EXAFS Study on the Phase Transition (Phase α' - δ) in CH_3NH_3I

Hiroyuki Ishida, Hironobu Maeda, Akiko Hirano, Tamotsu Fujimoto,
Yoshihiro Kubozono, Setsuo Kashino, and Shuichi Emura§

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700, Japan
§The Institute of Scientific and Industrial Research, Osaka University, Ibaraki 567, Japan

Z. Naturforsch. **50 a,** 876–880(1995); received June 16, 1995

The local structure of CH_3NH_3I around the I^- ion in Phase α' and δ was studied by iodine K-edge EXAFS. The crystal structure in Phase α' was redetermined by single crystal X-ray diffraction. The Debye-Waller factor $\sigma^{(2)}$ derived from EXAFS spectra shows an anomalous behavior around the order-disorder transition temperature from Phase δ to α'. The phase transition has been interpreted as the disordering process which involves not only the H atoms but also the C atoms in the cation.

Key words: Crystal structure; EXAFS; Phase transition; X-ray diffraction.

Introduction

Solid methylammonium iodide is known to exist in four different forms named α', δ [1, 2], β' [3], and ε [4, 5]. Phase α', stable at room temperature, has a tetragonal structure: space group P4/nmm with $Z = 2$, $a = 5.11$, $c = 8.95$Å [6]. The C–N axis coincides with the four-fold rotation axis parallel to the c-axis in the crystal, and hence the cation is orientationally disordered about this axis. Phase δ, existing below 166 K, is a metastable one. The structure, determined by neutron powder diffraction at 5 K, for the fully deuterated compound, CD_3ND_3I, is orthorhombic: Pbma with $Z = 4$, $a = 7.17143$, $b = 7.09673$, $c = 8.83232$Å [7]. The D atoms are ordered in an antiparallel manner along the b axis, and the C-N axis is slightly tilted with respect to the c-axis. The stable phase, β', is obtained by cooling the salt below 250 K under high pressure (200 MPa) [3] or by annealing it around 200 K for a long time (5 days [8] ~ 3 months [5]). Phase ε is an ionic plastic phase forming the CsCl-type cubic structure.

The α' - δ transition is reversible for cooling and heating at ambient pressure if the sample is carefully purified and dried [5]. This transition is of a higher-order nature and interpreted as an order-disorder process of the H atoms of $CH_3NH_3^+$ about the C-N axis [7, 8]. The dynamical behavior of the cation was studied by IR [1, 2], INS [9], ^{127}I NQR [10], and ^{1}H NMR [4, 5, 11]. Slight anomalies around the α' - δ phase transition were observed in the temperature dependences of ^{127}I NQR frequencies and spin-lattice relaxation times (T_1) of ^{1}H NMR. However, the changes in the cation dynamics through the phase transition are not fully understood.

In the present investigation we have measured iodine K-edge extended X-ray absorption fine structure (EXAFS) spectra in the temperature range 30 - 297 K in order to discuss the temperature dependence of the local structure around the I^- ion in terms of librational motions and disordering of the cation in relation to the α' - δ phase transition. In addition, we have redetermined the structure of Phase α' by single crystal X-ray diffraction to obtain the atomic parameters, especially the anisotropic displacement factors.

Experimental

CH_3NH_3I was prepared in the same manner as that for the ^{1}H NMR study [5] and filled in a quartz cell for EXAFS measurements. Single crystals for X-ray diffraction were obtained by slow evaporation of a methanol solution. Single-crystal X-ray measurements were carried out on Phase α' at 295 K using a Rigaku AFC-5R diffractometer with graphite monochromated Mo Kα radiation (50 kV, 200 mA). The structure was determined by the direct method using MITHRIL [12] and DIRDIF [13]. All calculations were performed on a Vax 3100 computer using TEXSAN [14]. Experimental conditions and crystal data are summarized in Table 1.

Reprint requests to Prof. Dr. H. Ishida.

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Iodine K-edge X-ray absorption spectra were collected in the transmission mode at BL-14A of the Photon Factory (KEK, Tsukuba) in the temperature range of 30 - 297 K. The energy of the injection beam was 2.5 GeV. The ring current was 200 - 350 mA. The incident beam was monochromatized by two Si(553) flat crystal monochromators. The sample temperature was regulated using a closed-cycle He refrigerator (Cryomech CP510) equipped with a temperature controller (Tristan Technologies LTC-10). The temperature was observed by a silicon diode sensor (Scientific Instruments Si-410). The programs "XAFS93" and "MBF93" were employed for the EXAFS data analysis [15].

Table 1. Experimental conditions for the crystal structure determination and crystal structure data in Phase α′ of CH_3NH_3I at 295 K.

Experimental conditions	
Crystal color, habit, and size	colorless, prismatic, $0.10 \times 0.15 \times 0.15$ mm^3
Diffractometer	Rigaku AFC-5R
Radiation and wavelength	Mo Kα, $\lambda = 0.71073$ Å
Absorption coefficient	$\mu = 6.51$ mm^{-1}
Scan	$\omega/2\theta$
$2\theta_{max}$	55.0°
Range of h, k, l	$0 \leq h \leq 6, 0 \leq k \leq 6,$ $0 \leq l \leq 11$
Cell parameters from 17 reflections ($2\theta = 22 - 28°$)	
Absorption correction	empirical, ψ-scan correction $T_{min} = 0.50, T_{max} = 1.00$
No. of measured reflections	357
No. of indepependent refls.	298 ($R_{int} = 0.05$)
3 standard reflections, (1 0 -2), (1 1 -2), (1 0 -1), monitored every 100 refls.	
intensity decrease	-11 %
Refinement on F	
$R = \sum \lVert F_o\rvert - \lvert F_c\rVert / \sum \lvert F_o\rvert$	0.041
$wR = \sqrt{\frac{\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2}{\sum wF_o^2}}$	0.045 [$w = 4F_o^2/\sigma^2(F_o^2)$]
S	2.14
No. of observed reflections	237 [$I > 3\sigma(I)$]
Number of parameters	10
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)	
No H atom was located in the difference Fourier map.	
Crystal data	
Space group	P4/nmm (#129)
Unit-cell dimensions	$a = 5.121(5)$ Å $c = 9.01\ (1)$ Å
Volume of the unit cell	$V = 236.2\ (6)$ Å^3
Formular units per unit cell	$Z = 2$
D_x	2.235 g/cm^3
$(\Delta/\sigma)_{max}$	0.004
$\Delta\rho_{max}, \Delta\rho_{min}$	1.47, -0.92 e Å^{-3}

Results and Discussion

The crystal structure of Phase α′ is shown in Fig. 1, and the obtained atomic parameters are listed in Table 2. Almost the same atomic positions as those of CD_3ND_3I determined by neutron powder-diffraction [7] were obtained. The C–N bond axis is parallel to the *c*-axis. Interestingly, the C atom has strongly anisotropic displacement factors in the plane perpendicular to the *c*-axis. This suggests the existence of a large-amplitude thermal libration of the C–N axis and/or disordering of the C atom caused by a precession of the C–N axis tilted slightly with respect to the *c*-axis. However, it was difficult to resolve the disordered position of the C atom.

Figure 2 shows the amplitude and the imaginary part of the radial structure function $\Phi(r)$, obtained

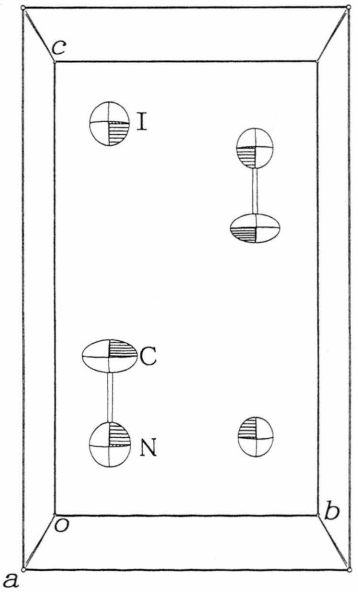

Fig. 1. An ORTEPII [16] view along the *a*-axis in Phase α′ of CH_3NH_3I. Thermal ellipsoids are drawn at the 50 % probability level.

Table 2. Positional and thermal parameters in Phase α′ of CH_3NH_3I. The coefficients U_{ij} of the anisotropic displacement factor expression are defined as follows:
$\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	1/4	1/4	0.8107(2)	0.0455(5)	0.0455	0.0577(8)	0	0	0
N	1/4	1/4	0.207(2)	0.049(5)	0.049	0.06(1)	0	0	0
C	1/4	1/4	0.374(2)	0.09(1)	0.09	0.03(1)	0	0	0

from the EXAFS oscillation $\chi(k)$ weighted by k^3 at 30 and 297 K. k is the wave number of the photoelectrons expressed as

$$k = [2m(E - E_0)/\hbar^2]^{1/2}.$$

Here E and E_0 denote the incident photon energy and the threshold energy of iodine K-edge absorption, respectively, and m is the electron mass. Referring to the crystal structures in Phase α′ (Fig. 3) and Phase δ [7], a pronounced peak around 3Å was assigned to the C and N neighbors of the I^- ion. The Fourier filtering technique was employed for the determination of structural parameters [15]. A non-linear least-squares fitting was applied to the filtered data according to the equation [17]

$$\chi(k) = \sum N_j |f_j(k;\pi)| \exp[-2r_j/\lambda_j(k)] \times \exp[-2k^2\sigma_j^{(2)}](kr_j^2)^{-1} \times \sin[2kr_j - \frac{2k}{r_j}(1 + 2\frac{r_j}{\lambda_j(k)})\sigma_j^{(2)} + \delta_j(k)].$$

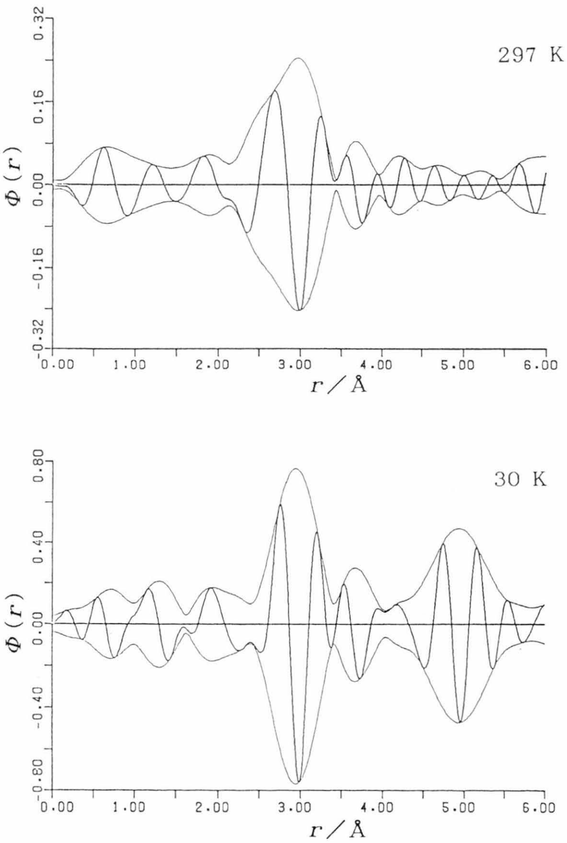

Fig. 2. Amplitude (thin line) and imaginary parts (thick line) of the Fourier transform, $\Phi(r)$, of the EXAFS oscillations at the iodide K-edge absorption in CH_3NH_3I observed at 30 and 297 K.

Each shell, j, has N_j scatterers at a distance r_j from the absorbing atom. The Debye-Waller term, $\sigma_j^{(2)}$, indicates the mean-square relative displacement between the absorbing and backscattering atoms. $\lambda_j(k)$ is the mean free path of the photoelectron. $f(k;\pi)$ is the backscattering amplitude of atom j, and $\delta_j(k)$ the total phase shift experienced by the excited photoelectron as it travels between the absorbing atom and its neighbors. Theoretical values were used for $|f_j(k;\pi)|$ and $\delta_j(k)$ [18].

As shown in Fig. 3, I^- is surrounded by five nearest backscattering C atoms: one first nearest C^i atom with a $C^i \cdots I$ distance of 3.94(2)Å and four second nearest C^{ii} atoms with a distance of 3.984(9)Å. Since it is difficult to distinguish the two distances by the EXAFS method, we used a one-shell model with the coordination number 5 for the C atoms, approximating that the C^i and C^{ii} atoms are equivalent with respect to the I^- ion. For the same reason we applied a one-shell model to the five backscattering N atoms. Consequently, the best fitting analysis for the peak in the region of 2.1 - 3.5Å observed in Phase α′ was carried out using the two-shells model; one shell is for five C atoms and the other shell is for the five N atoms. We also tried to analyze the peak using a four-shells model, but an improvement of R-factor was not obtained. The R-factor represents the fitting errors and is defined as

$$R = \sum |k_i^3 \chi^{\mathrm{obs}}(k_i) - k_i^3 \chi^{\mathrm{calc}}(k_i)| / \sum k_i^3 \chi^{\mathrm{obs}}(k_i),$$

where $\chi^{\mathrm{obs}}(k_i)$ and $\chi^{\mathrm{calc}}(k_i)$ are the experimental and calculated EXAFS oscillations, respectively.

According to the crystal data of CD_3ND_3I at 5 K [7], the structure around the I^- ion in Phase δ is similar to that in Phase α′. Thus, as a first approximation, the four C^{ii} atoms in Phase δ are treated as equidistant from the I^- ion. Since the C^{i} ••• I distance becomes shortened and is distinguishable from C^{ii} ••• I distance, we used a two-shells model for the C atoms. Moreover, we assumed the same value of the Debye-Waller term $\sigma^{(2)}$ for all C scattering atoms. The same approximation was made for the N atoms and, consequently, the peak in $\Phi(r)$ in Phase δ was analyzed by using a four-shells model. During the fitting calculation for Phase α′ and δ, the parameter $\lambda(k)$ and the correction value of the threshold energy (ΔE_0) were fixed to 1.097k Å and −0.013 keV, respectively, evaluated from the EXAFS spectrum at 30 K and the crystal data of Phase δ [7].

The temperature dependences of the C ••• I and N ••• I distances, and $\sigma^{(2)}$ for the C and N atoms are shown in Fig. 4 and 5, respectively. No remarkable change in the N ••• I distance was observed, which implies that the average distance of N ••• I is almost constant in the temperature range studied. On the other hand, a slight anomalous behavior was found for the C ••• I distance around the transition temperature. $\sigma^{(2)}$ obtained for C atoms was larger than $\sigma^{(2)}$

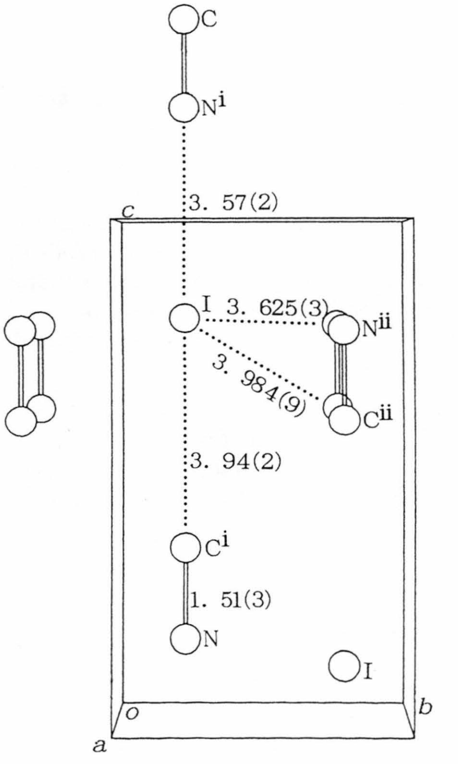

Fig. 3. The bond lengths and intermolecular distances (Å) around the I^- ion in Phase α′ of CH_3NH_3I.

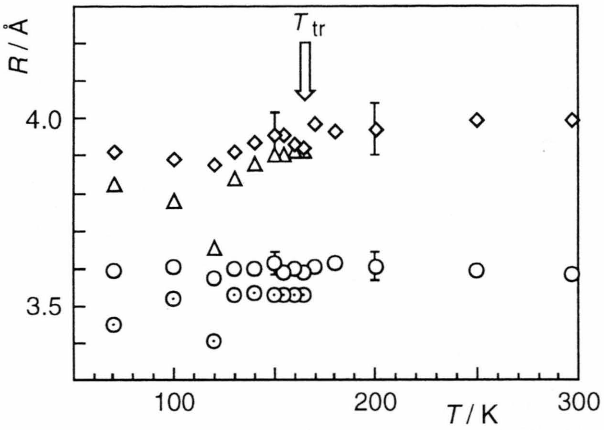

Fig. 4. Temperature dependence of the C ••• I (◇, △) and N ••• I (○, ⊙) distances.

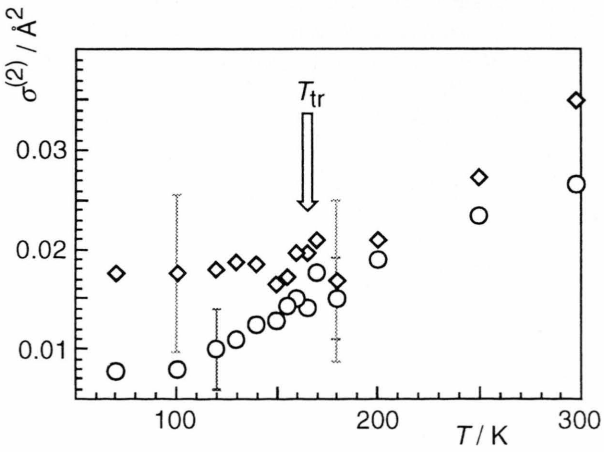

Fig. 5. Temperature dependence of the Debye-Waller factor $\sigma^{(2)}$ for C (◇) and N (○) backscattering atoms.

for N atoms; especially below 100 K the difference is large. This implies that the amplitude of the cationic libration around the C atom is much larger than that around the N atom even at low temperatures in Phase δ as observed by single X-ray diffraction in Phase α′, probably due to the weaker hydrogen bond of C – H ••• I type than that of N – H ••• I type. Both $\sigma^{(2)}$'s in Phase δ increased steeply with increasing temperature from ca. 120 K, where onset of anomaly in ^{1}H NMR T_1 [5] and ^{127}I NQR [10] was reported. This increase can, therefore, be explained by the increase in amplitude of the cationic libration and/or disordering of the cation due to the δ – α′ phase transition. Disordering of the cation accompanies breaking and forming hydrogen bonds between the cation and four neighboring I^- ions, which are located at different distances from the cation in Phase δ. This may cause precession of the cation tilted with respect to the *c*-axis or increase of the librational amplitude. As mentioned above, it is highly probable that the cation performs a precession of its C–N bond axis around the four-fold rotation axis in Phase α′. Therefore, the transition from Phase δ to α′ can be interpreted as an order-disorder process involving not only H atoms but also C atoms. The sudden decrease in $\sigma^{(2)}$ observed near the transition point can be related to the change in the cationic motion, probably because four conceivable hydrogen bonds around the cation become equivalent at the phase transition.

Acknowledgement

The authors are grateful to Dr. S. Kishimoto and Dr. T. Usami of the Photon Factory (KEK, Tsukuba) for their kind help in carrying out the measurements of EXAFS spectra. We wish to thank for the use of X-ray diffractometers (Rigaku AFC-5R) in the X-ray Laboratory of Okayama University. This work has been performed under a proposal of the Photon Factory Program Advisory Committee (No. 93G-189), and supported by a Grant-in-Aid for Scientific Research (No. 06640658) from the Ministry of Education, Science and Culture, Japan.

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