Modification of Crystal Structure of Ammonium Rochelle Salt [NaNH$_4$(+)-C$_4$H$_4$O$_6$.4H$_2$O] Owing to the Replacement of NH$_4$ Ions with K Ions

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Abstract

The crystal structures of NaK$_{1-x}$(NH$_4$)$_x$(+)-C$_4$H$_4$O$_6$.4H$_2$O (RS$_{1-x}$ARS$_x$, $x = 0.90$, 0.94 and 1.00) have been determined in the paraelectric phase ($T = 294$ K). The crystal data are: for ARS, orthorhombic, $P2_12_12$, $R = 0.038$, $wR = 0.032$, no. of reflections $= 3373$, $a = 12.206(7)$, $b = 14.451(6)$, $c = 6.250(4)$ Å, $V = 1102(1)$ Å^3, $Z = 4$, $D_x = 1.573$ g cm^{-3}, λ(Mo$K\alpha_1$) $= 0.70926$ Å, $F(000) = 552.00$; for RS$_{0.06}$ARS$_{0.94}$, orthorhombic, $P2_12_12$, $R = 0.040$, $wR = 0.030$, no. of reflections $= 2446$, $a = 12.172(4)$, $b = 14.421(4)$, $c = 6.239(2)$ Å, $V = 1095.2(6)$ Å^3, $Z = 4$, $D_x = 1.592$ g cm^{-3}, λ(Mo$K\alpha_1$) $= 0.70926$ Å, $F(000) = 553.92$; for RS$_{0.10}$ARS$_{0.90}$, orthorhombic, $P2_12_12$, $R = 0.036$, $wR = 0.027$, no. of reflections $= 1898$, $a = 12.165(9)$, $b = 14.420(7)$, $c = 6.239(4)$ Å, $V = 1094(1)$ Å^3, $Z = 4$, $D_x = 1.598$ g cm^{-3}, λ(Mo$K\alpha_1$) $= 0.70926$ Å, $F(000) = 555.20$. In the crystals there are two crystallographically nonequivalent cation sites occupied by K/NH$_4$ ions. The accommodation ratios of sites (1) [(2a) by the Wyckoff notation] and (2) [(2b)] are 0.94(1) and 0.92(1), respectively, in RS$_{0.06}$ARS$_{0.94}$, and 0.90(1) and 0.93(1), respectively, in RS$_{0.10}$ARS$_{0.90}$. As x increases, the location of site (2) displaces towards the origin. The hydrogen bonds around sites (1) and (2) are classified into two types: one is that the distances become longer as x increases, due to the difference in the ionic radii of K and NH$_4$ ions, while the other is that the distances are equal. Comparing the crystal structure of ARS to that of RS, the following differences occur: the position of site (2), the interatomic distances between cations of sites (1) and (2) and oxygens, the form of the tartrate molecule and the position of some water molecules. These differences seem to be mainly caused by the replacement of NH$_4$ ions by K.

1. Introduction

Sodium ammonium tartrate tetrahydrate, NaNH$_4$(+)-C$_4$H$_4$O$_6$.4H$_2$O (ammonium Rochelle salt, abbreviated as ARS) is isomorphous (orthorhombic, $P2_12_12$, $Z = 4$) in the paraelectric phase to sodium potassium ammonium tartrate tetrahydrate [Rochelle salt, abbreviated as RS (Jona & Shirane, 1962)].

However, a number of the physical properties of ARS on phase transitions are strikingly different from those of RS. For example, the polar axis of ARS is the b axis, while that of RS is the a axis; ARS has spontaneous polarization below $T_c = 109$ K (Takagi & Makita, 1958), while RS has a ferroelectric phase between the two transition temperatures $T_{c1} = 297$ and $T_{c2} = 255$ K. The dielectric constant of ARS does not follow the Curie–Weiss law above T_c and shows a small step-like anomaly at T_c, while that of RS shows two sharp peaks at the transition temperatures.

The reversal of the spontaneous polarization of ARS cannot be achieved by the application of even a very strong electric field, but it is easily realized by the application of the mechanical shearing stress. In the polar phase of ARS, Sawada & Takagi (1971) have reported X-ray superlattice reflections, indicating that the lattice constant a is doubled. Iizumi & Gesi (1978) have observed satellite reflections in the polar phase of the deuterated ARS by neutron diffraction and pointed out that the lattice is incommensurately modulated.

As is well known, ARS and RS form a continuous series of mixed crystals over the whole range of concentrations. These mixed crystals have been investigated by Makita & Takagi (1958). The mixed-crystal system of RS and ARS, NaK$_{1-x}$(NH$_4$)$_x$C$_4$H$_4$O$_6$.4H$_2$O (abbreviated as RS$_{1-x}$ARS$_x$), is divided into four compositional ranges according to the type of dielectric behavior. In RS ($x = 0$) the ferroelectric phase exists in the temperature range $T_{c1} = 297$ to $T_{c2} = 255$ K. The stable region of the ferroelectric phase becomes narrower as the content (x) of ARS increases. Then it completely disappears at $x = 0.025$. (This range is denoted as region I.) In the composition range $x = 0.025$–0.18, no ferroelectric phase transition is observed. (The range is denoted as region II.) In the range $x = 0.18$–0.90, another ferroelectric phase appears in a low-temperature region (denoted as region III). In the range $x = 0.90$–1.0, the polar phase equal to the low-temperature phase of ARS appears (denoted as region IV).

The NMR (Morimoto, 1974), elastic properties (Maeda & Ikeda, 1978), behaviors of the birefringences and dielectric properties (Ivanov, Khusravov, Shuvalov & Shchagina, 1979; Ivanov, Shuvalov, Khusravov & Shchagina, 1980), hydrostatic pressure effect (Gesi &

Table 1. *Experimental details*

	ARS	$RS_{0.06}ARS_{0.94}$	$RS_{0.1}ARS_{0.9}$
Crystal data			
Chemical formula	$Na(NH_4)C_4H_4O_6.4H_2O$	$NaK_{0.06}(NH_4)_{0.94}C_4H_4O_6.4H_2$	$NaK_{0.1}(NH_4)_{0.9}C_4H_4O_6.4H_2O$
Chemical formula weight	261.16	262.43	263.27
Cell setting	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12$	$P2_12_12$	$P2_12_12$
a (Å)	12.206 (7)	12.172 (4)	12.165 (9)
b (Å)	14.451 (6)	14.421 (4)	14.420 (7)
c (Å)	6.250 (4)	6.239 (2)	6.239 (4)
V (Å^3)	1102 (1)	1095.2 (6)	1094 (1)
Z	4	4	4
D_x (Mg m^{-3})	1.573	1.592	1.598
Radiation type	Mo $K\alpha_1$	Mo $K\alpha_1$	Mo $K\alpha_1$
Wavelength (Å)	0.70926	0.70926	0.70926
No. of reflections for cell parameters	65	76	55
θ range ($^\circ$)	22.5–30	22.5–30.5	23–30
μ (mm^{-1})	0.177	0.201	0.216
Temperature (K)	294	294	294
Crystal form	Sphere	Sphere	Sphere
Crystal size (diameter, mm)	0.45	0.25	0.25
Crystal color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Rigaku AFC-5	Rigaku AFC-5	Rigaku AFC-5
Data collection method	ω ($5<2\theta<30$), $2\theta-\omega$ ($30<2\theta<70$)	ω ($5<2\theta<30$), $2\theta-\omega$ ($30<2\theta<70$)	ω ($5<2\theta<30$), $2\theta-\omega$ ($30<2\theta<70$)
Absorption correction	Numerical integration (*DABEX*; Dwiggins, 1975)	Numerical integration (*DABEX*; Dwiggins, 1975)	Numerical integration (*DABEX*; Dwiggins, 1975)
T_{min}	0.887	0.927	0.922
T_{max}	0.888	0.928	0.923
No. of measured reflections	4125	3797	3033
No. of independent reflections	1825	1423	1056
No. of observed reflections	3373	2446	1898
Criterion for observed reflections	$F_o>3\sigma(F_o)$	$F_o>3\sigma(F_o)$	$F_o>3\sigma(F_o)$
R_{int}	0.0139	0.0149	0.0149
θ_{max} ($^\circ$)	35	35	35
Range of h, k, l	$0 \rightarrow h \rightarrow 21$	$0 \rightarrow h \rightarrow 21$	$0 \rightarrow h \rightarrow 21$
	$-26 \rightarrow k \rightarrow 26$	$0 \rightarrow k \rightarrow 26$	$-26 \rightarrow k \rightarrow 26$
	$0 \rightarrow l \rightarrow 11$	$-11 \rightarrow l \rightarrow 11$	$0 \rightarrow l \rightarrow 11$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections
Intensity decay (%)	1	1	1
Refinement			
Refinement on	F	F	F
Occupation ratio			
α (site 1)	1	0.94 (1)	0.90 (1)
β (site 2)	1	0.92 (1)	0.93 (1)
$x[x = (\alpha + \beta)/2]$	1	0.93	0.91
R	0.0380	0.0398	0.0355
wR	0.0320	0.0298	0.0272
S	1.2116	0.7314	0.8604
No. of reflections used in refinement	1825	1423	1056
No. of parameters used	211	213	213
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma(F_o)^2 + (0.01F_o)^2]$	$w = 1/[\sigma(F_o)^2 + (0.015F_o)^2]$	$w = 1/[\sigma(F_o)^2 + (0.01F_o)^2]$
$(\Delta/\sigma)_{max}$	<0.03	<0.03	<0.03
$\Delta\rho_{max}$ (e Å^{-3})	0.57	0.39	0.31
$\Delta\rho_{min}$ (e Å^{-3})	−0.46	−0.45	−0.25
Extinction method	Zachariasen (1967)	Zachariasen (1967)	Zachariasen (1967)
Extinction coefficient	$g = 5.06 \times 10^{-4}$	$g = 1.40 \times 10^{-4}$	$g = 8.69 \times 10^{-4}$
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV) and Stewart, Davidson & Simpson (1965)	*International Tables for X-ray Crystallography* (1974, Vol. IV) and Stewart, Davidson & Simpson (1965)	*International Tables for X-ray Crystallography* (1974, Vol. IV) and Stewart, Davidson & Simpson (1965)

Ozawa, 1980), dielectric relaxation (Horioka, Abe & Naka, 1980), Raman spectroscopy (Latush *et al.*, 1987) and thermal properties (Noda, Haga, Kikuta, Nozaki & Shiozaki, 1995) on the RS–ARS mixed crystal have been performed.

The crystal structure of RS ($x = 0.0$) has been studied by many workers (Beevers & Hughes, 1941; Iwata, Mitani & Shibuya, 1989, 1990; Suzuki & Shiozaki, 1996) and also that of ARS ($x = 1.0$) at room temperature (Shkuratova, Kiosse & Malinovskii, 1979;

Kuroda & Mason, 1981). Recently, the structural change due to the phase transition has been studied by Brożek & Stadnicka (1994) and Brożek, Mucha & Stadnicka (1994).

In the mixed crystals the cation sites and their neighboring oxygens will be strongly affected by replacing NH_4 ions with K, so that the dielectric properties and the transition mechanisms vary with the composition x. It is important to study the corresponding structural changes and it is expected that the precise studies of $RS_{1-x}ARS_x$ in region IV will prompt to understanding the mechanism of the phase transition in ARS.

We have studied the crystal structures of three different compositions of $RS_{1-x}ARS_x$ ($x = 1.00$, 0.94 and 0.90) at room temperature, which belong to region IV. In this paper we report their structures and compare them, and discuss the relation between the accommodation ratio of NH_4 ions and the change in crystal structure. Moreover, we compare the crystal structures of ARS and RS. The difference between these crystal structures and the influence of the replacement of NH_4 ions by K are discussed.

2. Experimental

Single crystals of $NaK_{1-x}(NH_4)_x(+)$-$C_4H_4O_6.4H_2O$ were grown from slow evaporation of three types of dextrorotatory aqueous saturated solutions of the natural L-(+)-tartrate acids containing the following corresponding ratios of the three salts; $2K_2(+)$-$C_4H_4O_6.H_2O$, $Na_2(+)$-$C_4H_4O_6.2H_2O$ and $(NH_4)_2(+)$-$C_4H_4O_6$. In the case of ARS the crystals were prepared by recrystallization several times; however, for the mixed crystals ($x \neq 1.00$), the recrystallization was not carried out because the content of K ions in the mixed crystals is different from that in the aqueous solutions. The three types of crystals were grown from the aqueous solutions $RS_{1-x}ARS_x$ ($x = 1.00$, 0.92 and 0.90), respectively. Atomic absorption spectrometry was employed to determine the fraction of ARS in the mixed crystals, resulting in the content of ARS in the sample grown from the aqueous solution $RS_{0.08}ARS_{0.92}$ being 0.94 (1) and that in the sample grown from the aqueous solution $RS_{0.10}ARS_{0.90}$ being 0.90 (1), i.e. $x = 0.94$ (1) and 0.90 (1) in the expression $NaK_{1-x}(NH_4)_x(+)$-$C_4H_4O_6.4H_2O$.

The sample crystals were sealed in a glass capillary tube to avoid dehydration and deliquescence and mounted on a Rigaku automatic four-circle X-ray diffractometer (AFC-5) with pyrolytic graphite-monochromated Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å). Corrections to the observed intensities were made for Lorentz–polarization, absorption and secondary extinction. The absorption correction (numerical integration) was made using the program DABEX (Dwiggins, 1975) in the

CHARGE system. Lattice parameters were calculated using the following function of systematic error of the lattice spacing: $\Delta d/d = \sin^2 \theta(1/\sin \theta + 1/\theta)$. Summaries of crystal data, data collection and refinement are listed in Table 1.

ARS has two nonequivlent NH_4 ion sites, site (1) [(2a) by Wyckoff notation] for NH_4 (1) and site (2) (2b) for NH_4 (2). The circumstances and the coordination around NH_4 (1) are different from those around NH_4 (2). It is natural to consider that in the mixed-crystal system, the accommodation of K ions for the two sites is different. In order to specify the accommodation rates of K ions in sites (1) and (2), the accommodation parameters α and β are introduced; α indicates the fraction of NH_4 ions accommodated in site (1) and β in site (2). These parameters fulfill the relation $\alpha + \beta = 2x$.

The values reported by Shkuratova, Kiosse & Malinovskii (1979) were used as the initial values of the positional and thermal parameters for the refinements of ARS. The final parameters of ARS were used as the initial values of the positional and thermal parameters of the refinements of $RS_{0.06}ARS_{0.94}$ and $RS_{0.10}ARS_{0.90}$. For the accommodation parameters of NH_4 ions in sites (1) and (2), the contents of ARS in the aqueous solutions were used for the initial parameters. Correction of the isotropic secondary extinction was made using AHRADY [(Sasaki, 1986) for ARS and $RS_{0.10}ARS_{0.90}$] and RADIEL [(Coppens et al., 1979) for $RS_{0.06}ARS_{0.94}$]. Full-matrix least-squares calculations were performed by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma(F_o)^2 + (aF_o)^2$.

The atomic and anomalous scattering factors were taken from International Tables for X-ray Crystallography (1974, Vol. IV). Two types of atomic scattering factor for the H atoms were used. The spherical-bonded H-atom scattering factor (Stewart, Davidson & Simpson, 1965) was used for H atoms bonded to C atoms and the free H-atom scattering factor (International Tables for X-ray Crystallography, 1974, Vol. IV) was used for H atoms bonded to O and N atoms. In the mixed crystals α and β were determined by least-squares calculations, together with the other structural parameters, including those of the hydrogen atoms. In the least-squares calculation, the atomic scattering factor $f_{KN(1)}$ of a hypothetical atom KN at site (1), defined as $f_{KN(1)} = (1 - \alpha)f_K + \alpha f_N$, was used, where f_K and f_N are the atomic scattering factors of the K and N atoms, respectively. The atomic scattering factor at site (2), defined as $f_{KN(2)} = (1 - \beta)f_K + \beta f_N$, was used in a similar manner. In order to determine the parameters α and β, the following constraints were applied in the refinements: $z(K \text{ atom}) = z(N \text{ atom})$, $U_{ij}(K \text{ atom}) = U_{ij}(N \text{ atom})$ ($i, j = 1 \sim 3$). The results of α and β are given in Table 1; the content of ARS, x for $RS_{0.06}ARS_{0.94}$, has been determined to be 0.93 and that for $RS_{0.10}ARS_{0.90}$ to be 0.91, respectively. These values are in good agreement with the results of atomic absorption spectrometry, within experimental error. The

final results of the atomic positions and the thermal parameters of the crystals are given in Table 2.*

3. Structure descriptions and discussions

3.1. Crystal structure of ARS

The crystal structure of ARS is composed of ammonium and sodium cations, tartrate molecules [(+)-$C_4H_4O_6^{2-}$] and water molecules† (Fig. 1). There are layers of cations (NH_4 and Na ions), perpendicular to the b axis, separated by layers of tartrate molecules connected by hydrogen bonds.

The N(1) atom is at the special position ($2a$) and is surrounded by six O atoms. Two of the H atoms in the ammonium ion N(1)H_4 are bonded to O(1) of the carboxyl oxygens. The remaining two H atoms seem to be weakly bonded to the O atoms of the water molecules $H_2O(9)$. The thermal ellipsoid of N(1) is very elongated along the direction of N(1)—O(9) and the U_{iso} value of H(N1b) is very large [$U_{iso} = 0.14\,(3)\,\text{Å}^2$].

On the other hand, the N(2) atom is at ($2b$) and surrounded by eight oxygens. Among the four H atoms of N(2)H_4, two are bonded to O(4) of the carboxyl oxygens and the remaining two are bonded to the O

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* Lists of atomic coordinates, anisotropic displacement parameters, values of the principal axes of the thermal ellipsoids for non-H atoms and structure factors have been deposited with the IUCr (Reference: OH0054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† In this paper, the numbers assigned to the atoms, except H atoms, are the same as used by Beevers & Hughes (1941), because of the merit of the descriptions and discussions of the physical properties in connection with RS. In the papers of Kuroda & Mason (1981), Brożek & Stadnicka (1994) and Brożek, Mucha & Stadnicka (1994), another numbering was used.
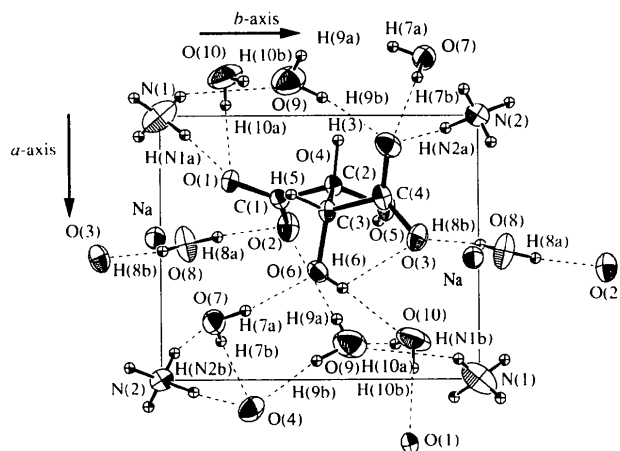

Fig. 1. Projection of the asymmetric unit of the paraelectric phase of ARS on (001). Thermal ellipsoids are drawn at the 50% probability level using ORTEPII (Johnson, 1976). H atoms are drawn as small spheres.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
ARS				
Na	0.2699 (1)	0.4917 (1)	0.4827 (1)	0.0268 (4)
N(1)	0.0	0.0	0.0480 (6)	0.0541 (19)
N(2)	0.0	1/2	0.1382 (5)	0.0292 (12)
C(1)	0.1568 (1)	0.1877 (1)	0.2825 (3)	0.0197 (8)
C(2)	0.1311 (1)	0.2729 (1)	0.4194 (3)	0.0192 (8)
C(3)	0.1803 (1)	0.2628 (1)	0.6435 (3)	0.0198 (8)
C(4)	0.1540 (2)	0.3494 (1)	0.7781 (3)	0.0231 (8)
O(1)	0.1220 (1)	0.1104 (1)	0.3508 (2)	0.0246 (6)
O(2)	0.2097 (1)	0.2010 (1)	0.1146 (2)	0.0310 (6)
O(3)	0.2312 (1)	0.4039 (1)	0.8161 (2)	0.0337 (7)
O(4)	0.0556 (1)	0.3591 (1)	0.8360 (2)	0.0341 (7)
O(5)	0.1719 (1)	0.3553 (1)	0.3235 (2)	0.0264 (7)
O(6)	0.2954 (1)	0.2469 (1)	0.6299 (4)	0.0271 (7)
O(7)	0.3908 (1)	0.0831 (1)	0.4800 (3)	0.0350 (8)
O(8)	0.2420 (1)	0.0402 (1)	0.8782 (2)	0.0408 (8)
O(9)	0.4333 (2)	0.2969 (2)	0.0478 (3)	0.0544 (11)
O(10)	0.4251 (2)	0.3970 (1)	0.4291 (4)	0.0602 (12)
$RS_{0.06}ARS_{0.94}$				
Na	0.2698 (1)	0.4917 (1)	0.4821 (1)	0.0265 (4)
N(1)*	0.0	0.0	0.0495 (39)	0.0518 (128)
N(2)†	0.0	1/2	0.1430 (16)	0.0282 (58)
C(1)	0.1561 (2)	0.1876 (1)	0.2827 (3)	0.0188 (10)
C(2)	0.1305 (2)	0.2731 (1)	0.4196 (3)	0.0181 (10)
C(3)	0.1805 (2)	0.2628 (1)	0.6434 (3)	0.0190 (10)
C(4)	0.1540 (2)	0.3495 (2)	0.7782 (3)	0.0222 (11)
O(1)	0.1219 (1)	0.1103 (1)	0.3508 (2)	0.0243 (8)
O(2)	0.2096 (1)	0.2011 (1)	0.1145 (2)	0.0298 (8)
O(3)	0.2315 (1)	0.4039 (1)	0.8154 (2)	0.0335 (8)
O(4)	0.0556 (1)	0.3592 (1)	0.8372 (3)	0.0334 (9)
O(5)	0.1718 (1)	0.3554 (1)	0.3233 (2)	0.0259 (9)
O(6)	0.2953 (1)	0.2469 (1)	0.6294 (3)	0.0276 (9)
O(7)	0.3910 (2)	0.0831 (1)	0.4795 (3)	0.0340 (10)
O(8)	0.2427 (2)	0.0400 (1)	0.8785 (3)	0.0409 (10)
O(9)	0.4331 (2)	0.2971 (2)	0.0473 (4)	0.0549 (14)
O(10)	0.4250 (2)	0.3974 (2)	0.4279 (4)	0.0603 (15)
$RS_{0.1}ARS_{0.9}$				
Na	0.2699 (1)	0.4918 (1)	0.4823 (2)	0.0272 (6)
N(1)‡	0.0	0.0	0.0480 (30)	0.0688 (127)
N(2)§	0.0	1/2	0.1443 (24)	0.0269 (83)
C(1)	0.1567 (2)	0.1873 (2)	0.2824 (4)	0.0202 (14)
C(2)	0.1299 (2)	0.2732 (2)	0.4195 (4)	0.0186 (13)
C(3)	0.1801 (2)	0.2629 (2)	0.6435 (5)	0.0206 (14)
C(4)	0.1538 (3)	0.3493 (2)	0.7784 (4)	0.0239 (15)
O(1)	0.1218 (1)	0.1104 (1)	0.3507 (3)	0.0250 (10)
O(2)	0.2097 (1)	0.2010 (1)	0.1146 (3)	0.0305 (10)
O(3)	0.2317 (1)	0.4040 (1)	0.8153 (3)	0.0340 (11)
O(4)	0.0552 (2)	0.3592 (1)	0.8374 (3)	0.0331 (11)
O(5)	0.1712 (2)	0.3556 (1)	0.3227 (3)	0.0269 (11)
O(6)	0.2957 (2)	0.2469 (1)	0.6298 (4)	0.0269 (11)
O(7)	0.3913 (2)	0.0831 (1)	0.4795 (4)	0.0341 (13)
O(8)	0.2428 (2)	0.0401 (1)	0.8792 (3)	0.0421 (13)
O(9)	0.4336 (3)	0.2973 (2)	0.0462 (5)	0.0556 (18)
O(10)	0.4253 (2)	0.3976 (2)	0.4269 (5)	0.0613 (19)

* Occupancy 0.94 (1).   † Occupancy 0.92 (1).   ‡ Occupancy 0.90 (1).
§ Occupancy 0.93 (1).

atoms of the water molecules $H_2O(7)$. The thermal ellipsoid of N(2) is isotropic.

The Na atom is at the general position and surrounded by six oxygens (Table 3).

Many hydrogen bonds connect the ammonium cations, tartrate and water molecules and they form the frame-

Table 3. *Interatomic distances (Å) around the Na atoms with e.s.d.'s in parentheses*

	ARS	$RS_{0.06}ARS_{0.94}$	$RS_{0.10}ARS_{0.90}$
Na—O(1^i)	2.401 (2)	2.398 (2)	2.397 (2)
Na—O(3)	2.485 (2)	2.479 (2)	2.477 (2)
Na—O(5)	2.512 (2)	2.504 (2)	2.508 (2)
Na—O(7^i)	2.376 (2)	2.371 (3)	2.374 (3)
Na—O(8^i)	2.367 (2)	2.360 (2)	2.366 (3)
Na—O(10)	2.361 (3)	2.352 (3)	2.353 (3)
Mean	2.417	2.411	2.413

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.

work of the crystal. In the tartrate molecule the O(1) atom accepts the two hydrogen bonds from N(1)H$_4$ and H$_2$O(10). O(2) accepts the three hydrogen bonds from H$_2$O(8), O(5)H and H$_2$O(9); among them the O(9)—H(9a)$\cdots$O(2) bond appears to be weak because of the long interatomic distance O(9)—O(2) (Table 6). O(3) and O(4) are also acceptors of the hydrogen bonds from H$_2$O(8) and O(6)H and from N(2)H$_4$, H$_2$O(7) and H$_2$O(9), respectively. O(6) accepts the hydrogen bond from H$_2$O(7) and also behaves as a donor to H$_2$O(10) and O(3).

The equivalent thermal parameters of N(1), O(9) and O(10) are extremely large (Table 2), as have been reported by Shkuratova, Kiosse & Malinovskii (1979) and also Brożek & Stadnicka (1994). The anisotropy in the thermal parameters of several atoms seems to be especially significant [U_{11} of C(4), O(5) and O(8), and U_{22} and U_{33} of O(10)]. Among the C atoms, the equivalent thermal parameter of C(4) is large and those of O(3) and O(4) are greater than those of the remaining O atoms in the tartrate molecule. The O atoms of the two carboxylate anions, O(1) and O(4), which are bonded to ammonium ions by hydrogen bonds, have the isotropic motions. On the other hand, O(2) and O(3), which are connected to each other through the water molecules H$_2$O(8), show anisotropic motion along the a axis.

3.2. *Crystal structural changes due to the replacement of NH_4^+ with K^+*

The thermal parameters of the individual atoms in the mixed crystals are similar to those in ARS. Remarkable changes of the z coordinates of several atoms are observed in the mixed crystals. As x increases, the values of the z coordinate of site (2) and O(4) become smaller. On the other hand, those of O(9) and O(10) become larger.*

The interatomic distances between Na atoms and the neighboring oxygens are presented in Table 3. The Na—O(3) and Na—O(10) distances increase as the parameter x increases. There are no significant differ-

* In this section, sites (1) and (2) are used as the name of cations, K(1) and K(2) in ARS and also KN(1) and KN(2) in $RS_{1-x}ARS_x$, respectively.

Table 4. *Interatomic distances (Å) and geometry of the hydrogen bonds around sites (1) and (2)*

	N$\cdots$O (Å)	N—H (Å)	O$\cdots$H (Å)	N—H$\cdots$O (°)
ARS				
N(1)—H(N1a)$\cdots$O(1)	2.889 (3)	0.90 (3)	2.00 (3)	171 (3)
N(1)—H(N1b^i)$\cdots$O(9^i)	3.104 (3)	0.74 (5)	2.50 (4)	141 (4)
N(2)—H(N2a)$\cdots$O(4^{ii})	2.859 (3)	1.00 (3)	1.86 (3)	174 (2)
N(2)—H(N2b^{iii})$\cdots$O(7^{iii})	2.985 (3)	0.78 (3)	2.31 (3)	145 (2)
N(1)—O(8^{ii})	3.192 (2)			
N(1)—O(10^{iv})	3.456 (4)			
N(2)—O(5)	3.181 (2)			
N(2)—O(8^v)	3.204 (2)			
$RS_{0.06}ARS_{0.94}$				
KN(1)—H(N1a)$\cdots$O(1)	2.875 (16)	0.77 (4)	2.10 (4)	175 (5)
KN(1)—H(N1b^i)$\cdots$O(9^i)	3.097 (6)	0.54 (6)	2.80 (7)	119 (8)
KN(2)—H(N2a)$\cdots$O(4^{ii})	2.867 (7)	0.89 (3)	1.98 (3)	172 (3)
KN(2)—H(N2b^{iii})$\cdots$O(7^{iii})	2.957 (8)	0.77 (4)	2.27 (3)	151 (3)
KN(1)—O(8^{ii})	3.193 (9)			
KN(1)—O(10^{iv})	3.449 (21)			
KN(2)—O(5)	3.160 (4)			
KN(2)—O(8^v)	3.187 (3)			
$RS_{0.10}ARS_{0.90}$				
KN(1)—H(N1a)$\cdots$O(1)	2.880 (12)	1.00 (5)	1.89 (5)	169 (4)
KN(1)—H(N1b^i)$\cdots$O(9^i)	3.089 (5)	0.87 (9)	2.49 (9)	127 (7)
KN(2)—H(N2a)$\cdots$O(4^{ii})	2.870 (10)	0.88 (4)	2.00 (3)	177 (3)
KN(2)—H(N2b^{iii})$\cdots$O(7^{iii})	2.948 (12)	0.78 (4)	2.28 (4)	144 (3)
KN(1)—O(8^{ii})	3.189 (7)			
KN(1)—O(10^{iv})	3.433 (16)			
KN(2)—O(5)	3.148 (6)			
KN(2)—O(8^v)	3.185 (3)			

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (ii) $x, y, z - 1$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.

ences between the remaining interatomic distances, within e.s.d.'s.

The interatomic distances and geometries of the hydrogen bonds around sites (1) and (2) are presented in Table 4. Around site (1) the site (1)—O(10) distance significantly increases with increments of x, while the site (1)—O(1) and site (1)—O(9) distances only increase by a small amount. The site (1)—O(8) distance is kept almost constant. The site (1)—O(9) distance seems to be slightly longer than that of an ordinary hydrogen bond, so that the strength of the hydrogen bond will be weak. Also, it is assumed that the site (1)—H(N1b)$\cdots$O(9) angle is much smaller than 180° and that the thermal parameter of the H atom is large.*

On the other hand, around site (2), the site (2)—O(5), site (2)—O(7) and site (2)—O(8) distances greatly increase, while that of site (2)—O(4) decreases slightly with increasing x. Hydrogen bonds are formed between

* The position of H(N1b) in $RS_{0.06}ARS_{0.94}$ is different from those in ARS and $RS_{0.10}ARS_{0.90}$, taking into account the atomic distances KN(1)—H(N1b) and H(N1b)$\cdots$O(9). It is, however, considered that the position of H(N1b) in $RS_{0.06}ARS_{0.94}$ should be located at similar positions in ARS and $RS_{0.10}ARS_{0.90}$. Thus, the authors regard the difference not as the important structural one but as the distinction resulting from the problems of the structural analysis.

Table 5. *Geometry of tartrate molecules in $RS_{1-x}ARS_x$, bonds lengths (Å) and angles (°) with e.s.d.'s in parentheses*

	ARS	$RS_{0.06}ARS_{0.94}$	$RS_{0.10}ARS_{0.90}$
C(1)—C(2)	1.532 (2)	1.532 (2)	1.540 (4)
C(2)—C(3)	1.531 (3)	1.530 (3)	1.532 (4)
C(3)—C(4)	1.542 (3)	1.541 (3)	1.537 (4)
C(1)—O(1)	1.269 (2)	1.264 (2)	1.261 (3)
C(1)—O(2)	1.247 (2)	1.250 (2)	1.245 (3)
C(2)—O(5)	1.423 (2)	1.422 (2)	1.424 (3)
C(2)—H(2)	1.05 (2)	1.02 (2)	1.11 (2)
C(3)—O(6)	1.426 (2)	1.418 (2)	1.428 (4)
C(3)—H(3)	1.00 (2)	0.96 (3)	1.09 (3)
C(4)—O(3)	1.250 (3)	1.249 (3)	1.254 (4)
C(4)—O(4)	1.262 (3)	1.261 (3)	1.263 (4)
O(2)—O(5)	2.624 (2)	2.619 (2)	2.622 (3)
O(5)—H(5)	0.73 (2)	0.78 (3)	0.81 (3)
H(5)···O(2)	2.16 (2)	2.15 (3)	2.11 (2)
O(3)—O(6)	2.668 (2)	2.660 (2)	2.660 (3)
O(6)—H(6)	0.69 (3)	0.60 (3)	0.75 (3)
H(6)···O(3)	2.40 (3)	2.38 (4)	2.38 (4)
O(1)—C(1)—O(2)	126.3 (2)	126.3 (2)	126.7 (2)
O(1)—C(1)—C(2)	116.8 (2)	117.1 (2)	116.6 (2)
O(2)—C(1)—C(2)	116.9 (1)	116.7 (2)	116.6 (2)
C(1)—C(2)—O(5)	111.4 (1)	111.4 (2)	111.1 (2)
C(1)—C(2)—C(3)	110.7 (1)	110.5 (2)	110.1 (2)
O(5)—C(2)—C(3)	109.1 (1)	109.0 (2)	109.1 (2)
C(2)—O(5)—H(5)	108 (1)	110 (2)	108 (2)
C(2)—C(3)—O(6)	110.3 (1)	110.6 (2)	110.7 (2)
C(2)—C(3)—C(4)	109.9 (1)	109.6 (2)	109.7 (2)
O(6)—C(3)—C(4)	111.6 (1)	111.8 (2)	111.6 (2)
C(3)—O(6)—H(6)	115 (2)	115 (3)	117 (3)
C(3)—C(4)—O(4)	116.4 (2)	116.6 (2)	116.7 (3)
C(3)—C(4)—O(3)	117.2 (2)	116.9 (2)	116.9 (3)
O(3)—C(4)—O(4)	126.3 (2)	126.4 (2)	126.4 (3)
O(5)—H(5)···O(2)	122 (2)	119 (3)	121 (3)
O(6)—H(6)···O(3)	106 (3)	112 (4)	103 (3)

Table 6. *Interatomic distances (Å) and angles (°) of oxygen–oxygen, creating hydrogen bonds*

	O—H	O···O	O···H	O—H···O
ARS				
O(6)—H(6)···O(10)	0.69 (3)	2.964 (3)	2.33 (3)	153 (3)
O(7)—H(7a)···O(6)	0.81 (3)	2.799 (2)	2.00 (3)	171 (2)
O(7)—H(7b)···O(4^i)	0.80 (3)	2.940 (2)	2.16 (3)	163 (2)
O(8)—H(8a)···O(3^{ii})	0.73 (3)	2.763 (2)	2.04 (3)	171 (3)
O(8)—H(8b)···O(2^{iii})	0.85 (3)	2.782 (2)	1.94 (3)	175 (2)
O(9)—H(9a)···O(2)	0.69 (4)	3.089 (3)	2.51 (4)	143 (5)
O(9)—H(9b)···O(4^i)	0.88 (3)	2.800 (3)	1.92 (3)	171 (2)
O(10)—H(10a)···O(9)	0.83 (3)	2.790 (3)	1.96 (3)	172 (2)
O(10)—H(10b)···O(1^i)	0.71 (3)	2.771 (3)	2.07 (2)	170 (3)

	Angle (°)
H(7a)—O(7)—H(7b)	105 (3)
H(8a)—O(8)—H(8b)	109 (3)
H(9a)—O(9)—H(9b)	95 (4)
H(10a)—O(10)—H(10b)	101 (3)

	O—H	O···O	O···H	O—H···O
$RS_{0.06}ARS_{0.94}$				
O(6)—H(6)···O(10)	0.60 (3)	2.964 (3)	2.44 (3)	145 (5)
O(7)—H(7a)···O(6)	0.74 (4)	2.795 (3)	2.06 (3)	173 (4)
O(7)—H(7b)···O(4^i)	0.91 (3)	2.934 (3)	2.05 (4)	165 (3)
O(8)—H(8a)···O(3^{ii})	0.79 (3)	2.756 (2)	1.98 (3)	168 (4)
O(8)—H(8b)···O(2^{iii})	0.80 (3)	2.780 (2)	1.98 (3)	178 (3)
O(9)—H(9a)···O(2)	0.76 (4)	3.081 (3)	2.48 (4)	137 (4)
O(9)—H(9b)···O(4^i)	0.84 (3)	2.797 (3)	1.96 (3)	173 (3)
O(10)—H(10a)···O(9)	0.92 (3)	2.782 (4)	1.88 (3)	168 (2)
O(10)—H(10b)···O(1^i)	0.70 (4)	2.768 (3)	2.07 (4)	172 (3)

	Angle (°)
H(7a)—O(7)—H(7b)	101 (4)
H(8a)—O(8)—H(8b)	103 (3)
H(9a)—O(9)—H(9b)	110 (4)
H(10a)—O(10)—H(10b)	98 (3)

	O—H	O···O	O···H	O—H···O
$RS_{0.10}ARS_{0.90}$				
O(6)—H(6)···O(10)	0.75 (3)	2.968 (4)	2.29 (4)	151 (4)
O(7)—H(7a)···O(6)	0.87 (3)	2.795 (3)	1.94 (3)	167 (3)
O(7)—H(7b)···O(4^i)	0.85 (4)	2.928 (3)	2.13 (4)	158 (3)
O(8)—H(8a)···O(3^{ii})	0.76 (3)	2.753 (3)	2.00 (3)	174 (4)
O(8)—H(8b)···O(2^{iii})	0.88 (4)	2.775 (3)	1.89 (3)	177 (3)
O(9)—H(9a)···O(2)	0.73 (3)	3.087 (5)	2.45 (4)	147 (5)
O(9)—H(9b)···O(4^i)	0.76 (3)	2.794 (4)	2.05 (4)	168 (4)
O(10)—H(10a)···O(9)	0.88 (3)	2.783 (5)	1.92 (5)	169 (4)
O(10)—H(10b)···O(1^i)	0.71 (4)	2.766 (4)	2.07 (4)	168 (4)

	Angle (°)
H(7a)—O(7)—H(7b)	96 (3)
H(8a)—O(8)—H(8b)	108 (4)
H(9a)—O(9)—H(9b)	103 (4)
H(10a)—O(10)—H(10b)	96 (4)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$; (iii) $x, y, 1+z$.

site (2) and O(7), and also site (2) and O(4). However, the two types of hydrogen bonds seem to have different characters: the former having a longer bond length seems to be weaker compared with the latter.

The bond lengths and angles in the tartrate molecules are given in Table 5. There are no significant differences among the three types of crystals. The bond lengths and angles of the hydrogen bonds are given in Table 6. The O(7)—O(4) and O(9)—O(2) bond lengths are slightly longer than the other O—H···O distances. Therefore, it seems that these hydrogen bonds are weak. There are no other significant differences within the e.s.d.'s.

4. Structural differences between ARS and RS in the paraelectric phase

The most remarkable difference is between the locations of the cations (NH_4 and K ions) of site (2). In ARS the coordinate of N(2) is [0, 0.5, 0.1382 (5)], while in RS that of K(2) is [0, 0.5, 0.1591 (4)]. The difference in the z-coordinate between the two locations is ca 0.1 Å. On the other hand, the locations of the site (1) cations in RS and ARS are almost equal.

In the mixed-crystal system $RS_{1-x}ARS_x$ the lattice constants a, b and c obey Vegard's law (Shiozaki, Nishimura, Amano, Suzuki & Nozaki, 1994): $a = 11.901 + 0.284x$, $b = 14.308 + 0.124x$ and $c = 6.240 - 0.001x$ Å. Taking into account not only the difference between the ionic radii of NH_4 and K ions [$r(NH_4) = 1.48$ and $r(K) = 1.33$ Å], but also the difference between the locations of the two cations, these relations are explained. These results show that the

crystal structure is modified by the replacement of NH_4 ions by K ions.

The four C atoms of the tartrate molecule form a plane in RS. The same features are also observed in ARS and the direction of the plane in ARS does not change from that in RS.

The tartrate molecule has two carboxylate anions. The lengths of the C—O bonds of the carboxylate anions are affected by crystal fields. It has been observed that the influence of the crystal fields in ARS is different from that in RS. The cause of the difference seems to mainly originate in the replacement of K with NH_4, so that in ARS the tartrate molecule interacts with the cations through hydrogen bonds. The characteristic features are as follows. In the carboxylate anion O(3)—C(4)—O(4) in ARS, C(4)—O(4) is longer than C(4)—O(3), however, C(4)—O(3) is longer than C(4)—O(4) in RS. On the other hand, in the other carboxylate anion O(1)—C(1)—O(2), C(1)—O(1) is longer than C(1)—O(2) in both ARS and RS.

There are several important characteristic features around sites (1) and (2). Between N(1) and O(1), N(2) and O(4) and also N(2) and O(7), the hydrogen-bond interactions are constructed in ARS. Among the distances between site (1) [K(1) and N(1)] and its neighboring oxygens, the site(1)—O(1) distance is almost equal to that in RS, however, the remaining lengths are significantly different [K(1)—O(9) 2.976 (7) and N(1)—O(9) 3.104 (3) Å]. Around site (2), the site (2)—O(4) distance is not substantially changed, however, that of site (2)—O(7) is different [K(2)—O(7) 2.830 (7) and N(2)—O(7) 2.985 (3) Å]. The site (2)—O(5) distance differs significantly [K(2)—O(5) 3.001 (7) and N(2)—O(5) 3.181 (2) Å]. The interatomic distances of site (1)—O(1) and site (2)—O(4) are unchanged in the course of the successive phase transition of RS (Suzuki & Shiozaki, 1996). Therefore, it is plausible that in the phase transition of ARS the role of these unchanged hydrogen bonding interactions will be different from those which are related to the water molecules [i.e. site(2)—O(7) etc.].

Among the four water molecules, the locations of $H_2O(9)$ and $H_2O(10)$ in the ARS crystal are displaced along the c axis from those in RS. The water molecule $H_2O(9)$ against tartrate molecules and the distances of O(9)—O(2) and O(9)—O(4) are shorter than those in RS. The O(9)—O(4) bond in ARS seems to be stronger than in RS.

The studies of the temperature dependence of the crystal structure and the accurate crystal structure in the polar phase are necessary to understand the nature of the structural phase transition of ARS and such studies are now in progress.

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