59 $(CH_2ClCOO)_2H \cdot NH_4$ family

59A Pure compounds

No. 59A-1 $CH_2ClCOONH_4$, Ammonium monochloroacetate

(M = 111.53)

1a $CH_2ClCOONH_4$ crystallizes either in the monoclinic or in the orthorhombic system. 57Pep
Ferroelectricity in monoclinic $CH_2ClCOONH_4$ was reported by Pepinsky et al. in 1957.

b

phase	II	I
state	F	P
crystal system	monoclinic *)	monoclinic
space group	$C2-C_2^3$ *)	$C2/c-C_{2h}^6$
Θ [°C]	–150	

57Pep

P_s || [010]. 57Pep
ρ = 1.5585 · 10^3 kg m^{-3} at RT. 57Pep
*) Speculated by Pepinsky et al. [57Pep].

2a Crystal growth: evaporation method from cold aqueous solution. 57Pep

3a Unit cell parameters: a = 8.42 Å, b = 11.63 Å, c = 9.82 Å, β = 110° at RT. 57Pep

b Z = 8. 57Pep

5a κ_b = 5 at RT, κ_b = 15 at –150 °C. 57Pep

c $P_s \approx 0.1 \cdot 10^{-2}$ C m^{-2} and $E_c \approx 1 \cdot 10^6$ V m^{-1} at –170 °C. 57Pep

Reference

57Pep Pepinsky, R., Okaya, Y., Mitsui, T.: Acta Crystallogr. **10** (1957) 600.

No. 59A-2 $(CH_2ClCOO)_2H \cdot NH_4$, Ammonium hydrogen bischloroacetate

(M = 206.03; [D: 215.08])

1a Ferroelectricity in $(CH_2ClCOO)_2H \cdot NH_4$ was discovered by Ichikawa and Mitsui in 1966. 66Ich

b

phase	II	I	66Ich
state	F	P	
crystal system	monoclinic [a])	monoclinic	[a]) 73Chi
space group	$Cc - C_s^4$	$C2/c - C_{2h}^6$	
Θ [K]	120.4(3) [a])		

Θ = 131.7(3) K for $(CH_2ClCOO)_2D \cdot ND_4$. 73Chi

P_s || [102]. 66Ich

$\rho = 1.528 \cdot 10^3$ kg m^{-3} at 18 °C. 66Ich

Transparent, colorless. 66Ich

2a Crystal growth: evaporation method from alcohol solution. 66Ich
Polycrystal is prepared by trickling concentrated aqueous ammonia into aqueous solution of monochloroacetic acid until pH 4.5 is reached. 73Chi

b Crystal form: Fig. 59A-2-001.

3a Unit cell parameters:
a = 10.521(4) Å, b = 11.576(4) Å, c = 8.387(3) Å, β = 119.48(3)° in phase I; 72Ich
a = 10.47(2) Å, b = 11.40(1) Å, c = 8.22(1) Å, β = 119.3(1)° in phase II. 74Ich

b Z = 4. 66Ich
Crystal structure: Table 59A-2-001, Table 59A-2-002, Table 59A-2-003, Table 59A-2-004, Table 59A-2-005; Fig. 59A-2-002, Fig. 59A-2-003, Fig. 59A-2-004, Fig. 59A-2-005, Fig. 59A-2-006.

5a $\kappa_{[102]} = C/(T - \Theta_p)$, $T > \Theta_{II-I}$, C = 44 K, Θ_p = –145 °C. 66Ich
Dielectric constant: Fig. 59A-2-007, Fig. 59A-2-008.

b Effect of E_{bias} on κ: Fig. 59A-2-009.

c Spontaneous polarization: Fig. 59A-2-010.
Coercive field: Fig. 59A-2-011.

6a Heat capacity: Fig. 59A-2-012, Fig. 59A-2-013.
Transition heat and transition entropy at Θ_t:

	ΔQ_m [J mol^{-1}]	ΔS_m [J K mol^{-1}]	76Chi
$(CH_2ClCOO)H \cdot NH_4$	300(21)	2.90(22)	
$(CH_2ClCOO)D \cdot ND_4$	340	2.95	

9a Infrared transmission: Fig. 59A-2-014.

13a NMR of ^{35}Cl: Table 59A-2-006, Table 59A-2-007; Fig. 59A-2-015, Fig. 59A-2-016, Fig. 59A-2-017, Fig. 59A-2-018.
NMR of ^1H and ^2H: Fig. 59A-2-019; see also 84Sun
Effect of hydrostatic pressure: Fig. 59A-2-020, Fig. 59A-2-021.

Table 59A-2-001. $(CH_2ClCOO)_2H \cdot NH_4$. Structure of phase I [72Ich]. Fractional coordinates at RT.

Atom	*x*	*y*	*z*
	[10^{-4}]		
Cl	1842(1)	4237(1)	–607(1)
O(1)	1770(2)	2548(2)	3340(3)
O(2)	3401(2)	3781(2)	3363(3)
N	0	453(3)	2500
C(1)	1161(3)	3404(3)	575(4)
C(2)	2242(3)	3255(2)	2580(4)
H(1)	2500	2500	5000
H(2)	727(37)	–45(31)	2366(47)
H(3)	351(40)	820(30)	3521(43)
H(4)	906(37)	2678(31)	–55(45)
H(5)	238(43)	3785(32)	479(50)

Table 59A-2-002. $(CH_2ClCOO)_2H \cdot NH_4$. Structure of phase I [72Ich]. Temperature parameters at RT. B_{ij} is defined by Eq. (a) in Introduction.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
	[10^{-4}]					
Cl	144(1)	127(1)	207(2)	–69(2)	76(2)	98(2)
O(1)	140(3)	96(2)	243(5)	–107(4)	182(6)	8(5)
O(2)	92(2)	69(2)	193(4)	–48(3)	121(5)	–4(4)
N	80(3)	55(2)	291(9)	0	126(9)	0
C(1)	106(3)	92(3)	232(7)	–61(5)	84(8)	30(7)
C(2)	89(3)	54(2)	208(5)	–21(4)	133(7)	–16(5)

Table 59A-2-003. $(CH_2ClCOO)_2H \cdot NH_4$. Fractional coordinates [$\cdot 10^{-4}$] and isotropic temperature parameters B [Å^2] in phase II [74Ich]. T = 80 K. B is defined by Eq. (e) in Introduction.

Atom	*x*	*y*	*z*	*B*
Cl(1)	1864(4)	4276(3)	–687(6)	1.57(5)
Cl(2)	3150(4)	797(3)	10733(6)	1.76(6)
O(11)	1663(11)	2527(9)	3162(15)	1.70(18)
O(12)	3412(12)	3679(10)	3312(16)	2.01(19)
O(21)	3179(12)	2446(10)	6572(16)	2.16(20)
O(22)	1600(10)	1175(8)	6693(14)	1.03(15)
N	0(17)	440(9)	2791(18)	1.44(20)
C(11)	1174(17)	3416(14)	458(23)	1.84(26)
C(12)	2164(13)	3240(11)	2421(18)	0.68(19)
C(21)	3915(16)	1622(12)	9495(21)	1.48(24)
C(22)	2723(15)	1713(13)	7350(20)	1.25(22)

Table 59A-2-004. $(CH_2ClCOO)_2H \cdot NH_4$. Interatomic distances [Å] and angles [°] in phase II (T = 80 K) and in phase I (T = RT) [74Ich].

	Distances [Å]			Bond angles [°]	
	80 K	RT		80 K	RT
C(11)–Cl(1)	1.742(21)	1.768(4)	Cl(1)–C(11)–C(12)	114.9(11)	113.4(2)
C(11)–C(12)	1.444(19)	1.506(4)	C(11)–C(12)–O(11)	112.7(12)	111.4(2)
C(12)–O(11)	1.272(20)	1.278(4)	C(11)–C(12)–O(12)	125.0(15)	123.2(3)
C(12)–O(12)	1.249(16)	1.225(3)	O(11)–C(12)–O(12)	122.2(12)	125.4(3)
C(21)–Cl(2)	1.833(20)		Cl(2)–C(21)–C(22)	109.3(11)	
C(21)–C(22)	1.589(19)		C(21)–C(22)–O(21)	108.4(12)	
C(22)–O(21)	1.279(23)		C(21)–C(22)–O(22)	122.2(15)	
C(22)–O(22)	1.196(17)		O(21)–C(22)–O(22)	129.4(13)	
O(11)...O(21)	2.457(16)	2.432(5)	C(12)–O(11)...O(21)	112.5(8)	114.8(3)
			C(22)–O(21)...O(11)	113.9(8)	
N...O(11)	2.876(17)	2.926(4)			
N^{iii}...O(12)	2.771(20)	2.880(3)			
N^{iv}...O(12)	3.369(19)	3.148(3)			
N^{iv}...O(21)	2.929(17)				
N^{ii}...O(22)	2.915(21)				
N...O(22)	2.923(17)				

Superscripts refer to atoms at:
(i) x, y, z; (ii) $x, -y, 1/2 + z$; (iii) $1/2 + x, 1/2 + y, z$; (iv) $1/2 + x, 1/2 - y, 1/2 + z$.

Table 59A-2-005. $(CH_2ClCOO)_2H \cdot NH_4$. Interatomic distances [Å] and angles [°] at RT [72Ich].

Distances [Å]		Bond angles [°]	
Ammonium ion			
N——H(2)	1.01(4)	H(2)–N——H(2^{ii})	110(4)
N——H(3)	0.86(3)	H(2)–N——H(3)	115(3)
		H(2)–N——H(3^{ii})	99(4)
		H(3)–N——H(3^{ii})	121(5)
Chloroacetate residue			
C(1)–Cl	1.768(4)	Cl——C(1)–C(2)	113.4(2)
C(1)–C(2)	1.506(4)	C(1)–C(2)–O(1)	111.4(2)
C(2)–O(1)	1.278(4)	C(1)–C(2)–O(2)	123.2(3)
C(2)–O(2)	1.225(3)	O(1)–C(2)–O(2)	125.4(3)
C(1)–H(4)	0.96(3)	Cl——C(1)–H(4)	104(3)
C(1)–H(5)	0.99(5)	H(4)–C(1)–H(5)	111(3)
		H(5)–C(1)–Cl	109(2)
		H(4)–C(1)–C(2)	112(2)
		H(5)–C(1)–C(2)	108(2)
Hydrogen bonds			
N...O(2^{iv})	2.880(3)	N——H(2)…O(2^{iv})	163(3)
H(2)...O(2^{iv})	1.90(4)	N——H(3)…O(2^{i})	161(3)
N...O(2^{i})	3.148(3)	N——H(3)…O(1)	108(3)
H(3)...O(2^{i})	2.32(3)		
N...O(1)	2.926(4)	C(2)–H(1)…O(1^{i})	114.8(3)
H(3)...O(1)	2.55(4)		
O(1)...O(1^{i})	2.432(5)		

Superscripts refer to atoms at:
(i) $1/2 - x, 1/2 - y, 1 - z$;
(ii) $-x, y, 1/2 - z$;
(iii) $-x, y, -1/2 - z$;
(iv) $1/2 - x, -1/2 + y, 1/2 - z$.

Table 59A-2-006. $(CH_2ClCOO)_2H \cdot NH_4$. Direction cosines of the principal axes of the electric field gradient tensors for ^{35}Cl with respect to the orthorhombic crystal axes *a*, *b* and *c** [73Chi].

	T	Principal axes		
	[K]	*X*	*Y*	*Z*
Cl	290	X_a = –0.515(67)	0.514(74)	0.686(7)
		X_b = 0.829(15)	0.097(116)	0.550(8)
		X_{c^*} = 0.217(124)	0.852(26)	–0.476(5)
Cl(1)	78	X_a = –0.501(51)	0.521(46)	0.692(8)
		X_b = 0.847(14)	0.131(86)	0.515(9)
		X_{c^*} = 0.177(86)	0.844(16)	–0.507(13)
Cl(2)	78	X_a = –0.489(91)	0.500(56)	0.714(9)
		X_b = 0.836(13)	0.038(144)	0.546(6)
		X_{c^*} = 0.247(144)	0.865(39)	–0.438(11)

Table 59A-2-007. $(CH_2ClCOO)_2H \cdot NH_4$. e^2qQ/h and η for ^{35}Cl [73Chi].

	T [K]	e^2qQ/h [MHz]	η
Cl	290	67.416(15)	0.064(10)
Cl(1)	78	69.774(13)	0.061(9)
Cl(2)	78	70.230(16)	0.054(12)

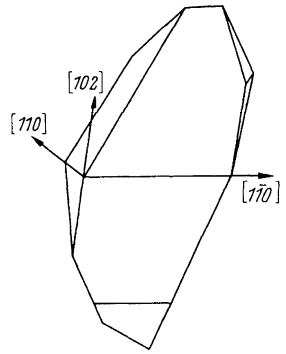

Fig. 59A-2-001. $(CH_2ClCOO)_2H \cdot NH_4$. Crystal form [66Ich].

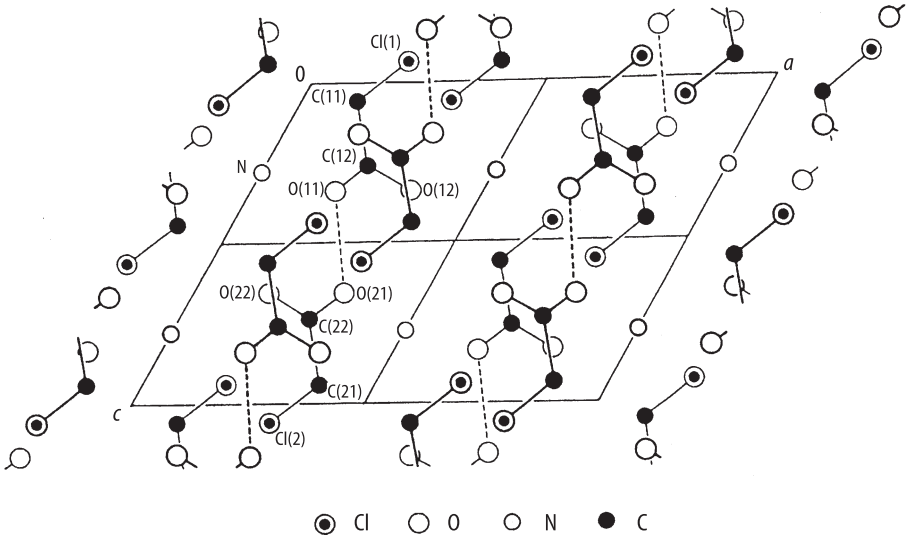

Fig. 59A-2-002. $(CH_2ClCOO)_2H \cdot NH_4$. Structure of phase II [74Ich]. $T = 80$ K. Projection along [010].

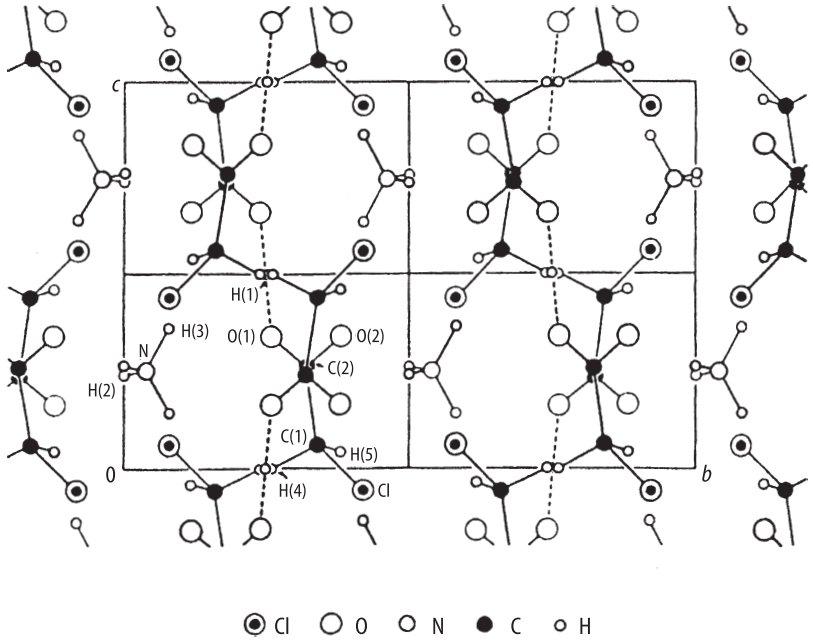

Fig. 59A-2-003. $(CH_2ClCOO)_2H \cdot NH_4$. Structure of phase I [72Ich]. T = RT. Projection along [100].

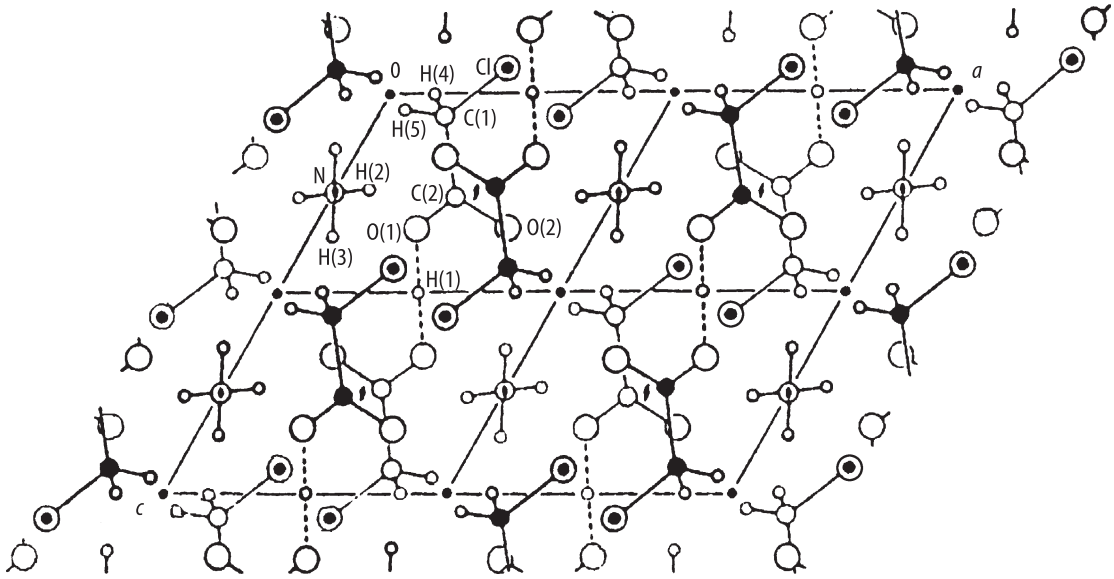

Fig. 59A-2-004. $(CH_2ClCOO)_2H \cdot NH_4$. Structure of phase I [72Ich]. T = RT. Projection along [010].

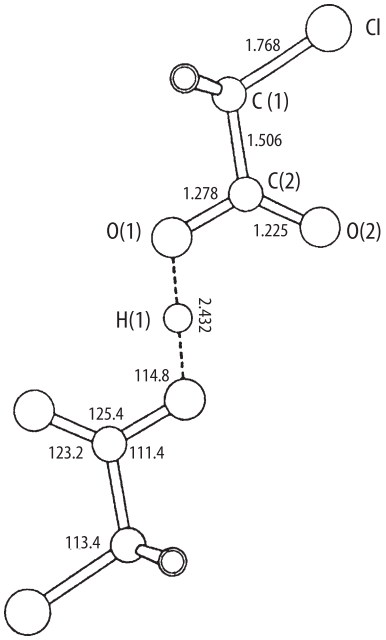

Fig. 59A-2-005. $(CH_2ClCOO)_2H \cdot NH_4$. Interatomic distances [Å] and bond angles [°] in chloroacetate residue in phase I [72Ich]. T = RT.

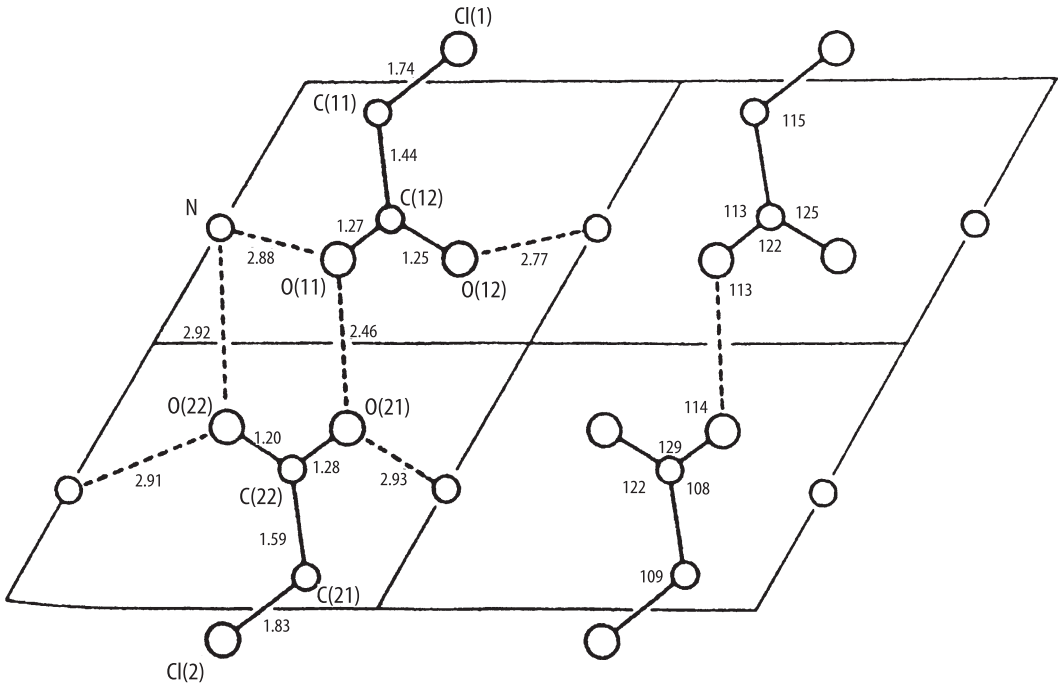

Fig. 59A-2-006. $(CH_2ClCOO)_2H \cdot NH_4$. Interatomic distances [Å] and bond angles [°] in chloroacetate residue in phase II [74Ich]. T = 80 K.

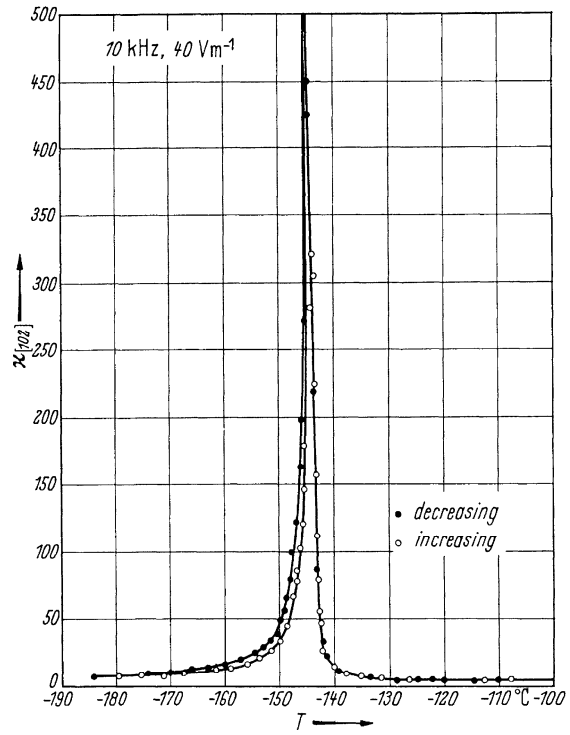

Fig. 59A-2-007. $(CH_2ClCOO)_2H \cdot NH_4$. $\kappa_{[102]}$ vs. T [66Ich]. Open circles: increasing temperature. Full circles: decreasing temperature.

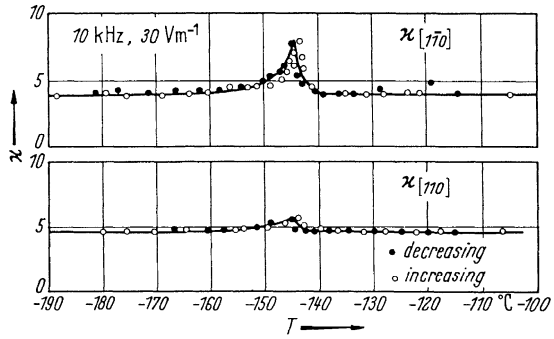

Fig. 59A-2-008. $(CH_2ClCOO)_2H \cdot NH_4$. $\kappa_{[1\bar{1}0]}$, $\kappa_{[110]}$ vs. T [66Ich].

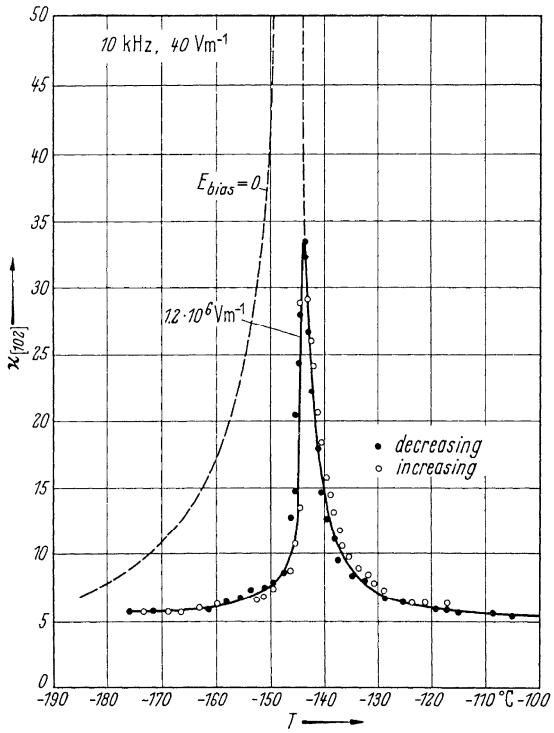

Fig. 59A-2-009. $(CH_2ClCOO)_2H \cdot NH_4$. $\kappa_{[102]}$ vs. T with dc bias field [66Ich].

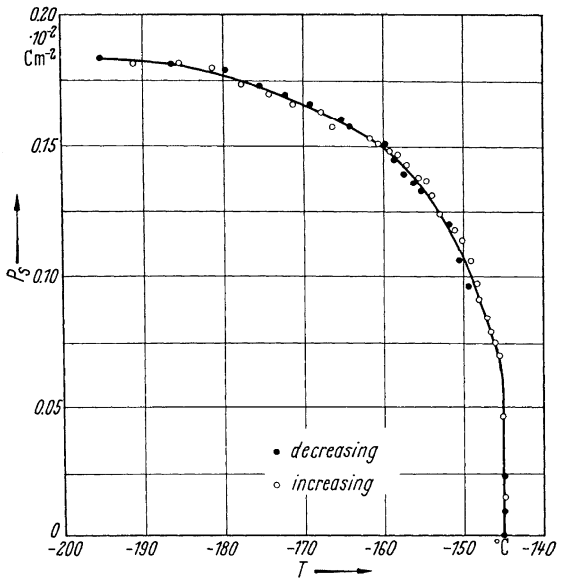

Fig. 59A-2-010. $(CH_2ClCOO)_2H \cdot NH_4$. P_s vs. T [66Ich].

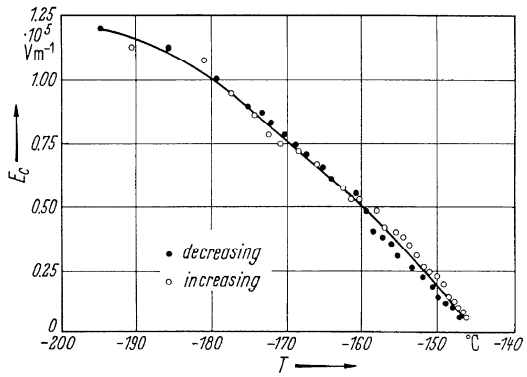

Fig. 59A-2-011. $(CH_2ClCOO)_2H \cdot NH_4$. E_c vs. T [66Ich].

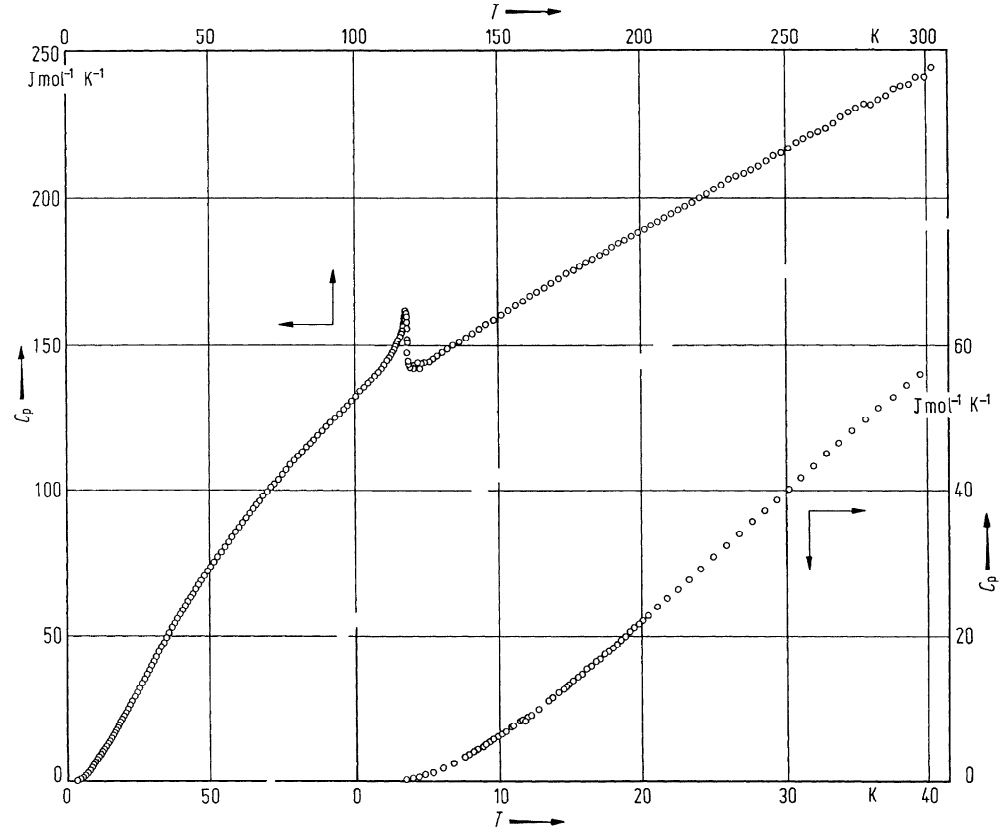

Fig. 59A-2-012. $(CH_2ClCOO)_2H \cdot NH_4$. C_p vs. T [72Chi].

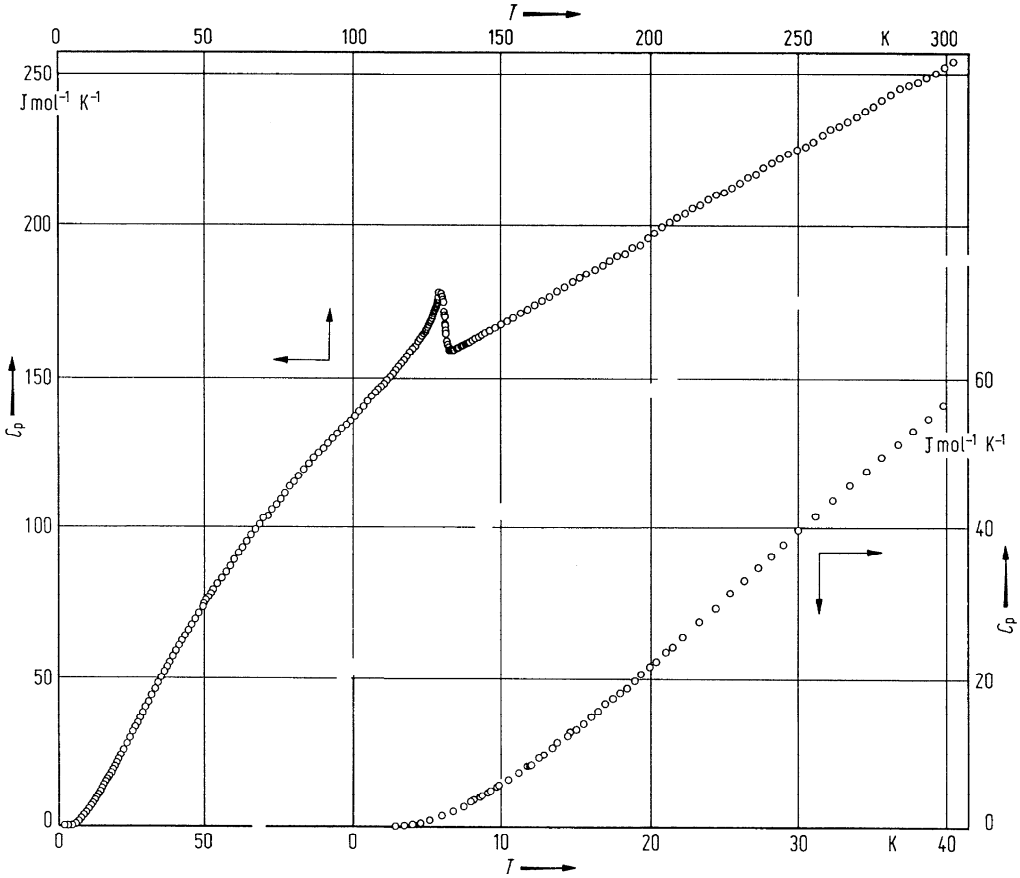

Fig. 59A-2-013. $(CH_2ClCOO)_2D \cdot ND_4$. C_p vs. T [72Chi].

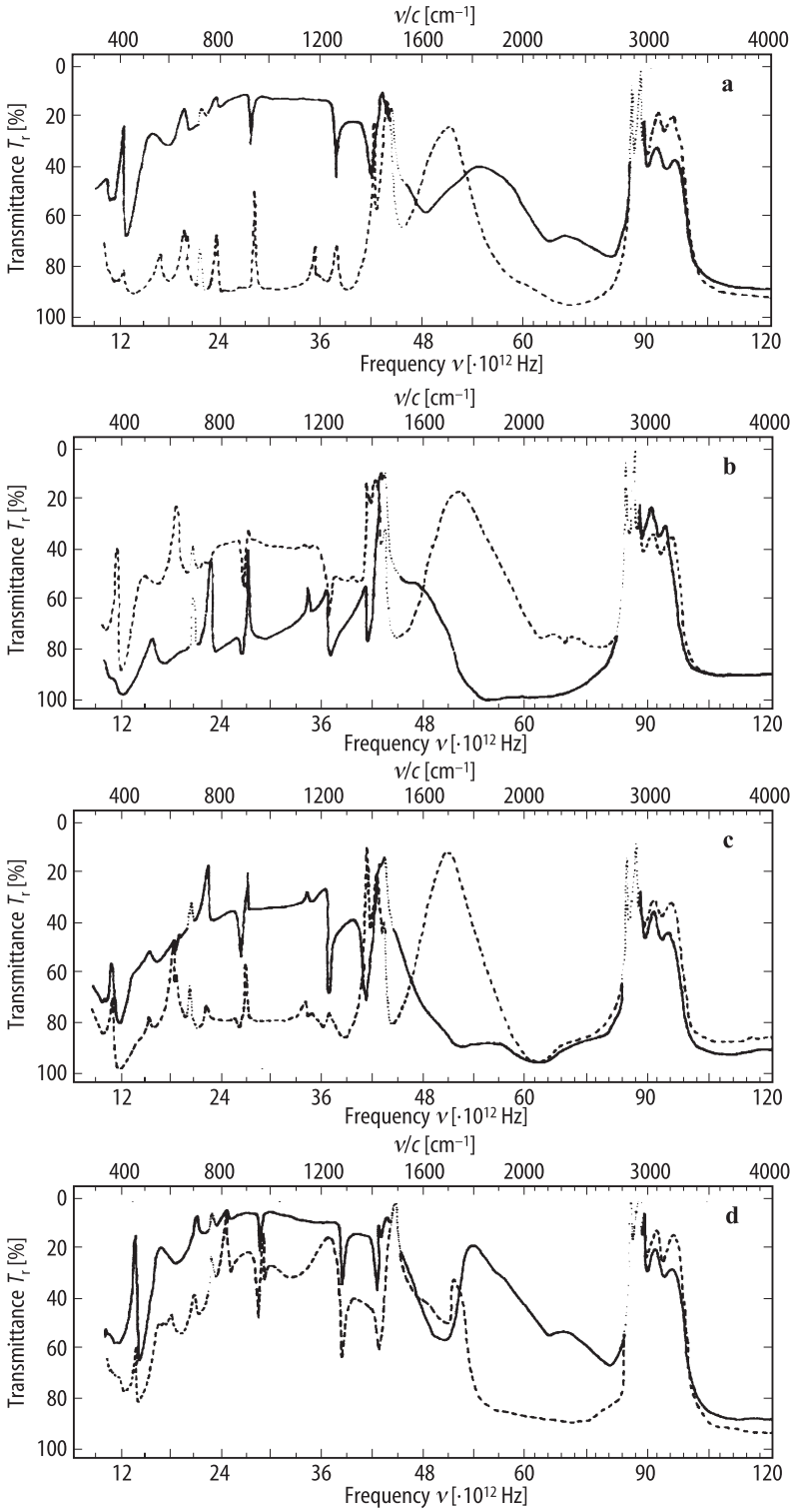

Fig. 59A-2-014. Continued.

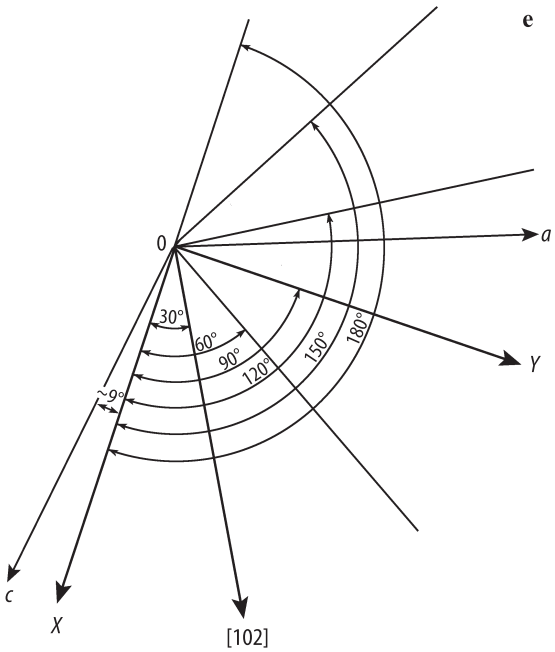

Fig. 59A-2-014. $(CH_2ClCOO)_2H \cdot NH_4$. T_r vs. ν [91Bar]. T_r: transmittance for polarized IR radiation. ***E***: polarization of IR radiation. *X*, *Y*, *Z*: optical principal axes. *a*, *b*, *c*: crystallographic axes. *T* = RT. (**a**) *ac* face, full line: ***E*** || ***X***, dashed line: ***E*** || ***Y*** (90° from ***X***). Dotted line: absorption by paraffin wax. (**b**) *ac* face, full line: ***E*** || 120° from ***X***, dashed line: ***E*** || 30° from ***X***. Dotted line: absorption by paraffin wax. (**c**) *ac* face, full line: ***E*** || 150° from ***X***, dashed line: ***E*** || 60° from ***X***. Dotted line: absorption by paraffin wax. (**d**) *bc* face, full line: ***E*** || ***c***, dashed line: ***E*** || ***b***. Dotted line: absorption by paraffin wax. (**e**) The relative orientations of the optical principal axes *X*, *Y*, *Z* with respect to the crystallographic axes *a*, *b*, *c* and the various polarizations.

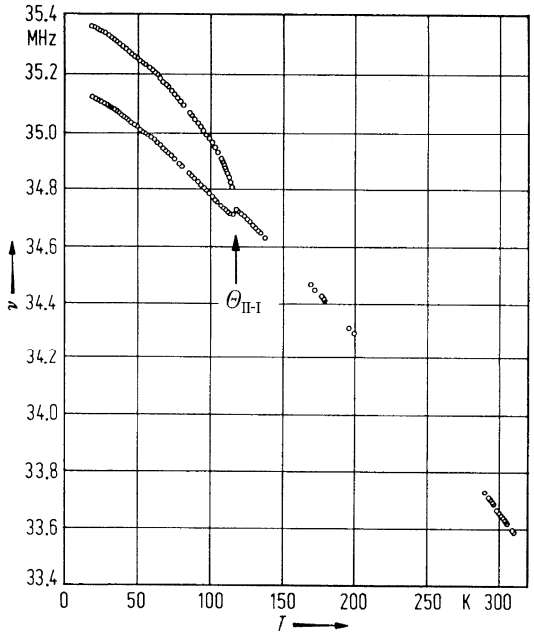

Fig. 59A-2-015. $(CH_2ClCOO)_2H \cdot NH_4$. ν vs. *T* [68Yam]. ν: ^{35}Cl nuclear quadrupole resonance frequency.

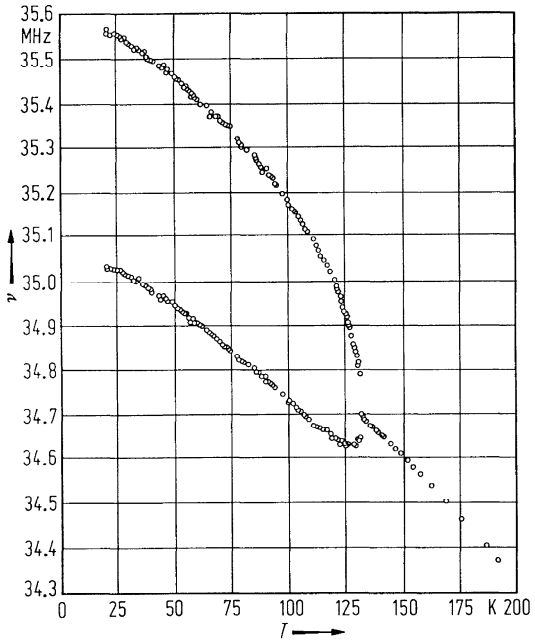

Fig. 59A-2-016. $(CH_2ClCOO)_2D \cdot ND_4$. ν vs. T [73Can]. ν: ^{35}Cl nuclear quadrupole resonance frequency. $\Theta_{II-I} = 131.7$ K.

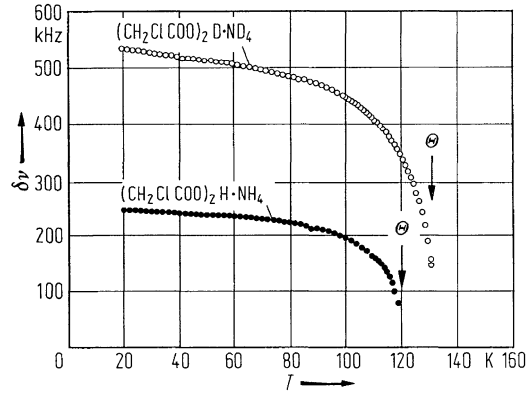

Fig. 59A-2-017. $(CH_2ClCOO)_2H \cdot NH_4$, $(CH_2ClCOO)_2D \cdot ND_4$. $\delta\nu$ vs. T [73Can]. $\delta\nu$: doublet separation of NQR spectrum for ^{35}Cl in the ferroelectric phase.

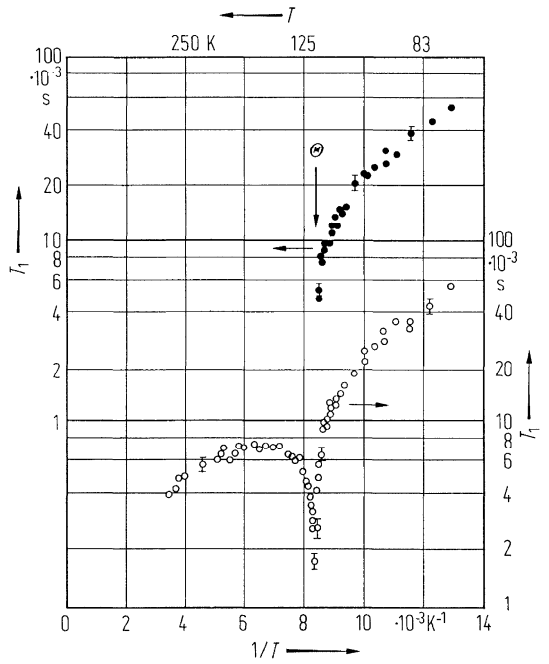

Fig. 59A-2-018. $(CH_2ClCOO)_2H \cdot NH_4$. T_1 vs. T^{-1} [74Chi]. T_1: ^{35}Cl spin lattice relaxation time. Open circles: for ν_1; full circles: for ν_2. Resonance line separates in two components corresponding to ν_1 and ν_2 in the ferroelectric phase.

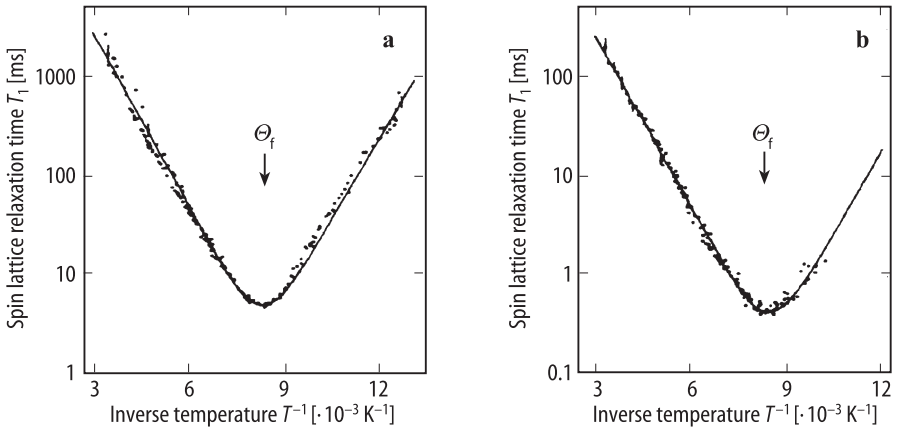

Fig. 59A-2-019. $(CH_2ClCOO)_2H \cdot NH_4$, $(CH_2ClCOO)_2D \cdot ND_4$. T_1 vs. T^{-1} [81Yam]. $f = 10$ MHz. (**a**) T_1: proton spin lattice relaxation time, (**b**) T_1: deuteron spin lattice relaxation time.

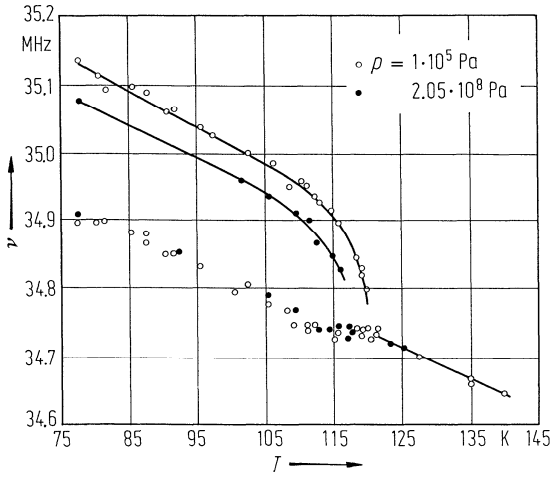

Fig. 59A-2-020. $(CH_2ClCOO)_2H \cdot NH_4$. ν vs. T [83Zda]. Parameter: p. ν: NQR frequency of ^{35}Cl.

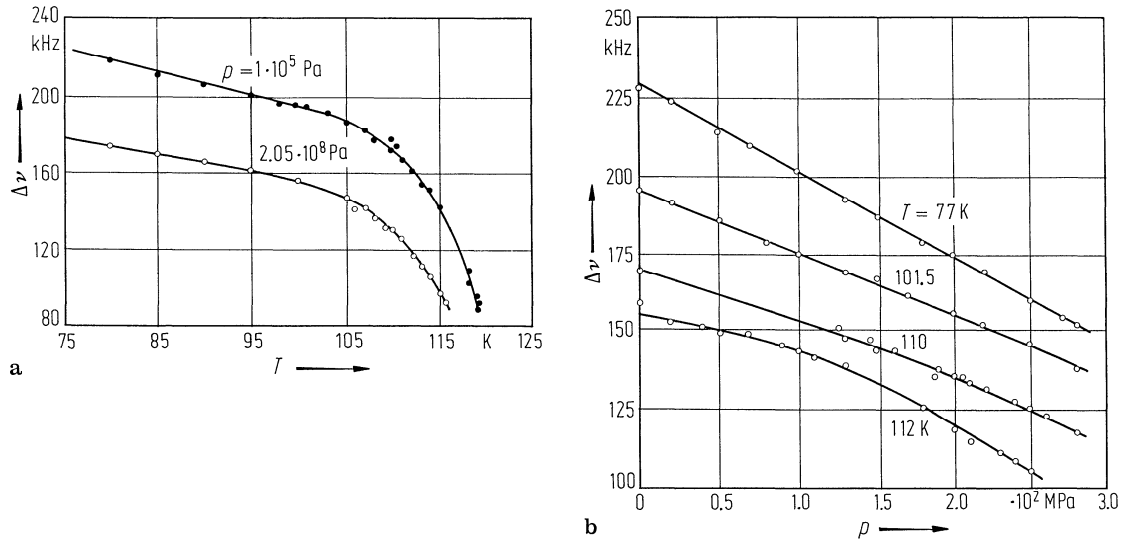

Fig. 59A-2-021. $(CH_2ClCOO)_2H \cdot NH_4$. $\Delta\nu$ vs. T and p [86Zda]. (**a**) $\Delta\nu$ vs. T. Parameter: p. (**b**) $\Delta\nu$ vs. p. Parameter: T. $\Delta\nu$: ^{35}Cl NQR line splitting.

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