No. 40A-5 NH_4HSO_4, Ammonium hydrogen sulfate

(M = 115.11; [D: 116.12])

1a Ferroelectricity in NH_4HSO_4 was discovered by Pepinsky et al. in 1958. 58Pep

phase	III	II	I	58Pep
state		F	P	
crystal system	triclinic	monoclinic	monoclinic	
space group	$P1-C_1^1$	$Pc-C_s^2$	$P2_1/c-C_{2h}^5$	
Θ [°C]	–119 [D: –115] [a])		–3 [D: –10.9] [a])	[a]) 70Kas

P_s || [001] in phase II.

T_{melt} = 147 °C. 70Oga

Transparent, colorless, deliquescent.

Cleavage plane: (011).

Before 1958, the crystal was believed to belong to the orthorhombic system. In this pseudoorthorhombic lattice, the crystallographic axes designated as a', b' and c' lie along the [201], [010] and [001] directions, respectively, in the above-mentioned crystal system. 71Nel

The volume of the pseudo-unit cell is twice that of the true unit cell. The space group is $B2_1/a$, Ba and B1 in phase I, II and III, respectively. 71Nel

2a Crystal growth: slow cooling of $(NH_4)_2SO_4$ dissolved in concentrated H_2SO_4, or slow hydrolysis of chloroacetate-amide in dilute H_2SO_4. The latter gave better crystals. 58Pep

3a Unit cell parameters:

phase I:

a = 14.51(1) Å, b = 4.54(0) Å, c = 14.90(2) Å, β = 120° 18′ at RT. Z = 8. 58Pep

in pseudoorthorhombic cell with $B2_1/a$:

a' = 24.66(2) Å, b' = 4.60(1) Å, c' = 14.82(2) Å, β' = 89.87(1)° at RT. Z = 16. 71Nel, 72Nel

phase II:

a = 14.26 Å, b = 4.62 Å, c = 14.80 Å, β = 121° 18′ at –30 °C. Z = 8. 71Nel

in pseudoorthorhombic cell with Ba:

a' = 24.37 Å, b' = 4.62 Å, c' = 14.80 Å, β' = 90.00(5)° at –70 °C. Z = 16. 71Nel

phase III:

a = 14.24 Å, b = 4.56 Å, c = 15.15 Å, $\alpha \approx 90°$, β = 123° 24′, $\gamma \approx 90°$ at –140 °C. Z = 8. 72Nel

in pseudoorthorhombic cell with B1:

a' = 24.43 Å, b' = 4.56 Å, c' = 15.15 Å, $\alpha' \approx 90°$, β' = 91° 12′, $\gamma' \approx 90°$ at –140 °C. Z = 16. 72Nel

b Crystal structure:

phase I: Table 40A-5-001, Table 40A-5-002; Fig. 40A-5-001, Fig. 40A-5-002, Fig. 40A-5-003, Fig. 40A-5-004.

phase II: Table 40A-5-003; Fig. 40A-5-005.

5a Dielectric constants:

Temperature dependence at $1.5 \cdot 10^3$ Hz: Fig. 40A-5-006, at $10 \cdot 10^3$ Hz: Fig. 40A-5-007.

κ_c' in a frequency range $1.0 \cdot 10^5$ ... $1.44 \cdot 10^9$ Hz: Fig. 40A-5-008.

κ_c'' in a frequency range $5.0 \cdot 10^5$ ... $1.44 \cdot 10^9$ Hz: Fig. 40A-5-009.

κ_c', κ_c'' in a frequency range $1.89 \cdot 10^{10}$ ... $3.7 \cdot 10^{10}$ Hz: Fig. 40A-5-010.

For deuterated crystals: $T > \Theta_{II-I}$; $\kappa_c = C/(T - \Theta_p)$, C = 250(10) K, $\Theta_p = \Theta_{II-I}$ = –10.9 °C. 70Kas

	Effect of hydrostatic pressure on temperature dependence of κ_c: Fig. 40A-5-011, Fig. 40A-5-012. κ_c at $7.0 \cdot 10^7$ Pa: Fig. 40A-5-013. Phase diagram: Fig. 40A-5-014. Dielectric relaxation time at high pressure: Fig. 40A-5-015. $d\Theta_{II-I}/dp = 13.8 \cdot 10^{-8}$ K Pa^{-1}, $d\Theta_{III-II}/dp = 75.5 \cdot 10^{-8}$ K Pa^{-1}.	68Pol
b	Coefficient ξ: Fig. 40A-5-016.	
c	Spontaneous polarization: Fig. 40A-5-017. Coercive field: Fig. 40A-5-018.	
d	Pyroelectric coefficient: Fig. 40A-5-019.	
6a	Heat capacity: Fig. 40A-5-020. ΔQ_m = 502 [a]), 602 [b]) J mol^{-1} for transition II–I, 1420 [a]) J mol^{-1} for transition III–II.	[a]) 58Pep [b]) 63Str
	ΔS_m = 2.1 [a]), 2.2 [b]), 1.66 [c]) J K^{-1}mol^{-1} for transition II–I, 8.8 [a]), 6.7 [c]) J K^{-1}mol^{-1} for transition III–II.	[a]) 58Pep [b]) 63Str [c]) 76Ale
9a	Infrared spectra: Fig. 40A-5-021. Refractive indices and optical angle: n_α = 1.463, n_β = 1.473, n_γ = 1.510, $2V = 60°$ for λ = 589 nm.	71Sch
10a	Raman scattering spectra at several temperatures: Fig. 40A-5-022.	
b	Temperature dependence of Brillouin scattering frequency shift and width: Fig. 40A-5-023.	
11	Proton conduction along the *c* axis. Activation energy: 0.58 eV ($T < 380$ K), 0.80 eV ($T > 380$ K).	82Red
13a	NMR: spin-lattice relaxation time of ^{1}H: Fig. 40A-5-024. See also Table 40A-1-001 in No. 40A-1. Spin-lattice relaxation time of ^{2}D in deuterated crystal: Fig. 40A-5-025.	
14a	Bragg reflection: Fig. 40A-5-026.	
b	Time-of-flight spectra of neutron scattering: Fig. 40A-5-027. See also	65Rus
15a	Domain structure; striped domains parallel to the (100) plane were observed at RT by polarized light.	74Kon