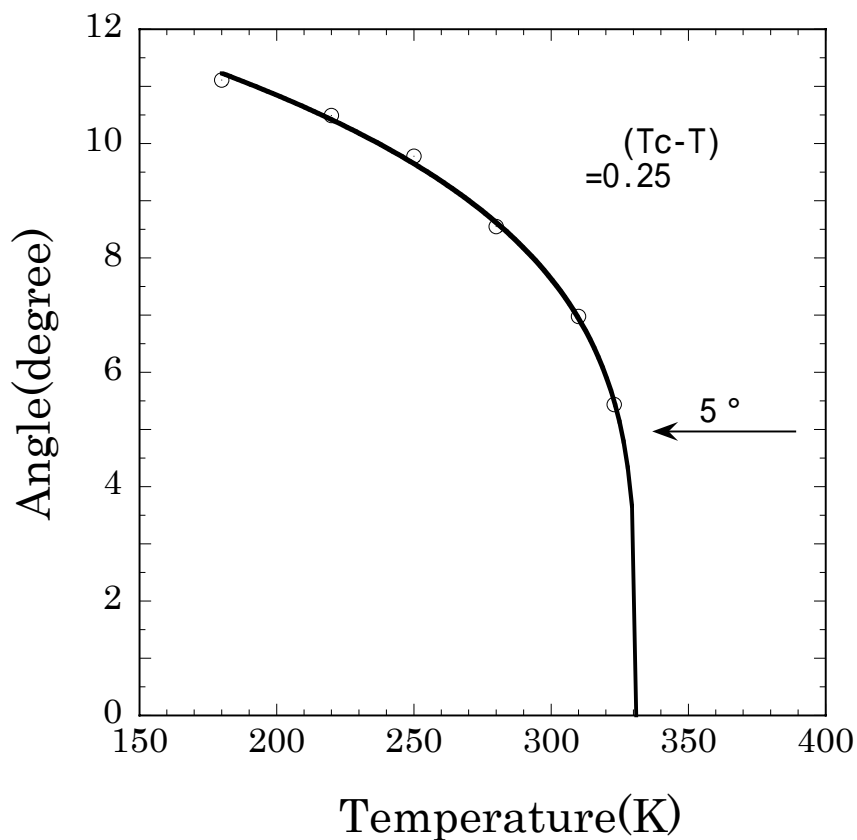


Fig. 5. The temperature dependence of the rotation angle of the  $\text{PbI}_6$  octahedron in the tetragonal phase of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . The arrow indicates the rotation angle in the cubic phase analyzed by the disordered model (after ref. 4).

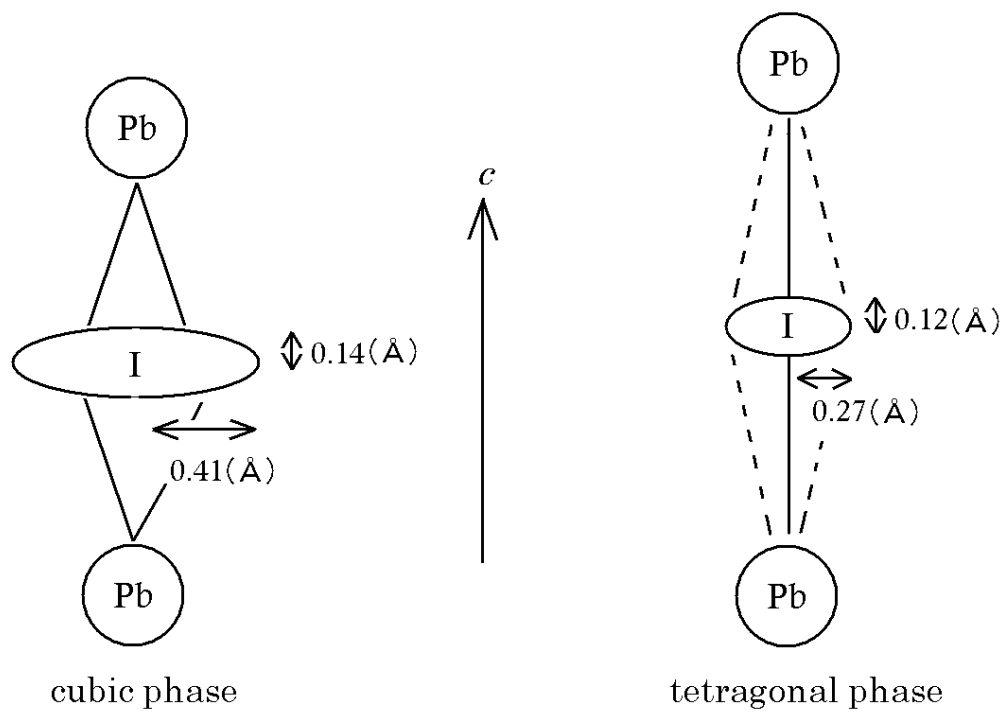


Fig. 6. Schematic picture of the Pb-I-Pb bond along the tetragonal  $c$ -axis.