No. 33A-5 $NH_4H_2PO_4$, Ammonium dihydrogen phosphate (ADP)

(M = 115.03; [D: 121.06])

1a Anomalous dielectric behavior of $NH_4H_2PO_4$ was first reported by Busch in 1937. 37Bus

b

phase	II	I	66Des
state	(A) *)	P	
crystal system	orthorhombic	tetragonal	
space group	$P2_12_12_1 - D_2^4$	$I\bar{4}2d - D_{2d}^{12}$	
Θ [K]	148 [D: 242]		

Effect of hydrostatic pressure on Θ: Fig. 33A-5-001, Fig. 33A-5-002.
Other phases III and IV were reported to exist under hydrostatic pressure, see Fig. 33A-5-001.
$d\Theta_{II-I}/dp = -3.4 \cdot 10^{-8}$ K Pa^{-1} [D: $-1.4 \cdot 10^{-8}$ K Pa^{-1}]. 69Ska
$T_{melt} \approx 190$ °C. 69Cla
$\rho = 1.803 \cdot 10^3$ kg m^{-3}. 66Bec
$\rho_X = 1.790 \cdot 10^3$ kg m^{-3}, $\rho = 1.800 \cdot 10^3$ kg m^{-3} at 22 °C. 73Kha
Transparent, colorless.
*) Antiferroelectric model in phase II was proposed by Nagamiya. 52Nag

2a Crystal growth: evaporation or cooling from aqueous solution. 73Kha
Solubility in H_2O: Fig. 33A-5-003; see also 58Oga
Mass production apparatus for growing large crystals, see 50Wal

b Crystal form: see subsection 2b in No. 33A-1.

3a Unit cell parameters: $a = b = 7.4997(4)$ Å, $c = 7.5494$ Å at 22 °C. 63Des
Table 33A-5-001, Table 33A-5-002;
see also Table 33A-1-003, Table 33A-1-004 in No. 33A-1.
c/a vs. radii of metallic or ammonium ions in KDP family: see Fig. 33A-11-002 in No. 33A-11.

b $Z = 4$ in phase I. 73Kha
Crystal structure: Fig. 33A-5-004, Fig. 33A-5-005, Fig. 33A-5-006.
Fractional coordinates and temperature parameters: Table 33A-5-003, Table 33A-5-004, Table 33A-5-005, Table 33A-5-006, Table 33A-5-007, Table 33A-5-008; Fig. 33A-5-007; see also Fig. 33B-1-004, Fig. 33B-1-005, Fig. 33B-1-006 in No. 33B-1.
Interatomic distances and bond angles: Table 33A-5-009.
Root mean square of thermal displacements: Table 33A-5-010.
Relation between Θ_{II-I} and structure of hydrogen bond: Fig. 33A-5-008.

4 Temperature dependence of lattice constants: Fig. 33A-5-009, Fig. 33A-5-010; see also 67Coo
Thermal expansion: Fig. 33A-5-011, Fig. 33A-5-012; see also Table 33A-1-029 in No. 33A-1.
Effect of hydrostatic pressure: Fig. 33A-5-013.

5a κ vs. T: Fig. 33A-5-014, Fig. 33A-5-015, Fig. 33A-5-016.
Curie-Weiss law: $\kappa_c = \kappa_\infty + C/(T - \Theta_p)$, $T > \Theta_{II-I}$, where $C = 2.67 \cdot 10^3$ K, $\Theta_p = -14$ K, $\kappa_\infty = 7.0$. 46Mas
Dielectric anomaly around 100 °C: see 83Sub
κ' and $\tan\delta$ at 9.2 GHz: Fig. 33A-5-017, Fig. 33A-5-018.
κ for 10 kHz…36 GHz: Table 33A-5-011.

κ' and κ'' of $ND_4D_2PO_4$ between 0.1 GHz and 4 GHz: Fig. 33A-5-019, Fig. 33A-5-020.
κ' and κ'' in submillimeter region: Fig. 33A-5-021.
κ in far-infrared region: see 9a.
Phase diagram: see Fig. 33A-5-001 in 1b.
Θ_{I-I} vs. p: see Fig. 33A-5-002 in 1b.
Effect of p on κ_a: Fig. 33A-5-022.

6a Heat capacity: Fig. 33A-5-023, Fig. 33A-5-024, Fig. 33A-5-025.
Transition heat and transition entropy at Θ_{I-I}:

ΔQ_m [J mol^{-1}]	ΔS_m [J K^{-1} mol^{-1}]	
644	4.4	44Ste
690 [D: 727]	4.6 [D: 3.05]	70Ami

7a Piezoelectricity: Table 33A-5-012; Fig. 33A-5-026, Fig. 33A-5-027.

8a Elastic compliance and stiffness: Table 33A-5-013; Fig. 33A-5-028, Fig. 33A-5-029, Fig. 33A-5-030, Fig. 33A-5-031, Fig. 33A-5-032.
Phonon damping coefficient measured by the phonon echo method: see 77Bil
For discrepancy between c_{44} and c_{55}: see 61Jaf
Isotope effect on sound velocity: see 86Ber

9a Refractive indices: Table 33A-5-014, Table 33A-5-015, Table 33A-5-016; Fig. 33A-5-033, Fig. 33A-5-034, Fig. 33A-5-035.
$n_o = 1.521$ for $ND_4D_2PO_4$ at RT for $\lambda = 550$ nm. 69Adh
Sellmeier coefficients: see Table 33A-1-040, Table 33A-1-041 in No. 33A-1.
$\partial n/\partial T$ for several λ: see Table 33A-1-042 in No. 33A-1.
Birefringence: Fig. 33A-5-036.
κ'' obtained from far-infrared spectra: Fig. 33A-5-037, Fig. 33A-5-038, Fig. 33A-5-039.
Transmission in vacuum ultraviolet region: see Fig. 33A-1-151 in No. 33A-1.
Far-infrared reflection spectra: Fig. 33A-5-040, Fig. 33A-5-041, Fig. 33A-5-042.
Transmission spectra between 300 nm and 2000 nm: Fig. 33A-5-043.
Optical absorption of γ-irradiated SeO_4^{2-} doped ADP: see 88Rat

b Electrooptic effect: Table 33A-5-017, Table 33A-5-018; Fig. 33A-5-044, Fig. 33A-5-045, Fig. 33A-5-046, Fig. 33A-5-047, Fig. 33A-5-048, Fig. 33A-5-049.
See also Fig. 33A-1-185 in No. 33A-1.
Electrooptic effect in ultraviolet region near the absorption edge: see 76Ona
Quadratic electrooptic effect: see 85Sab

c Piezooptic effect: Table 33A-5-019, Table 33A-5-020;
see also Fig. 33A-1-190, Fig. 33A-1-191 in No. 33A-1.
Effect of p on refractive indices: Fig. 33A-5-050.

d Optical activity: Fig. 33A-5-051, Fig. 33A-5-052.
Verdet constant $V = 234(11)$ K m^{-1} for $\lambda = 632.8$ nm. 76Kor
see also Fig. 33A-1-206 in No. 33A-1.

e Nonlinear susceptibility for SHG:
$|d_{36}| = 0.53 \cdot 10^{-12}$ m V^{-1}. 72Lev
$|d_{36} / d_{36}^{KDP}| = 1.21(5)$ at RT for $\lambda = 1.064$ μm.
$|d_{14} / d_{14}^{KDP}| = 1.02(5)$ or $1.07(5)$ at RT for $\lambda = 0.6943$ μm, and $1.17(5)$ at RT for $\lambda = 1.0582$ μm.

[D: $|d_{36} / d_{36}^{KDP}| = 1.10$ for $\lambda = 0.6943$ μm]. 69Bec
Second harmonic generation near $\lambda = 250$ nm: see 76Jai, 77Nik
Third and fourth harmonic generation of Nd-glass laser at $\lambda = 1.06$ μm: see 77And
Two phonon absorption: see 77Rei

10a Raman scattering: Fig. 33A-5-053, Fig. 33A-5-054, Fig. 33A-5-055; see also Fig. 33A-1-214 in No. 33A-1.

11 Electrical conductivity: Fig. 33A-5-056, Fig. 33A-5-057, Fig. 33A-5-058.
Conductivity σ and activation energy ΔU at RT:

	σ [Ω^{-1} m^{-1}]	ΔU [kJ mol^{-1}]	76Per
$NH_4H_2PO_4$	$2.9 \cdot 10^{-8}$	53.2 (0.55 eV)	
$ND_4D_2PO_4$	$1.3 \cdot 10^{-8}$	54.4 (0.56 eV)	

For additional data: see 73Har, 50Mas
Electrical conductivity of γ-irradiated crystal and effect of thermal annealing on the conductivity: see 85Sab
Conductivity of a ADP crystal doped with $(HSO_4)^-$: see 74Kha
Conductivity of Co^{2+} doped ADP crystals: see 77Sha
Conductivity of MoO_4^{2-} doped ADP crystals: see 87Rat1
Breakdown field: Fig. 33A-5-059, Fig. 33A-5-060; see also 50Mas
Electroluminescence of SO_4^{2-} doped ADP: see 90Ale

13a NMR: Table 33A-5-021, Table 33A-5-022, Table 33A-5-023.
T_1 vs. T^{-1}: Fig. 33A-5-061;
see also 75Kas, 74Gro
$(\Delta\omega^2)$ vs. θ: Fig. 33A-5-062.
Chemical shift of ^{30}P: see Table 33A-1-056 in No. 33A-1.
Double resonance study of ^{14}N of ADP: see 69Har
^{31}P NMR: see 94Eic

b ESR of Cr^{3+}: Table 33A-5-024.
ESR of CrO_4^{3-}: Fig. 33A-5-063, Fig. 33A-5-064;
see also Fig. 33A-11-023 in No. 33A-11 and 88Dal
ESR of γ-ray irradiated crystal: see Table 33A-1-069 in No. 33A-1
and also 71Suz1, 71Suz2, 72Kaw, 75Owe
ESR of irradiated ADP doped with K_2SeO_4: see 73Kaw1, 74Kaw
ESR of SeO_4^{3-}: see 85Fuk, 86Fuk, 88Fuk1, 88Rat
ESR of MoO_4^{2-}: see 87Rat2
ESR of Tl^{2+}: see 83Dom

c	Mössbauer effect: Fig. 33A-5-065. No anomaly is observed in the temperature dependence of isomer shift and normalized resonance intensity at Θ_{II-I}. However, a sudden increase in the linewidth near Θ_{II-I} is observed, consistent with the expected increase in electric field gradient created by the onset of antiferroelectric ordering.	72Sas
14b	Neutron diffuse scattering: Fig. 33A-5-066. Inelastic neutron scattering: Fig. 33A-5-067, Fig. 33A-5-068; see also Fig. 33B-5-075 in No. 33B-5.	
16	Etchant for revealing etch pits: a saturated solution of potassium acid phthalate. X-ray topographic study of twin boundaries and dislocations: see Vickers hardness: see Etchant for revealing etch pits due to dislocations: a saturated solution of potassium acid phthalate.	66Des 78Oki 87Anb 66Des