

# STRUCTURAL STUDY OF $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ IN THE LOW-TEMPERATURE PHASE

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*(Received October 7, 1999, revised version December 21, 1999)*

The crystal structure of tetraammonium dihydrogen triselenate,  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ , in the low-temperature phase at 141 K is studied by X-ray diffraction. The space group symmetry (triclinic  $P1$ ) and the structure parameters are determined. By the shift of the Se atom from the center of the  $\text{SeO}_4$  tetrahedron, it is suggested that the  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  crystal in the low-temperature phase is ferroelectric with the electric dipole moment along the  $c$ -axis. The rotation of the  $\text{SeO}_4$  tetrahedron suggested by electron paramagnetic resonance measurements is discussed.

PACS numbers: 61.66.Fn, 64.60.Fr

## 1. Introduction

Hydrogen sulfate and selenate family crystals of the general formula  $\text{M}_x\text{H}_y(\text{XO}_4)_z$  ( $\text{M}=\text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ ;  $\text{X}=\text{S}, \text{Se}$ ) exhibit interesting physical properties. They undergo a series of structural phase transitions to incommensurate, ferroelectric, ferroelastic, and superionic phases. Especially, the ammonium salts of the above family exhibit some of these properties. Ammonium hydrogen selenate crystals are grown from solutions of  $(\text{NH}_4)_2\text{SeO}_4$  and  $\text{H}_2\text{SeO}_4$ . Depending on the molar ratio of these two compounds, one can obtain  $\text{NH}_4\text{HSeO}_4$ ,  $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$  or  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  crystals [1]. The non-stoichiometry in mother solution and deuteration of the above-mentioned crystals have some effects on the physical properties of the crystals such as the size and shape of the crystal, unit cell dimensions and phase transition temperatures [2, 3].

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The crystal structure of tetraammonium dihydrogen triselenate,  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$ , at room temperature is found to be triclinic with space group  $P\bar{1}$  with two molecular units in a unit cell [4, 5]. It exhibits a phase transition at 378 K and melts at 432 K as observed by thermal and electrical conductivity measurements [5, 6]. A substantial increase in electrical conductivity from  $10^{-5}$  to  $4 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$  occurs at the transition [6]. The high-temperature phase is recognized as a superionic state with a low activation energy (0.11 eV) [6–11]. Recently, from the Raman measurements, it has been found that a change in dynamics of  $\text{SeO}_4$  and  $\text{HSeO}_4$  entities begins about 15 K below the superionic transition temperature and the temperature hysteresis of its transition temperature is about 30 K [10, 11].

In the previous paper [12], we have performed differential scanning calorimetry (DSC) and electron paramagnetic resonance (EPR) measurements for the  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  crystal below room temperature. The temperature dependence of the DSC curve and  $^{77}\text{Se}$  hyperfine line-positions of  $\text{SeO}_3^-$  radicals shows the existence of a low-temperature structural phase transition at about 182 K. The parameters of the spin Hamiltonian obtained from the angular dependence of the line-positions indicate that one of the three inequivalent  $\text{SeO}_4$  tetrahedra in the unit cell rotates with decreasing temperature in the low-temperature phase, and the angle of rotation at 140 K is about  $17^\circ$  as compared with that at room temperature. The purpose of this paper is to report the crystal structure of  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  in the low-temperature phase and to confirm the angle of rotation of the  $\text{SeO}_4$  tetrahedron.

## 2. Experimental

Single crystals of  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  were grown by slow evaporation from aqueous solutions containing  $(\text{NH}_4)_2\text{SeO}_4$  and  $\text{H}_2\text{SeO}_4$  in the molar ratio of 1.3 : 1 at room temperature (about 293 K). The X-ray measurement was carried out by using an Enraf–Nonius CAD-4 four-circle automatic diffractometer with an express software and graphite monochromated  $\text{Mo } K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The sample temperature was controlled by using cold  $\text{N}_2$  gas with a low-temperature apparatus of Enraf–Nonius, and the temperature fluctuation was kept within  $\pm 0.5$  K. The intensity data were corrected for both Lorentz-polarization and absorption effects. The structure was refined by the full-matrix least-squares method using a SDP crystallographic software package for Windows on a personal computer. All nonhydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms involved in the hydrogen  $\text{O}\cdots\text{O}$  bonds were refined isotropically. However, the isotropic thermal parameter of the hydrogen atoms of the  $\text{NH}_4$  ions was fixed with 0.02. The basic crystallographic data, and the details of the measurement and refinement are summarized in Table I.

TABLE I

Basic crystallographic data, data collection, and structure refinement parameters.

Crystal data	
Compound/chemical formula weight	$(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3/M_r = 503.04$
Crystal system/space group	Triclinic/ $P1$
Lattice constants	$a = 7.6379(9) \text{ \AA}$ $b = 10.3207(13) \text{ \AA}$ $c = 10.5262(11) \text{ \AA}$ $\alpha = 114.389(10)^\circ$ $\beta = 93.257(9)^\circ$ $\gamma = 107.545(10)^\circ$
Volume of unit cell	$V = 704.7(2) \text{ \AA}^3$
Formula unit per cell	$Z = 2$
Linear absorption coefficient	$\mu = 7.81 \text{ mm}^{-1}$
Crystal shape/colour	Prism/colourless
Sample shape/size in diameter	Sphere/ $2r = 0.34 \text{ mm}$
Data collection	
Measurement of temperature	141 K
Data collection method	$\theta/2\theta$ scans
Absorption correction type	Empirical via $\psi$ scans
Transmission factor	$T = 0.9112-0.9995$
Number of reflections measured	6557 ( $\theta_{\max} = 35.0^\circ$ )
Range of $h$ , $k$ , and $l$ for measured intensities	$h = 0 \rightarrow 12$ $k = -16 \rightarrow 15$ $l = -16 \rightarrow 16$
Number of standard reflections	3
Interval time/intensity decay	120 min/2.16%
Refinement	
$R$ factor/ $wR$ factor (refinement on $F$ )	$R = 0.033/wR = 0.039$
Goodness of fit	$S = 0.705$
Number of reflections used in refinement	3279 ( $I > 3\sigma(I)$ )
Number of parameters refined	488
Weighting scheme	$w = 1/[\sigma^2(F) + (0.02F)^2 + 1.0]$
Maximum of shift/esd	$(\Delta/\sigma)_{\max} = 0.12$
Difference density (peak/hole)	1.23/ $-1.94 \text{ e\AA}^{-3}$
Extinction coefficient	$5.2(3) \times 10^{-7}$

## 3. Results and discussion

The lattice parameters of  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  at 141 K are very close to those obtained at room temperature. No systematic absences for the observed reflections can be observed as similar to those at room temperature. Then, the possible space group is proposed to be triclinic  $P\bar{1}$  or  $P1$ . The space group at room temperature is  $P\bar{1}$  [4, 5] and the structural phase transition occurs at about 182 K [12]. Therefore, the space group in the low-temperature phase is believed to be  $P1$ .

TABLE II

Positional parameters in fractions of a unit cell, equivalent isotropic  $U_{\text{eq}}$  (Se, O and N) or isotropic  $U_{\text{iso}}$  (H) thermal parameters ( $\text{\AA}^2$ ) at 141 K, where  $U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_j$ . The isotropic thermal parameter of the H atoms around the  $\text{NH}_4$  ions was fixed with  $U_{\text{iso}} = 0.02$ .

Atom	x	y	z	$U_{\text{eq}}$	Atom	x	y	z	$U_{\text{iso}}$
Se(1)	.14503	.73059	.36683	.0221(3)	H(o1)	-.01(2)	.10(2)	.68(2)	.02(5)
Se(2)	.4464(1)	.62985(9)	.72705(9)	.0260(3)	H(o2)	.26(2)	.60(2)	.53(2)	.02(5)
Se(3)	.1588(1)	.13353(9)	.88447(8)	.0121(3)	H(o3)	.99(2)	.94(2)	.31(2)	.02(5)
Se(4)	.8427(1)	.26887(8)	.63199(8)	.0288(2)	H(o4)	.72(2)	.43(2)	.44(2)	.03(5)
Se(5)	.5400(1)	.36541(8)	.26845(8)	.0068(2)	H(1)	.30(2)	.46(2)	-.03(2)	.02
Se(6)	.8311(1)	.86368(8)	.11044(8)	.0140(2)	H(2)	.21(2)	.54(2)	-.05(2)	.02
O(1)	.3360(9)	.8204(8)	.3258(7)	.066(2)	H(3)	.37(2)	.60(2)	.05(2)	.02
O(2)	.0369(10)	.5540(8)	.2217(7)	.014(3)	H(4)	.21(2)	.53(2)	.05(2)	.02
O(3)	.0040(11)	.8194(8)	.3920(7)	.066(3)	H(5)	.34(2)	.91(2)	.22(2)	.02
O(4)	.1969(8)	.7127(8)	.5104(6)	.032(2)	H(6)	.47(2)	.94(2)	.10(2)	.02
O(5)	.5131(10)	.5053(6)	.7571(7)	.024(2)	H(7)	.40(2)	1.02(2)	.18(2)	.02
O(6)	.3434(9)	.7263(7)	.8430(7)	.019(2)	H(8)	.24(2)	.88(2)	.07(2)	.02
O(7)	.2914(10)	.5186(7)	.5636(7)	.012(2)	H(9)	-.07(2)	.19(2)	.19(2)	.02
O(8)	.6191(7)	.7528(6)	.7026(6)	.019(2)	H(10)	.00(2)	.36(2)	.26(2)	.02
O(9)	.3225(9)	.2511(8)	.8639(7)	.033(2)	H(11)	-.02(2)	.31(2)	.36(2)	.02
O(10)	.2373(9)	.0263(7)	.9270(7)	.022(2)	H(12)	.12(2)	.29(2)	.29(2)	.02
O(11)	.0464(8)	.2293(7)	.9902(6)	.009(2)	H(13)	.42(2)	.16(2)	.58(2)	.02
O(12)	-.0014(9)	.0137(6)	.7278(7)	.012(2)	H(14)	.35(2)	.21(2)	.46(2)	.02
O(13)	.6509(10)	.1608(7)	.6509(7)	.044(2)	H(15)	.41(2)	.29(2)	.62(2)	.02
O(14)	.9278(11)	.4231(8)	.7608(7)	.027(3)	H(16)	.21(2)	.18(2)	.56(2)	.02
O(15)	.9823(8)	.1656(6)	.5952(7)	.040(2)	H(17)	.73(2)	.58(2)	1.08(2)	.02
O(16)	.7921(11)	.2938(7)	.4931(7)	.044(2)	H(18)	.75(2)	.41(2)	1.04(2)	.02
O(17)	.4720(11)	.4724(8)	.2272(8)	.047(3)	H(19)	.63(2)	.40(2)	.95(2)	.02
O(18)	.6628(9)	.2942(7)	.1597(7)	.026(2)	H(20)	.78(2)	.45(2)	.91(2)	.02
O(19)	.6856(10)	.4773(7)	.4299(8)	.048(3)	H(21)	.62(2)	.09(2)	.81(2)	.02
O(20)	.3692(10)	.2400(8)	.2881(7)	.032(3)	H(22)	.51(2)	.06(2)	.89(2)	.02
O(21)	.6498(9)	.7458(7)	.1438(7)	.021(2)	H(23)	.63(2)	-.02(2)	.84(2)	.02
O(22)	.7719(9)	.9748(6)	.0575(6)	.037(2)	H(24)	.72(2)	.10(2)	.92(2)	.02
O(23)	.9687(10)	.7882(8)	.0206(8)	.023(3)	H(25)	1.07(2)	.78(2)	.80(2)	.02
O(24)	.9659(9)	.9931(6)	.2799(6)	.018(2)	H(26)	.98(2)	.64(2)	.73(2)	.02
N(1)	.2757(10)	.5324(7)	.0061(7)	.027(2)	H(27)	1.03(2)	.71(2)	.65(2)	.02
N(2)	.3646(12)	.9371(10)	.1361(9)	.018(3)	H(28)	.85(2)	.72(2)	.72(2)	.02
N(3)	.0100(10)	.2969(7)	.2772(7)	.016(2)	H(29)	.60(2)	.84(2)	.46(2)	.02
N(4)	.3386(13)	.2142(9)	.5487(9)	.049(3)	H(30)	.64(2)	.78(2)	.52(2)	.02
N(5)	.7244(11)	.4571(8)	.9848(9)	.014(3)	H(31)	.61(2)	.74(2)	.41(2)	.02
N(6)	.6162(12)	.0553(7)	.8653(7)	.048(3)	H(32)	.79(2)	.80(2)	.42(2)	.02
N(7)	.9719(10)	.7162(7)	.7272(8)	.023(2)					
N(8)	.6461(10)	.8020(9)	.4582(8)	.033(3)					

TABLE III  
Selected bond lengths in Å (a) and bond angles in degree (b) at 141 K.

(a) Bond lengths				(b) Bond angles	
Se(1)-O(1)	1.661(7)	Se(4)-O(13)	1.631(7)	O(1)-Se(1)-O(2)	106.9(3)
Se(1)-O(2)	1.728(5)	Se(4)-O(14)	1.513(6)	O(1)-Se(1)-O(3)	110.6(4)
Se(1)-O(3)	1.581(9)	Se(4)-O(15)	1.678(7)	O(1)-Se(1)-O(4)	111.6(3)
Se(1)-O(4)	1.637(8)	Se(4)-O(16)	1.631(8)	O(2)-Se(1)-O(3)	108.2(4)
Se(2)-O(5)	1.650(8)	Se(5)-O(17)	1.547(10)	O(2)-Se(1)-O(4)	110.7(4)
Se(2)-O(6)	1.636(7)	Se(5)-O(18)	1.604(7)	O(3)-Se(1)-O(4)	108.7(4)
Se(2)-O(7)	1.731(6)	Se(5)-O(19)	1.688(6)	O(5)-Se(2)-O(6)	117.7(4)
Se(2)-O(8)	1.648(6)	Se(5)-O(20)	1.628(8)	O(5)-Se(2)-O(7)	103.1(3)
Se(3)-O(9)	1.554(7)	Se(6)-O(21)	1.707(7)	O(5)-Se(2)-O(8)	112.5(3)
Se(3)-O(10)	1.602(9)	Se(6)-O(22)	1.625(8)	O(6)-Se(2)-O(7)	109.3(3)
Se(3)-O(11)	1.632(7)	Se(6)-O(23)	1.614(8)	O(6)-Se(2)-O(8)	107.7(3)
Se(3)-O(12)	1.709(5)	Se(6)-O(24)	1.738(5)	O(7)-Se(2)-O(8)	105.8(3)
O(1)-O(2)	2.724(9)	O(13)-O(14)	2.612(9)	O(9)-Se(3)-O(10)	109.7(4)
O(1)-O(3)	2.666(11)	O(13)-O(15)	2.621(10)	O(9)-Se(3)-O(11)	106.7(4)
O(1)-O(4)	2.728(11)	O(13)-O(16)	2.646(11)	O(9)-Se(3)-O(12)	110.8(3)
O(2)-O(3)	2.681(10)	O(14)-O(15)	2.683(10)	O(10)-Se(3)-O(11)	119.0(4)
O(2)-O(4)	2.769(9)	O(14)-O(16)	2.554(9)	O(10)-Se(3)-O(12)	105.4(3)
O(3)-O(4)	2.615(13)	O(15)-O(16)	2.678(12)	O(11)-Se(3)-O(12)	105.0(3)
O(5)-O(6)	2.812(11)	O(17)-O(18)	2.582(12)	O(3)-H(o3)-O(24)	170(17)
O(5)-O(7)	2.648(11)	O(17)-O(19)	2.585(13)	O(4)-H(o2)-O(7)	169(16)
O(5)-O(8)	2.743(10)	O(17)-O(20)	2.640(13)	O(13)-Se(4)-O(14)	112.3(4)
O(6)-O(7)	2.748(8)	O(18)-O(19)	2.645(9)	O(13)-Se(4)-O(15)	104.8(4)
O(6)-O(8)	2.652(9)	O(18)-O(20)	2.716(11)	O(13)-Se(4)-O(16)	108.4(4)
O(7)-O(8)	2.696(7)	O(19)-O(20)	2.658(8)	O(14)-Se(4)-O(15)	114.4(4)
O(9)-O(10)	2.581(12)	O(21)-O(22)	2.797(10)	O(14)-Se(4)-O(16)	108.6(4)
O(9)-O(11)	2.558(10)	O(21)-O(23)	2.827(11)	O(15)-Se(4)-O(16)	108.1(4)
O(9)-O(12)	2.687(7)	O(21)-O(24)	2.696(7)	O(17)-Se(5)-O(18)	110.0(4)
O(10)-O(11)	2.786(11)	O(22)-O(23)	2.704(11)	O(17)-Se(5)-O(19)	106.0(4)
O(10)-O(12)	2.634(11)	O(22)-O(24)	2.605(10)	O(17)-Se(5)-O(20)	112.5(4)
O(11)-O(12)	2.652(8)	O(23)-O(24)	2.681(9)	O(18)-Se(5)-O(19)	106.9(3)
O(3)-O(24)	2.591(12)	O(12)-O(15)	2.515(12)	O(18)-Se(5)-O(20)	114.3(4)
O(3)-H(o3)	1.77(21)	O(12)-H(o1)	1.25(21)	O(19)-Se(5)-O(20)	106.6(4)
H(o3)-O(24)	0.83(22)	H(o1)-O(15)	1.28(21)	O(21)-Se(6)-O(22)	114.1(4)
O(4)-O(7)	2.569(13)	O(16)-O(19)	2.569(13)	O(21)-Se(6)-O(23)	116.7(4)
O(4)-H(o2)	1.50(22)	O(16)-H(o4)	1.96(21)	O(21)-Se(6)-O(24)	103.0(3)
H(o2)-O(7)	1.08(21)	H(o4)-O(19)	0.61(22)	O(22)-Se(6)-O(23)	113.2(4)
				O(22)-Se(6)-O(24)	101.5(3)
				O(23)-Se(6)-O(24)	106.2(3)
				O(12)-H(o1)-O(15)	167(12)
				O(16)-H(o4)-O(19)	171(19)

The positional parameters in fractions of the unit cell and the thermal parameters are listed in Table II. Selected bond lengths in Å and bond angles in degrees are given in Table III. Figure 1 shows a perspective view of the crystal structure of  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  at 141 K. The observed structure is very close to that previously reported at room temperature [4,5].

The comparison of the Se-O bond lengths at room temperature with 141 K indicates as follows: In the structure of the room-temperature phase, the  $\text{Se}(2)\text{O}_4$  and  $\text{Se}(3)\text{O}_4$  tetrahedra are slightly distorted from the regular ones. The  $\text{Se}(1)\text{O}_4$  tetrahedron is nearly regular. On the other hand, all  $\text{SeO}_4$  tetrahedra in the

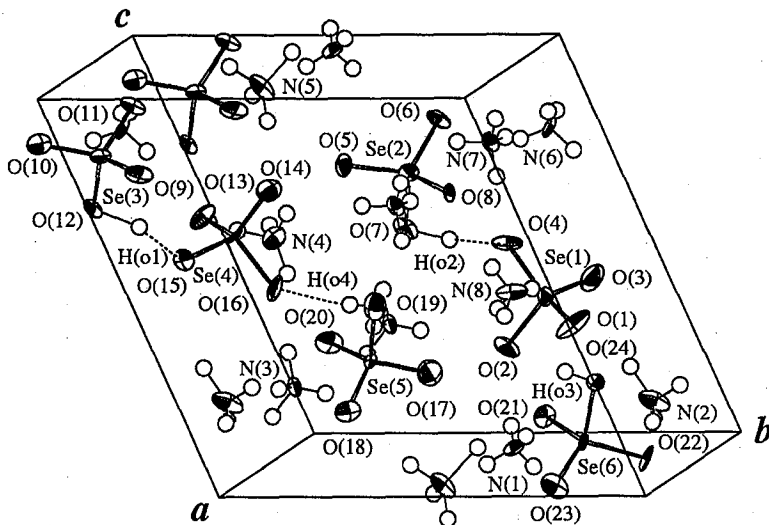


Fig. 1. Perspective view of the structure of  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  at 141 K with 70% probability-displacement thermal ellipsoids.

low-temperature phase are deviated from the regular ones. The magnitudes of the deviation at 141 K are larger than those at room temperature. The averaged  $\text{O}\cdots\text{O}$  hydrogen bond at 141 K is 2.56 Å and is almost equal to that (2.55 Å) at room temperature [5].

The bond distance between the Se atom and the O atom ended with the  $\text{O}\cdots\text{O}$  hydrogen bond is the longest in the  $\text{SeO}_4$  tetrahedra except the  $\text{Se}(1)\text{O}_4$  and  $\text{Se}(4)\text{O}_4$  tetrahedra which have two hydrogen bonds connected. It implies that there exists a strong drawing force between the O atoms which are connected by the hydrogen bond. Therefore, the bond distances between these Se and O atoms are longer than the other Se–O bonds in the  $\text{SeO}_4$  tetrahedron. This is also seen in the structure of  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  at room temperature and in the  $\text{Na}_3\text{H}(\text{SO}_4)_2$  crystal structure which contains very short hydrogen bonds [5, 13–15]. The averaged shift of the Se atom from the center of the  $\text{SeO}_4$  tetrahedron at 141 K along the *c*-axis is found of about  $-0.01$  Å and along the other axes it is almost equal to the magnitude of the error of the atomic positions. Since the electric dipole moment is produced by the electric charges of ions and their distances from the center, it is suggested that an electric dipole moment of the  $\text{SeO}_4$  tetrahedron is produced along the *c*-axis.

It has been pointed out that one of the three inequivalent  $\text{SeO}_4$  tetrahedra of the sample crystal rotates with decreasing temperature [12]. In this paper, the corresponding  $\text{SeO}_4$  tetrahedra which undergo rotation in the low-temperature phase are  $\text{Se}(1)\text{O}_4$  and  $\text{Se}(4)\text{O}_4$  tetrahedra. We examine in detail the difference between these  $\text{SeO}_4$  tetrahedra at room temperature and 141 K. It is found that both  $\text{Se}(1)\text{O}_4$  and  $\text{Se}(4)\text{O}_4$  tetrahedra do not rotate at 141 K as compared with those at room temperature, but the O(1) atom is shifted from the position of the room-temperature phase. A schematic drawing of the  $\text{Se}(1)\text{O}_4$  tetrahedra at

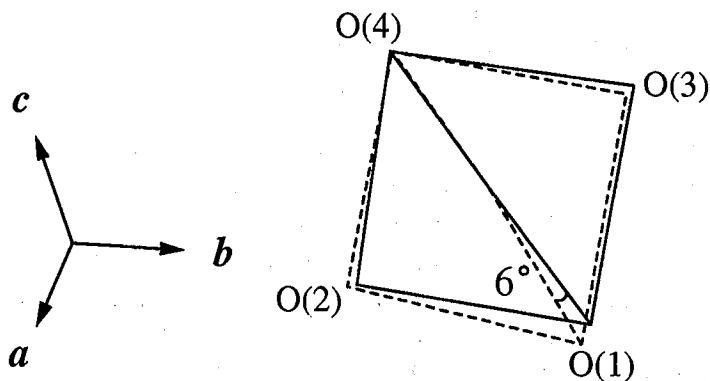


Fig. 2. Projection on the plane along the direction perpendicular to the O(1)–O(4) and O(2)–O(3) bonds for the Se(1)O<sub>4</sub> tetrahedra. The solid and dashed lines show the Se(1)O<sub>4</sub> tetrahedra at room temperature [5] and 141 K, respectively.

room temperature and 141 K is shown in Fig. 2, as viewed along the direction which is perpendicular to the two mutually perpendicular bonds of O(1)–O(4) and O(2)–O(3). Since the principal directions of the EPR parameter of the spin Hamiltonian are almost perpendicular to the O–O bonds, the shift of the O(1) atom indicates that the principal directions of the parameter rotate along the perpendicular axis. Therefore, it is considered that the temperature dependence of the <sup>77</sup>Se hyperfine line-positions in the low-temperature phase is produced by an increase in the shift of the O(1) atom with decreasing temperature. The angle of deviation of the O(1) atom from the Se–O(1) direction of the room-temperature phase is observed to be about 6°, as shown in Fig. 2. However, the observed value of the angle is rather different from that (about 17°) obtained from the EPR measurements [12]. This difference is probably caused by the error in the angular dependence of the <sup>77</sup>Se hyperfine line-positions.

Finally, we summarize the results of the X-ray measurements for  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  at 141 K. The observed structure is almost the same as that at room temperature. The  $(\text{NH}_4)_4\text{H}_2(\text{SeO}_4)_3$  crystal in the low-temperature phase could be ferroelectric with the electric dipole moment along the *c*-axis. The SeO<sub>4</sub> tetrahedra do not rotate with decreasing temperature in the low-temperature phase. However, the shift of the O(1) atom produces the rotation of the principal directions of the EPR parameter.

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