PHASE TRANSITION AND FREEZING OF IONIC DISORDER IN C_SNO₂ AND TINO₂ CRYSTALS[†]

KEIICHI MORIYA, TAKASUKE MATSUO and HIROSHI SUGA

Department of Chemistry and Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

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Abstract—The heat capacities of CsNO₂ and TlNO₂ have been measured in the temperature region between 13 and 350 K. The phase transitions of CsNO₂ and TlNO₂ were found at (209.16 ± 0.10) K and (282.4 ± 0.1) K. The enthalpy and entropy of the phase transition were (3.45 ± 0.20) kJ mol⁻¹ and (17.2 ± 1.0) JK⁻¹ mol⁻¹ for the former, and (6.44 ± 0.31) kJ mol⁻¹ and (23.8 ± 1.1) JK⁻¹ mol⁻¹ for the latter. The glass transitions were found around 42 K in CsNO₂ and around 60 K for TlNO₂, respectively. The corresponding dielectric relaxations were observed between 58 and 130 K for CsNO₂ in the frequency range between 10^2 and 10^5 Hz and between 80 and 180 K for TlNO₂ in the frequency range between 2×10^2 and 10^5 Hz. The calorimetric and dielectric relaxation times yielded a straight line in the Arrhenius plot over a wide time scale ranging from 10^{-6} to 10^5 sec. The slope gave the activation enthalpy of 13.8 kJ mol⁻¹ and 19.5 kJ mol⁻¹ for the orientational entropy of the NO₂⁻ ion in the high-temperature phase. Based on the packing and symmetry considerations, these entropies were interpreted by the model which included two different sets of orientations of the NO₂⁻ ions parallel to [110] and [111] in the CsCl type unit cell. The existence of the different sets of orientations was proved by the double ($\Delta v \sim 10$ cm⁻¹) of the Raman spectrum of the bending mode of the NO₂⁻ ion in the cubic phase of the CsNO₂ crystal. The band narrowed to an ordinary singlet with increasing temperature. This observation was accounted for a stem mode and narrowed to an ordinary singlet with increasing temperature.

1. INTRODUCTION

The crystal structures of cesium(I) and thallium(I) nitrites are of the cesium chloride type (space group O_{h}^{1} —Pm3m) with z = 1 at room temperature [1-3]. The NO₂⁻ ions are orientationally disordered in conformity with the octahedral symmetry of anion site. A phase transition is therefore expected to occur at a temperature below the room temperature. This offers a possibility of studying an order-disorder phase transition due to ionic orientations in structurally simple crystals. In fact, Richter and Pistorius reported that the CsNO₂ crystal transformed at (179 ± 2) K to a low-temperature rhombohedral phase (space group $D_{3d}^3 - R\overline{3}m$ [2]. Mraw and Staveley measured the heat capacities of CsNO2 between 83 and 479 K, and found the transition temperature $T_t = 208.85$ K and transition entropy $\Delta s_t = 13.28 \text{ JK}^{-1} \text{ mol}^{-1}$ [4]. However, the symmetry of the low-temperature phase of CsNO₂ crystal requires that orientational disorder of the nitrite ion still persists in this phase. This gives rise to the possibility of another phase transition or freezing of the disorder into an immobile state at a lower temperature. In fact, we found a glass transition around 42 K and ascertained the phase transition at 209.16 K [5]. For TINO₂ crystal, we found a phase transition at 282.4 K due to disordering of the NO2⁻ orientation [6]. The dielectric dispersion in TINO₂ was observed in the frequency range 2×10^2 and 10^5 Hz between 80 and 180 K [6]. The long relaxation time of the ionic reorientation will hinder the crystal's attainment of the equilibrium state at low temperatures. Thus we can expect a heat capacity anomaly at a temperature where the frequency of maximum absorption becomes about 10^{-4} Hz, the inverse of the calorimetric time scale. In the present study we investigated dynamic and thermodynamic properties of CsNO₂ and TINO₂ crystals by calorimetry in the static and ultra-low frequency region, by dielectric spectroscopy in the audio and radio frequency and by Raman scattering in the mid-IR region. The results were interpreted in terms of a site disorder model.

2. EXPERIMENTAL

2.1 Sample preparation

Cesium and thallium nitrites crystals were prepared by the double decomposition of $Ba(NO_2)_2$ ·H₂O and Cs_2SO_4 (from Merck Co. Ltd., suprapur) and Tl₂CO₃ (from Mitsuwa Pure Chemicals) aqueous solutions, respectively. Tl₂CO₃ was recrystallized in advance from aqueous solution. The $Ba(NO_2)_2$ ·H₂O crystal was prepared from extra-pure grade reagents of NaNO₂ and BaCl₂·2H₂O (both from Wako Pure Chemicals Co. Ltd.) by salting out [7]. Colorless CsNO₂ and rose-orange TlNO₂ crystals were obtained by slow evaporation of the double decomposition solutions at 298 K. The crystals were purified by recrystallization from aqueous solutions and washed with a small amount of ethanol. The products were dried *in vacuo* at 120°C. There was no anomaly in the

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Fig. 1. The molar heat capacity of CsNO₂.

heat capacity which might have been attributed to the melting of a eutectic temperature of occluded mother liquor. The crystals of CsNO₂ were further purified by 20 passes of zone-melting. The crystals were handled in the nitrogen gas. Impurity ions for Cs salt found by atomic absorption spectra were Rb; 0.01°_{0} , Na; 0.02°_{0} , and K; 0.002°_{0} , respectively. The nitrogen determined by gravimetric method was 7.78°_{0} (calc. 7.83°_{0}). The elemental analysis for Tl gave (81.7 ±

 $0.4)_{0}^{\circ}$ by Tl₂CrO₄ gravimetric method in agreement with the calculated value of 81.63%. Nitrate ions in the nitrites in both compounds were analyzed by the ratio of the intensities of internal symmetric vibration (A₁) of NO₃⁻⁻ and NO₂⁻⁻ ions in the Raman spectra[8]. They were less than 0.1_{0}° .

2.2 Heat capacity measurement

The heat capacities of CsNO₂[5] and TINO₂[6]



Fig. 2. The molar heat capacity of TlNO₂.

were measured with an adiabatic low-temperature calorimeter with a built-in cryo-refrigerator [9, 10] and another adiabatic calorimeter [11-14] between 13 and 355 K, respectively. The sample crystals were 26.641 g (0.14894 mol) for CsNO₂ and 102.074 g (0.40764 mol) for TINO2. They were loaded in calorimeter cells with a small amount of helium gas to aid the heat transfer. Figures 1 and 2 give the molar heat capacities of the crystals. Their numerical values are given in Tables 1 and 2. Graphically smoothed heat capacities and derived thermodynamic functions are given in Tables 3 and 4. A large heat capacity peak associated with the orientational disordering of the nitrite ions was found at (209.16 \pm 0.10) K for CsNO₂ and at (282.4 ± 0.1) K for TlNO₂. In the CsNO₂ crystal, the transition temperature is 0.31 K higher than that reported by Mraw and Staveley [4]. The heat capacity data agree with their results within 0.15% above the transition temperature and within 0.2% below. The excess part due to the phase transition became significant around 100 K for CsNO2 and 130 K for TINO₂. It increased gradually as the temperature increased to the normal value above the quasi-isothermal transition at (209.16 ± 0.10) K for the Cs salt without possessing any excess part that would be attributable to residual short-range order effect. Similar behavior was found in the phase transition of other nitrites: KNO₂ [15], and RbNO₂ [16]. The time required for thermal equilibration in the neighborhood of the transition becomes long compared with 10 min usually required in the normal region. Typical thermal relaxation times are 25 hr at 209.16 K for the temperature increment of $\Delta T = 0.055$ K in the Cs salt and 27 hr at 282.12 K for that of $\Delta T = 0.188$ K in the Tl salt, respectively. Figure 3 shows the cooling curve of TINO₂ obtained by slow removal of heat. The cooling rate of 0.7 Kh⁻¹ was effected by applying an appropriate back-up potential in the cell-shield thermocouple circuit. Undercooling of 0.4 K was encountered in the cooling process and this attested the first-order nature of the phase transition [17].

For the estimation of the enthalpies and entropies of the phase transitions, the normal heat capacities given by the solid lines in Figs. 1 and 2 were determined by adding the following five con-

Table 1. Heat capacity of CsNO₂

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	T	C_	Tav.	Cn	T_{av}	C _p	Tav	C
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	15.26	7.679	78.02	61.31	206.26	98.53	330.37	91.74
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19.72	12.79	89.65	65.49	209.80	414.7	345.77	91.84
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25 24	30 04	120.00	75.67	242.25	90,91	47.38	42.50
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	20.07	34 30	142 09	77.72	254 11	91.10	Third	series
41.0133.00144.9278.89260.2191.2128.2922.5543.1038.23150.9179.46260.2191.2129.4123.8044.4439.63153.8980.11266.0291.2129.4123.8045.5341.01156.8580.75268.9391.2230.5825.1746.6442.07159.3481.24271.8391.1531.7926.4747.8543.11161.7981.63274.7391.1732.9527.4849.1144.02164.2282.26277.6391.2034.0328.6650.3645.03166.6582.77279.6891.2535.0629.7651.5745.90169.0783.30281.7491.3436.0530.7752.8146.92171.4883.90284.6391.3737.0831.7654.0647.87173.8784.49287.5291.3538.2032.7555.2748.85176.2685.17290.4191.4739.3133.9856.4849.69178.6485.75293.3091.4540.3735.2457.8250.66181.0086.48296.1891.4341.4137.3359.3551.66183.3687.23299.0691.5042.5038.0060.9952.74185.7087.91301.9491.4843.5839.0162.6753.84186.0488.80304.	39.07	35 50	142.08	70 27	257.30	91.09	(anne	aleð)
42.1037.24147.9270.83203.1231.2728.2922.5543.3038.23150.9179.46263.1291.2729.4123.8044.4439.63153.6980.11266.0291.2129.4123.8045.5341.01156.8580.75268.9391.2230.5825.1746.6442.07159.3481.24271.8391.1531.7926.4747.8543.11161.7981.63274.7391.1732.9527.4849.1144.02164.2282.26277.6391.2034.0328.6650.3645.03166.6582.77279.6891.2535.0629.7651.5745.90169.0783.30281.7491.3436.0530.7752.8146.92171.4883.90284.6391.3737.0831.7654.0647.87173.8784.49287.5291.3538.2032.7555.2748.85176.2685.17290.4191.4739.3133.9856.4849.69178.6485.75293.3091.4540.3735.2457.8250.66181.0086.48296.1891.4341.4137.3359.3551.66183.3687.23299.0691.5042.5038.0960.9952.74185.7087.91301.9491.4843.5839.0162.6753.84188.0488.80304.	41.01	37 24	144.74	70.27	260.21	91.21		
43.5035.2.5150.9173.40266.0291.2129.4123.8044.4439.63155.8980.11266.0291.2230.5825.1745.5341.01156.8580.75268.9391.2230.5825.1746.6442.07159.3481.24271.8391.1531.7926.4747.8543.11161.7981.63274.7391.1732.9527.4849.1144.02164.2282.26277.6391.2034.0328.6650.3645.03166.6582.77279.6891.2535.0629.7651.5745.90169.0783.30281.7491.3436.0530.7752.8146.92171.4883.90284.6391.3737.0831.7654.0647.87173.8784.49287.5291.3538.2032.7555.2748.85176.2685.17290.4191.4739.3133.9856.4849.69178.6485.75293.3091.4540.3735.2457.8250.66183.3687.23299.0691.5042.5038.0960.9952.74185.7087.9130.9491.4843.5839.0162.6753.84188.0488.80304.8391.4044.6339.8464.4354.86190.3689.67307.7091.5145.6640.8566.2955.94192.6890.57310.	42.10	29 23	147.92	70.07	263 12	91.27	28.29	22.55
44.4453.67153.8960.11208.0211.1230.5825.1745.5341.01156.8580.75268.9391.2230.5825.1746.6442.07159.3481.24271.8391.1531.7926.4747.8543.11161.7981.63274.7391.1732.9527.4849.1144.02164.2282.26277.6391.2034.0328.6650.3645.03166.6582.77279.6891.2535.0629.7651.5745.90169.0783.30281.7491.3436.0530.7752.8146.92171.4883.90284.6391.3737.0831.7654.0647.87173.8784.49287.5291.3538.2032.7555.2748.85176.2685.17290.4191.4739.3133.9856.4849.69178.6485.75293.3091.4540.3735.2457.8250.66181.0086.48296.1891.4341.4137.3359.3551.66183.3687.23299.0691.5042.5038.0960.9952.74185.7087.9130.9491.4843.5839.0162.6753.84190.3689.67307.7091.5145.6640.8566.2955.94190.3689.67307.7091.6346.6541.7868.1456.90194.9791.65313.4	43,30	39.63	150.91	/9.40	266 02	91.21	29.41	23.80
43.3341.32130.8360.73200.2321.1531.7926.4746.6442.07155.3481.24271.8391.1531.7926.4747.8543.11161.7981.63274.7391.1732.9527.4849.1144.02164.2282.26277.6391.2034.0328.6650.3645.03166.6582.77279.6891.2535.0629.7651.5745.90169.0783.30281.7491.3436.0530.7752.8146.92171.4883.90284.6391.3737.0831.7654.0647.87173.8784.49287.5291.3538.2032.7555.2748.85176.2685.17290.4191.4739.3133.9256.4849.69178.6485.75293.3091.4540.3735.2457.8250.66181.0086.48296.1891.4341.4137.3359.3551.66183.3687.23299.0691.5042.5038.0960.9952.74185.7087.91301.9491.4843.5839.0162.6753.84190.3689.67307.7091.5145.6640.8564.4354.86190.3689.67307.7091.6346.6541.7868.1456.90194.9791.65313.4391.6447.7242.82	44.44	A1 01	103.89	00.11	200.02	91.22	30.58	25.17
47.8543.11161.79 81.63 274.73 91.17 32.95 27.48 49.1144.02164.22 82.26 277.63 91.20 34.03 28.66 50.3645.03166.65 82.77 279.68 91.25 35.06 29.76 51.5745.90169.07 83.30 281.74 91.34 36.05 30.77 52.8146.92171.48 83.90 284.63 91.37 37.08 31.76 54.0647.87173.87 84.49 287.52 91.35 38.20 32.75 55.27 48.85 176.26 85.17 290.41 91.47 39.31 33.98 56.48 49.69 178.64 85.75 293.30 91.45 40.37 35.24 57.82 50.66 181.00 86.48 296.18 91.43 41.41 37.39 59.3551.66183.36 87.23 290.69 91.50 42.50 38.09 60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.71 48.87 43.61	43.33	42 07	100.00	Q1 24	271.83	91.15	31.79	26.47
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	40.04	43 11	159.34	01.24	274.73	91.17	32.95	27.48
49.11 44.02 104.22 04.26 279.68 91.25 35.06 29.76 50.36 45.03 166.65 82.77 279.68 91.25 35.06 29.76 51.57 45.90 169.07 83.30 281.74 91.34 36.05 30.77 52.81 46.92 171.48 83.90 284.63 91.37 37.08 31.76 54.06 47.87 173.87 84.49 287.52 91.35 38.20 32.75 55.27 48.85 176.26 85.17 290.41 91.47 39.31 33.98 56.48 49.69 178.64 85.75 293.30 91.45 40.37 35.24 57.82 50.66 181.00 86.48 296.18 91.43 41.41 37.33 59.35 51.66 183.36 87.23 299.06 91.50 42.50 38.09 60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.84 188.04 88.80 304.83 91.40 44.63 39.84 64.43 54.96 190.36 89.67 307.70 91.51 45.66 40.85 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82	40 11	44 02	101.79	01.07	277 63	91.20	34.03	28.66
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	47.11	45.03	104.22	02.20	279 68	91.25	35.06	29.76
52.81 46.92 171.48 83.90 284.63 91.37 37.08 31.76 54.06 47.87 173.87 84.49 287.52 91.35 38.20 32.75 55.27 48.85 176.26 85.17 290.41 91.47 39.31 33.98 56.48 49.69 178.64 85.75 293.30 91.45 40.37 35.24 57.82 50.66 181.00 86.48 296.18 91.43 41.41 37.33 59.35 51.66 183.36 87.23 299.06 91.50 42.50 38.09 60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.84 190.36 89.67 307.70 91.51 45.66 40.85 66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82	51 57	45.90	100.03	92.77	281.74	91.34	36.05	30.77
54.06 40.797 171.48 80.90 287.55 51.35 38.20 32.75 55.27 48.85 176.26 85.17 290.41 91.47 39.31 33.98 56.48 49.69 178.64 85.75 293.30 91.45 40.37 35.24 57.82 50.66 181.00 86.48 296.18 91.43 41.41 37.33 59.35 51.66 183.36 87.23 299.06 91.50 42.50 38.09 60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.84 188.04 88.80 304.83 91.40 44.63 39.84 64.43 54.96 190.36 89.67 307.70 91.51 45.66 40.85 66.29 55.94 192.68 90.57 310.57 91.64 47.72 42.82 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82	57 91	46 92	107.07	93 00	284.63	91.37	37.08	31.76
55.27 48.85 176.26 85.17 290.41 91.47 39.31 33.98 56.48 49.69 178.64 85.75 293.30 91.45 40.37 35.24 57.82 50.66 181.00 86.48 296.18 91.43 41.41 37.33 59.35 51.66 183.36 87.23 299.06 91.50 42.50 38.09 60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.84 188.04 89.67 307.70 91.51 45.66 40.85 64.43 54.86 190.36 89.67 307.70 91.51 45.66 40.85 66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.71 48.87 43.61	54.06	47.87	173 07	04 40	287.52	91.35	38,20	32.75
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	55 27	49.85	1/3.8/	04.47	290.41	91.47	39.31	33.98
57.82 50.66 170.64 60.73 295.30 21.43 41.41 37.33 57.82 50.66 181.00 86.48 296.18 91.43 41.41 37.33 59.35 51.66 183.36 87.23 299.06 91.50 42.50 38.09 60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.84 188.04 88.80 304.83 91.40 44.63 39.84 64.43 54.86 190.36 89.67 307.70 91.51 45.66 40.85 66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82 316.29 91.71 48.87 43.61 34.61 34.61 34.61	55.27	40.00	170.20	03.17	203 30	91 45	40.37	35.24
59.35 51.66 183.36 87.23 299.16 91.50 42.50 38.09 60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.84 188.04 88.80 304.83 91.40 44.63 39.84 64.43 54.86 190.36 89.67 307.70 91.51 45.66 40.85 66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82 316.29 91.71 48.87 43.61 34.61 34.61	JO.40 57 97	50.66	101 00	03./3	293,50	91.43	41.41	37.33
60.99 52.74 185.70 87.91 301.94 91.48 43.58 39.01 62.67 53.84 188.04 88.80 304.83 91.40 44.63 39.84 64.43 54.86 190.36 89.67 307.70 91.51 45.66 40.85 66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82	59 35	51.66	103 24	00.10	299 06	91.50	42.50	38.09
62.67 53.84 188.04 88.80 304.83 91.40 44.63 39.84 64.43 54.86 190.36 89.67 307.70 91.51 45.65 40.85 66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82 316.29 91.71 48.87 43.61 31.62 91.71 48.87	60.99	52 74	105.30	07.43	301 94	91.48	43.58	39.01
64.43 54.86 190.36 89.67 307.70 91.51 45.66 40.85 66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82 316.29 91.71 48.87 43.61 31.62 91.71 48.87	60.77	53 84	100.01	00 00	307.54	91.40	44,63	39.84
66.29 55.94 192.68 90.57 310.57 91.63 46.65 41.78 68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82 316.29 91.71 48.87 43.61 316.29 91.71 48.87 43.61	64 43	54.86	188.04	88.80	307 70	91.51	45.66	40.85
68.14 56.90 194.97 91.65 313.43 91.64 47.72 42.82 316.29 91.71 48.87 43.61	66 70	55.94	103 60	07.07	310 57	91.63	46.65	41.78
316.29 91.71 48.87 43.61	68 14	56.90	104 07	90.57	313 43	91.64	47.72	42.82
	00.14	20020	124.3/	71.05	316.29	91.71	48.87	43.61

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Table 2. Heat capacity of TlNO₂

Tav	C _p	Tav	C _p	Tav	C p	T av	C _
							-1 -1
К	JK MOI	К	JK mol	K	JK mol	K	JK *mol *
		2		212 22	82.90	327.65	103.38
First	series	Secor	nd series	215,52	83 49	330.61	103.48
14 00	0 607	00 (7	50 70	218 89	83.99	333.59	103.46
14.05	0.057	00.07	50.04	221.66	84.44	336.58	103.44
14.00	3.210	96 27	57.04	224.40	84.72	339.57	103.52
12.42	11 08	00.37	62.62	227.13	85.07	342.57	103.38
17 93	12.04	03 2 7.	62.03	229.85	85,60	345.35	103.40
19 40	14 18	96 66	64 69	232.65	86.25	348.58	103.45
20 44	15 21	99 51	65 52	235.49	86.69	351.58	103.28
21 40	16 14	102 39	66 30	238.33	87.28	354.59	103.37
22.46	17.12	105.23	66 89	241.16	88.02		
23.63	18.35	108.12	67.65	243.97	87.88	Third	series
24.73	19.44	110.01	68.00	246.77	89.02		
26.01	20.70	112.97	68.62	249.54	89.77	54.45	43.60
27.57	22.06	115.79	69 17	252.30	90.39	55.57	44.31
29.22	23.66	118.59	69.72	255.04	91.09	56.67	44.99
30.83	25.17	121.35	70.16	257.76	91.78	57.75	45.60
32.42	26.58	124.08	70.57	260.47	92.62	58.81	46.29
34.00	28.02	126.87	71.13	263.16	93.45	59.86	47.23
35.58	29.40	129.71	71.63	265.83	94.21	60.89	48.16
37.20	30.86	132.52	71.90	268.49	95.17	61.90	48.91
38.25	31.78	135.32	72.37	271.14	96.25	62.90	49.50
40.26	33.36	138.09	72.74	273.70	97.37	63.89	50.19
41.77	34.61	140.83	73.15	276.34	98.49	64.87	50.77
43.29	35.80	143.56	73.62	278.67	137.75	65.84	51.33
44.90	37.03	146.38	73.96	280.56	375.6	66.30	51.82
46.54	38.26	149.31	74.38	280.90	576.8	17 - 14 h	
48.20	39.45	152.22	74.76	281.44	1103.2	rortn	alod
49.93	40.66	154.04	75.01	281./4	1960.1	(anne	areu/
51.64	41.83	156.91	75.50	281.94	3058	51 63	43 70
53.46	43.00	159.77	75.78	282.12	4859	54.05	40.50
55.40	44.18	162.61	76.20	282.29	5902	57 26	45.41
50.00	40.22	105.43	76.50	282.43	101 55	58 05	46.42
57.27	40,33	168.23	76.88	284.41	181.55	58 84	47.15
62.67	47.00	171.02	77.29	287.00	103.65	59.62	47.66
65 97	51 44	173.79	/7.56	290.04	103.69	60 39	48.22
68 42	52 76	170.34	77.97	292.30	103.02	61.17	48.49
70 79	54 03	1/9.20	78.32	294.90	103.60	61.95	48.99
73 17	55 29	102.00	/8./5	297.97	103.03	62.73	49.66
75.61	56.47	187 20	78.92	302.43	103.61	63.51	49.77
78.16	57.70	190 46	79.30	304.85	103.51	64.28	50.42
80.79	58.89	193.38	/ 3. / L 80 15	307.69	103.45	65.06	50.81
83.40	59.97	196 28	80.45	310.49	103.47	65,83	51.24
86.01	61.09	199.16	80.89	313.30	103.62	66.60	51.72
88.69	62.10	202.02	81 35	316.11	103.48	67.35	52.17
91.40	63.05	204.87	81.61	318.94	103.51	68.11	52.65
94.08	63.95	207.70	82.05	321.79	103.49	68.85	52.96
		210.52	87 52	324.69	103.46	69.59	53.36

tributions: the acoustic translational vibrations C(ac. translation, 3D), the optical translational vibrations C(opt. translation, 3E), the librational oscillations of the anions C (rotation, 3), the internal vibrations of the anions C(internal, 3E) and the $C_p - C_r$ term.

$$C_{p} = C(\text{ac. translation, 3D}) + C(\text{opt. translation,} 3E) + C(\text{rotation, 3}) + C(\text{internal, 3E}) + C_{p} - C_{v}.$$
(1)

Here, E and D mean the Einstein and Debye functions, respectively. The numbers in parentheses give the degrees of freedom included in each term. The internal vibration frequencies of NO_2^- ions in Cs NO_2 and TINO₂ are 1315 cm⁻¹ (A₁), 1248 cm⁻¹ (B₁) and 803 cm⁻¹ (A₁); 1306 cm⁻¹(A₁), 1267 cm⁻¹(B₁) and 769 cm⁻¹(A₁), respectively. These values were determined by Raman and infrared absorption spectra. The wave number of the internal vibration in Cs NO_2 was consistent with the Brooker and Irish's

data within 2 cm⁻¹ [18]. The anisotropic threedimensional librational heat capacity of the NO2 ion was approximated by three independent onedimensional hindered rotors for which the barrier height was 13.8 kJ mol⁻¹ for the Cs salt and 19.5 kJ mol⁻¹ for the Tl salt. These values were obtained by the dielectric measurements described below. The contributions from the acoustic and optical translational modes of CsNO2 (each 3 degrees of freedom) were calculated with the Debye and Einstein temperatures 79.9 K and 176.9 K. These characteristic temperatures were determined by fitting the Debye and Einstein equations between 15 and 40 K to the heat capacities from which other contributions due to internal and librational modes were subtracted. They were taken account of by the use of Einstein functions. Similar fitting for TINO2 between 15 and 60 K gave 64.7 K and 189.5 K for the Debye and Einstein temperatures. The last $C_p - C_r$ term was estimated by the Lindemann's law [19]. The melting temperature, the only essential constant in



Fig. 3. Cooling curve of TlNO₂.

T	C°p	s; - s°	[H° - H°]/T	-[G° - H ₀ °]/T
ĸ	Jk ⁻¹ mol ⁻¹	JK ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻¹	JK ⁻¹ mol ⁻¹
10	(2.33)	(0.78)	(0.58)	(0.20)
20	13.09	5.52	4.03	1.49
30	24.34	12.96	8.93	4.03
40	35.07	21.45	14.14	7.31
50	44.48	30.32	19.30	11.02
60	52.09	39.13	24.15	14.98
70	57.89	47.62	28.58	19.04
80	62.23	55.65	32.53	23.12
90	65.61	63.18	36.02	27.16
100	68.42	70.24	39.12	31.12
110	70.94	76.88	41.90	34.98
120	73.27	83.16	44.42	38.74
130	75.42	89.11	46.72	42.39
140	77.40	94.77	48.85	45.92
150	79.30	100.17	50.81	49.36
160	81.28	105.35	52.65	52.70
170	83,52	110.35	54.40	55.95
180	86.20	115.19	56.09	59.10
190	89.54	119.94	57.76	62.18
200	94.19	124.64	59.46	65.18
210	176.50	141.44	73.30	68.14
220	90.68	146.27	74.67	71.60
230	90.79	150.30	75.37	74.93
240	90.91	154.16	76.01	78.15
250	91.03	157.88	76.61	81.27
260	91.13	161.45	77.17	84.28
270	91.23	164.89	77.69	87.20
280	91.31	168.21	78.17	90.04
290	91.41	171.42	78.63	92.79
300	91.51	174.52	79.06	95.46
310	91.63	177.52	79.46	98.06
320	91.74	180.43	79.84	100.59
330	91.81	183.25	80.20	103.05
340	91.88	185.99	80.55	105.44
350	91.95	188.66	80.87	107.79
273.15	91.26	165.94	77.85	88.09
298.15	91.43	173.95	78.98	94.97

Table 3. Thermodynamic functions of CsNO₂

	Table 4. Th	ermodynamic fu	nctions of TINC	D ₂
Т	C°p	S° - S°	$\left[H^{\circ} - H^{\circ}_{0}\right]/T$	- [G° - H°]/T
ĸ	$JK^{-1}mol^{-1}$	J K ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻¹	JK ⁻¹ mol ⁻¹
10	(3.11)	(1.04)	(0.78)	(0.26)
20	14.77	6.95	5.00	1.95
30	24.34	14.78	9.88	4.90
40	33.00	22.99	14.60	8.39
50	40.77	31.20	19.07	12.14
60	47.60	39.26	23.27	15.99
70	53.46	47.05	27.17	19.87
80	58.36	54.52	30.78	23.74
90	62.35	61.63	34.07	26.56
100	65.54	68.37	37.07	31.31
110	68.07	74.74	39.77	34.97
120	70.08	80.75	42.22	38.53
130	71.74	86.43	44.43	42.00
140	73.16	91.80	46.43	45.37
150	74.46	96.90	48.26	48.64
160	75.73	101.74	49.93	51.80
170	77.00	106.37	51.49	54.88
180	78.32	110.81	52.94	57.86
190	79.67	115.08	54.31	60.76
200	81.08	119.20	55.62	63.58
210	82.53	123.19	56.86	66.33
220	84.07	127.06	58.06	69.00
230	85.71	130.84	59.23	71.61
240	87.57	134.52	60.37	74.15
250	89.74	138.14	61.50	76.64
260	92.41	141.71	62.64	79.07
270	95.81	145.26	63.80	81.46
280	340.50	149.36	65.56	83.80
290	103.67	168.09	81.57	86.52
300	103.58	171.60	82.30	89.30
310	103.51	175.00	82.99	92.01
320	103.49	178.29	83.63	94.66
330	103.45	181.47	84.23	97.24
340	103.45	184.56	84.79	99.76
250	102 24	197 56	95 33	100 00

146.38

170.96

64.18

82.17

Lindemann's equation was determined as 693 K for CsNO₂ and 465 K for TlNO₂ by DSC [20]. Successive steps in the determination of the normal heat capacities are shown in Figs. 1 and 2 as solid lines. The enthalpies and entropies of the phase transitions of CsNO₂ and TlNO₂ crystals thus calculated are (3.45 ± 0.20) kJ mol⁻¹ and (17.2 ± 1.0) JK⁻¹ mol⁻¹, and (6.44 ± 0.31) kJ mol⁻¹ and (23.8 ± 1.1) JK⁻¹ mol⁻¹, respectively. These results are summarized in Tables 5 and 6. The difference of the

273.15 298.15

97.09

entropies of transition of $CsNO_2$ crystal reported here and Ref. [3] arises from the different estimations of the normal heat capacity.

82.20

88.79

In addition to the phase transition, an increase of the heat capacity by $\sim 1 \, JK^{-1} \, mol^{-1}$ was found around 42 K for CsNO₂ [5] and around 60 K for TINO₂. The heat capacity anomalies have relaxational nature: exothermic and endothermic temperature drifts were found around these temperatures. The average temperature drift rates at

Table 5. Enthalpy and entropy of the phase transition of $CsNO_2$

[™] t ∕ K	ΔH _t / kJ mol ⁻¹	Δs _t / JK ⁻¹ mol ⁻¹
209.16 ± 0.10	3.45 ± 0.20	17.2 ± 1.0

Table 6.	Enthalpy	and	entropy	of	the	phase	transition	of	TINO ₂
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[™] t / K	∆H _t / kJ mol ⁻¹	$\Delta s_t / J K^{-1} mol^{-1}$
282.4 ± 0.1	6.44 ± 0.31	23.8 ± 1.1



Fig. 4. Temperature drift of CsNO₂ in the glass transition region.



Fig. 5. Temperature drift of TINO₂ in the glass transition region.

25 min after the heating period for different series of measurement are plotted against temperature in Figs. 4 and 5. The encraties (C_p/T) around the glass transitions of CsNO₂ and TlNO₂ were plotted as in Figs. 6 and 7 against temperature, respectively. In Fig. 6 series 1 shows the heat capacities measured with the heating rate of 1 Khr⁻¹ after, rapid cooling (1 Kmin⁻¹). Series 2 was obtained by the heating rate of 2 Khr^{-1} after rapid cooling (1 Kmin⁻¹). The heat capacities of the sample after slow cooling (0.1 Kmin⁻¹) and annealing at 40.5 K for 36 hr are shown as series 3. In Fig. 7, series 1 is the heat capacities measured with the heating rate of 4 Khr⁻¹ after quenching the sample at the rate of 1 Kmin^{-1} . Series 2 was obtained by the heating rate of 1 Khr⁻¹ after similar quenching. In series 3, the heat capacities were measured with the heating rate of 1 Khr⁻¹ after slow cooling (0.1 Kmin^{-1}) and annealing at 57.3 K for 53 hr. We found that the temperature at which the drifts changed from exothermic to endothermic was the lower, the more the sample was stabilized in the previous thermal history. This behavior is the characteristics of the glass transition. The small increases of heat capacities $\sim 1 \, JK^{-1} \, mol^{-1}$ in both compounds suggest that the energy involved in the disorder is small compared with those in the glassy liquid $(\Delta C_p > 20 \text{ JK}^{-1} \text{ mol}^{-1})$ [21]. We expect that these small heat capacity anomalies are related to the freezing of orientational disorder of the NO₂⁻ ion which is believed to exist in the low-temperature phases. The dotted lines of Figs. 6 and 7 are normal heat capacities calculated above. The excess entropies assuming T^{-2} law for the excess heat capacities are 1.3 JK⁻¹ mol⁻¹ for CsNO₂ and 0.9 JK⁻¹ mol⁻¹ for TINO₂.



Fig. 6. The encraty (C_p/T) of CsNO₂ in the glass transition region. Series 1 and 2 measured without annealing and series 3 after annealing at 40.5 K for 36 hr. The dotted line correspond to the calculated one.



Fig. 7. The encraty of $TINO_2$ in the glass transition region. Series 1 and 2 measured without annealing and series 3 after annealing at 57.3 K for 53 hr. The dotted line corresponds to the calculated one.

2.3 Dielectric measurement

The complex dielectric permittivities of CsNO₂ and TINO₂ crystals were measured with capacitance bridge (General Radio Co. Ltd.) and a cryostat [22] at 12 frequencies ranging from 100 Hz to 100 kHz for the former and 9 frequencies ranging from 200 Hz to 100 kHz for the latter. Experimental detail is described elsewhere [5, 6]. The real (ϵ') and imaginary (ϵ'') parts of the relative dielectric permittivities of CsNO₂ and TlNO₂ crystals were shown in Figs. 8 and 9. The dielectric relaxations were observed between 58 and 150 K in CsNO₂ [5] and 80 and 180 K in TINO₂ [6]. The magnitudes of the dispersions $(\Delta \epsilon' \sim 2.5 \text{ for the Cs salt and } \sim 10 \text{ for the Tl salt})$ suggest that ionic reorientation is involved in the polarization as expected from the polarity of the nitrite ions. The magnitude of the absorptions in both compounds increased with the temperature rise. These will be interpreted in Discussion.

Another dispersion apparently related to the phase transition at 282.4 K became significant at high temperatures. The dielectric loss increased rapidly as the temperature approached the phase transition from below. This is an effect of dielectric loss caused by the d.c. conductivity with increase of the temperature.

In Figs. 10 and 11, temperature dependence of the dielectric losses for CsNO₂ and TlNO₂ are plotted against the decadic logarithm of the frequency, *f*. The line shapes of the dielectric losses are slightly broader than the simple Debye theory predicts as shown in Figs. 12 and 13. The normalized dielectric losses of both compounds, $\epsilon''/\epsilon''_{max}$, are plotted against f/f_{max} in a logarithmic scale where f_{max} is the frequency of maximum absorption. The solid lines in the figures represent the Debye-type absorption with single relaxation times. The average relaxation time τ_d can be calculated by the expression [23] of

$$\tau_{\rm d} = \frac{1}{2\pi f_{\rm max}}.$$
 (3)

As is well known, the complex dielectric permittivity ϵ^* can be represented by the following equation for usual polar liquids and solids [24]

$$\epsilon^* - \epsilon_{\omega} = \frac{\epsilon_0 - \epsilon_{\omega}}{1 + i\omega \tau_d^{1-\omega}},\tag{4}$$

where ϵ_{∞} and ϵ_0 are the limiting high- and lowfrequency permittivities and ω the angular frequency with $\omega = 2\pi f$, respectively. The exponential factor of α is the distribution parameter which is equal to 0 for a system of single relaxation time. Cole and Cole have pointed out that a plot of ϵ' vs ϵ'' for different frequen cies at a given temperature should give an arc of a circle according to eq (4)[24]. The Cole-Cole plots of the ϵ' and ϵ'' at three different temperatures are shown in Figs. 14 and 15. The distribution parameters α determined from the arc plots are given in the same figures. The values of $\alpha \sim 0.2$ show that the relaxation deviate from the single dispersion processes. They decreased with the increasing temperature. Similar behavior is found in crystals such as ice [25, 26] and some organic crystals [27, 28],

2.4 Raman spectra of the high-temperature phase

An NO_2^{-1} ion has three internal vibrations, the symmetric (A_1) and antisymmetric (B_1) stretching and bending (A_1) modes. In the low-temperature phases of CsNO₂ and TINO₂ crystals, all of the three modes were observed as sharp singlets. They became slightly broader as the transition temperatures were approached from below. In the high-temperature phases the antisymmetric stretching vibration was very weak and smeared out. The symmetric stretching modes in both compounds and bending mode in TINO₂ broadened further with the temperature rise in the high-temperature phases and had no structures. This behavior is common in orientationally disordered crystals [29, 30]. However, the bending mode in CsNO₂ split into an ill-resolved doublet as shown in



Fig. 8. Upper: dielectric constant of CsNO2 at various frequencies. Lower: dielectric loss of CsNO2.



Fig. 9. Upper: dielectric constant of $TINO_2$ at various frequencies. Lower: dielectric loss of $TINO_2$.





Fig. 10. Dielectric loss of $CsNO_2$ against the decadic logarithm of the frequency.

Fig. 11. Dielectric loss of $TINO_2$ against the decadic logarithm of the frequency.



Fig. 12. The normalized plots of the dielectric loss of $CsNO_2$ against frequency at several temperatures; \triangle , 73 K; \bigcirc , 83 K. The solid line is the theoretical curve for a single Debye-type relaxation.



Fig. 13. The normalized plots of the dielectric loss of TlNO₂ against frequency at several tempratures; \triangle , 109 K; \bigcirc , 125 K. The solid line is the theoretical curve for a single Debye-type relaxation.



Fig. 14. The Cole–Cole plot of $CsNO_2$ at some temperatures with the distribution parameters.



Fig. 15. The Cole–Cole plot of $TlNO_2$ at some temperatures with the distribution parameters.



Fig. 16. Raman line shape of the bending vibration (A_1) of the NO₂⁻ ion in CsNO₂.



Fig. 17. Arrhenius plot of the relaxation time of $CsNO_2$ determined by dielectric loss measurement and calorimetry.



Fig. 18. Arrhenius plot of the relaxation time of $TINO_2$ determined by dielectric loss measurement and calorimetry.

Fig. 16. The component bands were broad and their relative intensity changed with temperature so that at 222 K the spectra resembled unusually broad band with a flat top. As the temperature increased further the doublet coalesced finally into an ordinary singlet at 301 K. The overall width of the band decreased with increasing temperature. The spectra taken between 210 and 252 K were resolved into two Lorentzian components by the use of a Curve Resolver 310 (Dupont Co. Ltd.). The separation of the splitting at 210 K was about 10 cm⁻¹ and it became slightly smaller at 252 K ($\Delta v \sim 8 \text{ cm}^{-1}$). The itensities of two bands were slightly different at 210 K, but they became equal above 222 K. The frequency of the bending mode in the low-temperature phase at 204 K was close to that of the lower component of the doublet above the phase transition. Apparent broadening and the subsequent narrowing of the bending mode of the NO_2^- ion with the increase of temperature in the high-temperature phase of CsNO₂ were also shown in IR spectra.

As was previously discussed [5], the splitting of the bending mode was interpreted in terms of two nonequivalent orientations for an NO₂ ion in the simple cubic lattice of CsNO2. Stable orientations of the NO_2 ion relative to the crystal axis are not known. But there are two possibilities for the NO₂ orientations with O-O axis parallel to [110] and [111] of the cubic lattice from entropic and packing considerations as described in Discussion. The NO2 ion at two different orientations will feel different crystal fields of the lattice. These crystal fields can influence the internal vibration of the NO_2^- ion resulting in the splitting of the spectra. The bending mode with the smallest force constant among the internal vibrations will be most sensitively affected by the different crystalline environments.

Similar doublets were observed by infrared spectra in the CN stretching mode of NaCN · 2H₂O [31] and the OH stretching mode in benzoic acid [32, 33]. In the LiNO₂ crystal, a doublet having large splitting $(\Delta v \sim 30 \text{ cm}^{-1})$ was observed in the bending mode of the NO_2^- ion by IR and Raman spectra. This was interpreted as the difference of chemical bond which contains nitorito and nitro linkages [18]. In these experiments doublet due to the different configurations was found but any such narrowing of the line width within the same crystalline phase as in the CsNO₂ crystal was not observed. Origin of the unusual narrowing will be described in Discussion.

3. DISCUSSION

3.1 The dielectric and calorimetric relaxation times Kinetic parameters associated with the enthalpy relaxation can be obtained by analyzing the calorimetric temperature vs time curves in the glass transition region. In the analysis of temperature drift curves, it is important to recognize that the thermometer measures the temperature of the lattice system as distinct from the configurational temperature of the system. The time lags between the lattice NO₂^{**} vibrational systems of sample crystals and the thermometer unit including the calorimeter cell are typically 10 min and almost independent of temperature. In contrast, the relaxation time of the NO₂ configurational system is strongly temperature dependent. At higher temperature the configurational system equilibrates instantaneously with the lattice. The different situation occurs at lower temperature where the relaxation time increases practically without limit, leading to freezing of the NO2 ions into immobile glassy state. At an intermediate temperature, the relaxation time becomes short enough for the energy flow between the lattice and configurational systems to occur in an experimentally practical time and at the same time long enough for the time constant of the thermal conduction in the calorimeter cell to be negligibly small in comparison. The exothermic or endothermic relaxation occurs depending on whether the configurational enthalpy of the NO_2^- ion is larger or smaller than that appropriate to the current lattice temperature. The

calorimetric relaxation time τ_c is defined as follows by assuming an exponential law for the approach of the enthalpy to the equilibrium value,

$$\frac{\mathrm{d}H_{\mathrm{c}}(T,t)}{\mathrm{d}t} = -\frac{H_{\mathrm{c}}(T,t)}{\tau_{\mathrm{c}}},\tag{5}$$

where $H_i(T, t)$ is configurational enthalpy to be relaxed to the equilibrium value at temperature T and time t. The l.h.s. of eqn (5) is related to the temperature drift rate dT/dt by the equation;

$$\frac{\mathrm{d}H_{\mathrm{c}}(T,t)}{\mathrm{d}t} = -Cf\frac{\mathrm{d}T}{\mathrm{d}t},\tag{6}$$

where f is the conversion factor to the molar quantity and C the apparent heat capacity. Configurational enthalpy is written as follows;

$$H_{c}(T,t) = Cf[T(\infty) - T(t)], \qquad (7)$$

where $T(\infty)$ is the temperature after the relaxational behavior is over. Combining eqns (5)-(7) we obtain;

$$T(\infty) - T(t) = (T(\infty) - T(0)) \exp\left(-\frac{t}{\tau}\right).$$
(8)

The calorimetric relaxation time was determined by fitting an exponential function to the drift curve of the calorimetric temperature.

The dielectric relaxation times τ_d of CsNO₂ and TlNO₂ determined by eqn (3) are plotted against inverse temperature in Figs. 17 and 18. The calorimetric relaxation times τ_c as determined above were also plotted in the same figures. Two points of the calorimetric relaxation times at the lowest temperatures in both compounds were determined from the exothermic and six points in high temperature regions from the endothermic drifts. The calorimetric and dielectric relaxation times lie on a straight line in both compounds over a wide relaxation time ranging 10^{-6} -10⁵ sec. The slopes give the activation enthalpies, 13.8 kJ nmol⁻¹ for CsNO₂ and 19.5 kJ mol⁻¹ for TINO₂. It should be pointed out that the equalities of the calorimetric and dielectric relaxation times implied in Figs. 17 and 18 are not a priori expected. In fact, in a power series expansion of the enthalpy in the electric polarization, only the even order terms exist because of the symmetry. Therefore the enthalpy is proportional to P^2 in the lowest order. It follows that

$$\tau_{\rm c} = 2\tau_{\rm d}.\tag{9}$$

Thus, τ_d and τ_c will be different by a factor of two in this approximation. However, a small difference of ln 2 cannot be discussed with any significance in Figs. 17 and 18.

From the structural and dielectric evidences, the NO_2^- orientations are in dynamic disorder at high temperature in the low-temperature phase. At lower

temperatures, the dynamic disorder will change to a static disorder by falling out of thermal equilibrium with other degrees of the crystal. If we take 10 ksec arbitrarily as the boundary between dynamic and static disorder by using the Arrhenius parameter obtained above, the glass transition will occur at 42 K for CsNO₂ and 60 K for TlNO₂.

3.2 Dynamic and static nature of the orientational disorder in the $CsNO_2$ crystals

We conclude from the occurrence of the glass transition that disorder remains in the lowtemperature rhombohedral phase of the CsNO₂ crystal. The simplest model for the structure of the low-temperature phase consistent with the crystal data [2] puts the Cs^+ ion at the 1a position (0, 0, 0) of $D_{3d}^5 - R\overline{3}m$, the N at 3g positions, $(x\overline{x_2^1}; \overline{x_2^1}x;$ $\frac{1}{2}\bar{x}$) to distribute the two O atoms among the two triplets of 6h positions (xxz; xzx; zxx; $\bar{x}x\bar{z}$; $\bar{x}z\bar{z}$; $\bar{z}\bar{x}\bar{x}$) where the NO_2^{-} ion is maintained in the crystal. This model corresponds to the structure with the smallest number of the symmetry elements among those consistent with the X-ray diffraction data. We will take this three state model for the NO_2^- orientation around C₃ axis of the rhombohedral structure in which the NO_2^- ions accommodated in the unit cell with O-O axis parallel to the C_3 axis. The model involves three distinct orientations of the nitrite group, and therefore has a configurational entropy of $R \ln 3$. Interactions among the nitrite ions will deform the three-fold potential, leading ultimately to a hypothetical phase transition into an orientationally ordered state that would satisfy the third law of thermodynamics. However, the relaxation time of the reorientational motion increases exponentially with decreasing temperature and prolonged relaxation time hinders the dipolar system from reaching the equilibrium configuration before the hypothetical phase transition is reached. The situation is the same as in a few crystals (CO [34], N₂ [35], H₂O [36], SnCl₂. $2H_2O$ [37], H_3BO_3 [38], pinacol hydrate [39], etc.) which are believed to be in a frozen-in state with respect to some degrees of freedom. The relaxation time for molecular rearrangement becomes so long at the temperature where short-range or long-range order continues to develop that small amount of relaxational heat-capacity is observed experimentally.

The experimental entropy of the phase transition is 17.2 JK⁻¹ mol⁻¹. However, the residual entropy of $R \ln 3 = 9.1 \text{ JK}^{-1} \text{ mol}^{-1}$ inferred from the crystal structure of the low-temperature phase is to be added to this value in the estimation of the orientational disorder in the high-temperature phase. The total entropy due to the orientational disorder of the NO_2^{-1} ion has a value $17.2 + 9.1 = 26.3 \text{ JK}^{-1} \text{ mol}^{-1}$. If one assumes that the orientation of the ion is uniquely fixed in the hypothetical lowest-temperature phase, the orientational entropy S_{or} of the nitrite ions is related to the number of complexions W in the high-temperature phase by the equation, $\Delta S_{\rm or} = R \ln W$. The configurational entropy of NO₂⁻

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ions, (26.3 ± 1.0) JK⁻¹ mol⁻¹, corresponds to $W = 23.6 \pm 2.9$.

We will make a model of disorder which is in accordance with the calorimetric and spectroscopic data and packing consideration. The maximum dimension of the nitrite ion is along the two oxygen atoms. The actual size including the van der Waals radii is 0.49 nm. This value is calculated from the crystal structural data of NaNO₂ [40] in the orientationally ordered phase by taking into account the ionic radius of Na⁺ ion. The size is slightly larger than the lattice constant 0.44 nm, of the high-temperature phase of the CsNO₂ crystal (CsCl structure). There are two possible modes of accommodation of an NO₂⁻ ion in the unit cell based on packing and symmetry considerations. These two possible orientations are such that the O-O axis of the NO_2^{-1} ion is parallel to the body-diagonal axis or parallel to the face diagonal axis in the cubic structure as shown in Fig. 19. We suppose that the O-O axis of the triangular anion is parallel to the bodydiagonal of the cubic lattice in analogy with the low-temperature rhombohedral phase. There are four body-diagonals in the unit cell. Each of them has three orientations because the body-diagonal is a three-fold axis of the crystal. In total there are $3 \times 4 = 12$ equivalent orientations of this type. We assume additional stable orientations in which the O-O axis is parallel to the face-diagonal, as mentioned above. There are six of them, each with weight two because the face-diagonal is a two-fold axis, giving rise to additional $2 \times 6 = 12$ orientations. The two sets of orientation are non-equivalent crystallographically so that anion in the orientations belonging to the different sets are generally in different crystal fields. They will thus have different vibrational frequencies if the surrounding cations exert large enough forces to the central anion. The orientational entropy calculated by this model is equal to $R \ln 24 = 26.4 \text{ JK}^{-1} \text{ mol}^{-1}$. The experimental value of the orientational entropy, 26.3



Fig. 19. Orientational disorder of the NO_2^- ion in the cubic phase of C_8NO_2 .

(=17.2 + 9.1) JK⁻¹ mol⁻¹ is in excellent agreement with the model entropy. We believe this model is fundamentally correct but it should be pointed out that this exact agreement may be fortuitous by three reasons. Firstly, the entropy due to volume change at the phase transition is not known, secondly more than the three possible orientations might be allowed for the rhombohedral low-temperature phase, and thirdly the possibility of another configurational disorder will be allowed for the high-temperature phase.

The Raman spectra of the bending mode of the NO_2^- ion as shown in Fig. 16 are consistent with the same disorder model of different two sets of orientations with equal probability. The low frequency component of the doublet is assigned to the ions whose O-O axis is parallel to the body-diagonal because it occurs at the frequency approximately equal to that in the low-temperature phase in which all of the anions are packed in such a way. The approximately same intensity of the two components of the doublet supports the model of the random distribution of the ions over the two sets orientations with the same degeneracies.

Narrowing of the vibrational spectrum with increasing temperature is unusual and requires explanation. We interpret it as a motional narrowing caused by increasingly rapid ionic reorientation as the temperature is increased. We assume that the frequencies of the component bands of the doublet of the NO₂⁻ ion are v_1 and v_2 corresponding to the two different sets of orientations as mentioned above and that the NO₂⁻ ions can change these orientations with the correlation time τ . When we assume the Markovian process for the present non-equivalent reorientation of the NO₂⁻ ion, the scattered intensity of the Raman spectra is written as follows [41];

$$I(v) = \frac{P_1^0 P_2^0}{\pi} \frac{(v_1 - v_2)^2}{(v - v_1)^2 (v - v_2)^2 + v_c^2 (v - \tilde{v})^2},$$
 (10)

where $\bar{v} = P_1^{0}v_1 + P_2^{0}v_2$ is the equilibrium average of the two frequencies and P_1^{0} and P_2^{0} are equilibrium probabilities in the form of $P_1^0 = v_c'/v_c$, $P_2^0 = v_c''/v_c$ and $v_c = v'_c + v''_c$. v'_c^{-1} and v''_c^{-1} are the life times of the each state, respectively. This equation shows that if v_c is small compared with $|v_1 - v_2|$, the spectrum is composed of two separate Lorentzians. They merge into one for larger v_c . In the intermediate v_c , the line shape changes from the former to the latter. As mentioned in the experimental section, the temperature dependence of the NO₂⁻⁻ bending mode of Raman spectra corresponds to different v_c in the equation. The increase of v_c corresponding to the shorter correlation time $(2\pi v_c)^{-1}$ is caused by the disordering of the NO_2^- ion's orientation. As the temperature is raised the correlation time decreases so that $2\pi\tau < |v_1 - v_2|^{-1}$. Then the rapid reorientation will average out the different crystal fields felt by the anion at different instants [41]. As a result of this motional narrowing a singlet spectrum is observed at $(v_1 + v_2)/2$ in place of the doublet. In other words, in

order for the effective averaging to be attained, the mean life time of an orientation should be shorter than the inverse of the frequency difference to be averaged, $\Delta v \sim 10 \text{ cm}^{-1}$. The average life time should be less than 1 psec at 250 K. At the same time such a shortened correlation time will affect the line widths of the respective spectra, as it does in some plastic crystals [42]. Salient feature of the NO₂⁻ Raman spectrum, especially its temperature dependence, is thus reproduced by this equation with larger v_c values for higher temperatures. However, well-resolved doublets expected at lower temperatures could not be confirmed because of the phase transition at 209 K.

Such a motional narrowing is also observed in some high-resolutional NMR spectra with different chemical environments in solution state. One example is the hindered rotation of N,N-dimethyl formamide in carbon tetrachloride solution where two kinds of methyl protons can exchange their environments by internal rotation with correlation time τ [43]. In this case motional narrowing can be observed at the correlation time of $\tau \sim 1$ msec. In spite of the 10⁹ difference in the Raman and NMR correlation times, the fundamental mechanisms underlying the two spectral observations are very close to each other. Very little has so far been reported on the motional narrowing in the Raman spectrum in contrast to the similar effect in NMR and this is the first experimental evidence known to us. There are several reasons for this difference. First, the eigenstates are much more well defined in nuclear spin systems than in the vibrational systems. Therefore very high resolution has been attained in NMR. In the vibrational spectroscopy there are many mechanisms for line broadening to overshadow the motional narrowing. Second, the rapid ionic reorientation with $\tau \sim 1$ ps is found in a limited type of orientationally disordered crystal in a small temperature range.

3.3 Orientational disorder and phase transition in the $TINO_2$ crystal

Two possibilities of the space group, Cmm2 and Cmmm, were derived from the X-ray photograph for the low-temperature phase of TlNO₂, as shown in Appendix. The space group of Cmmm requires that orientational disorder exists in the low-temperature phase. When we adopt this space group, the two state model having equally probable orientations of the NO_2 ion is maintained as shown in Fig. A3. The model involves two distinct orientations of the nitrite ion in the low-temperature phase and therefore has the orientational entropy of $R \ln 2$. The other space group Cmm2 does not necessarily require the orientational disorder of the NO_2^- ion. In view of the dielectric dispersion that occurs in the lowtemperature phase, the space group Cmmm is the preferred one. However, if one allows partial disorder for the orientation of the NO_2^{-1} ion, one has also to take into consideration the other possibility. More definite conclusion from structural study is obviously desirable. The freezing of the orientation of NO₂⁻

ion from the equilibrium crystalline state to the glassy state occurred around 60 K in the TlNO₂ crystal before it undergoes ultimately a hypothetical phase transition to an orientationally ordered state.

The magnitude of the dielectric absorption increases with increasing temperature as shown in Fig. 9. This behavior can be interpreted with two alternative ways. Firstly, we suppose that the distribution factor α increases with decreasing temperature as in CsNO₂. The dielectric loss at maximum absorption $\epsilon_{max}^{"}$ would then decrease with the decreasing temperature. In the other explanation of dielectric behavior at low temperatures, we assume two non-equivalent orientations for the NO₂ ion corresponding to the space group *Cmm*₂. If there is an enthalpy difference of ΔH_0 in the two nonequivalent orientations, the magnitude of the dielectric dispersion is given by the expression [44];

$$\epsilon'_0 - \epsilon'_\infty = \frac{C}{T} \left(1 + \cosh \frac{\Delta H_0}{RT} \right)^{-1} \tag{11}$$

where C is constant. In this model, when there is an enthalpy difference larger than RT between the two minima which is separated by the activation enthalpy 19.5 kJ mol⁻¹, the dielectric loss decreases with the decreasing temperature. Calculation by fitting the data of ϵ' and ϵ'' to eqn (11) indicates that the enthalpy difference of the two minima is (100 ± 20) J mol⁻¹. The experimental and theoretical values are shown in Fig. 20. With this enthalpy difference the heat capacity jump at 60 K of TINO₂ crystal is calculated by the Schottky heat capacity equation [45];

$$C_{\rm sch} = R \left(\frac{\delta}{T}\right)^2 \frac{g_0}{g_1 [1 + (g_0/g_1) \exp(\delta/T)]^2}$$
(12)

in which $\delta = \Delta H_0/R$ is the enthalpy separation in K and g_0 and g_1 are degeneracies of the lower and upper energy levels, respectively. The contribution below 60 K is truncated by the freezing of the process. With T = 60 K and $g_0/g_1 = 1$, $C_{\rm sch}$ is equal to



Fig. 20. The maximum value of dielectric loss ϵ'' against the temperature.

 $1.5 \text{ JK}^{-1} \text{ mol}^{-1}$ in satisfactory agreement with the experimental heat capacity jump of ~ $1 \text{ JK}^{-1} \text{ mol}^{-1}$. There are thus two models for accounting for the dielectric properties of TINO₂ at low temperatures. To distinguish these two models, accurate crystal structure data will be valuable.

The experimental entropy of the phase transition is (23.8 ± 1.1) JK⁻¹ mol⁻¹. If we take this entropy as of entirely orientational origin, the residual entropy of $R \ln 2 = 5.8 \text{ JK}^{-1} \text{ mol}^{-1}$ has to be added to it in order to obtain the total orientational entropy of the NO_2^{-} ion in the cubic phase. In the symmetric potential for reorientation of NO₂⁻ ion compatible with the space group Cmmm, the corresponding entropy $R \ln 2$ is retained in the low-temperature phase. Even in the non-symmetric potential comparable with Cmm2, the residual entropy close to $R \ln 2$ is expected to be retained in the crystal if the orientational freezing occurs at higher temperature compared with $\Delta H_0/R$. The total entropy due to orientational disorder in the high-temperature phase is (29.6 ± 1.1) JK⁻¹ mol⁻¹. A model of the orientational disorder is constructed as follows, as in C_{sNO_2} crystal. The Tl⁺ ion is located at la position and the NO_2^{-1} ion at 1b position in the cubic unit cell of the CsCl structure. The allowable orientations of the NO_2^- ion are limited to those having the O-O axis parallel to [110] and [111]. In total there are 24 orientations of the NO_2^{-1} ion in the high-temperature phase of TINO₂. The experimental entropy assuming two possible orientations in the low-temperature phase, (29.6 ± 1.1) JK⁻¹ mol⁻¹, is slightly larger than the model value of 26.4 JK⁻¹ mol⁻¹ and that of $CsNO_2$, (26.3 ± 1.0) JK⁻¹ mol⁻¹. However, in the TINO₂ crystal $\Delta S / \Delta V$ term may be larger than in CsNO₂ and the orientational disorder of the NO₂⁻ ion in the high-temperature phase is expected to be comparable with the CsNO₂ crystal. In TlNO₂, no splitting appeared in Raman spectra in the hightemperature phase between 285 and 350 K in the bending mode of the NO_2^- ion. Only the motional broadening of the band appeared in this temperature region. This indicates that reorientational motion of the NO_2^- ion in TINO₂ among the different sets of orientations is more frequent than in CsNO₂. Closer consideration to this problem will be given in the future.

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APPENDIX

Structure of the low-temperature phase of the TINO₂ crystal Existence of the residual entropy is expected in the low-temperature phase of TINO₂ from the observations of glass transition and dielectric relaxation. In order to examine the structural aspect of the residual disorder in the lowtemperature phase and to confirm the structure of the hightemperature phase proposed earlier, X-ray photographs were taken in both phases of the TINO2 crystal. The photographs are reproduced in Fig. A1 (the room temperature phase) and A2 (the low-temperature phase at 240 K), respectively. The high-temperature phase was found to have the CsCl structure, in agreement with the result by Cavalca et al. [3]. The crystal used for the measurement of X-ray study at low temperature was obtained by cooling the hightemperature phase single crystal which was taken out of the aqueous solution at room temperature ($\sim 0.2 \text{ mm}$ cube). This crystal was not a single crystal but twinned. The analysis of the low-temperature photograph was difficult because of extra lines due to twinning. However, by the comparison of the pattern in Fig. A1 with that of Fig. A2 at 240 K, the space group of the low-temperature phase was determined as one or the other of the possible two space groups $C_{2b}^{11} - Cmm2$ and $D_{2b}^{19} - Cmmm$. Both of these space groups belong to orthorhombic system (Z = 2) with C facecentering. Addition of center of symmetry to the former gives rise to the latter. The unit cell and a model of the disordered NO₂⁻⁻ ions in the low-temperature phase is given in Fig. A3, together with the unit cell of the high-temperature phase. In the low-temperature phase the unit cell is deformed by 2° in the direction of face-diagonal in the (001) plane and face-diagonal of the high-temperature cubic unit cell becomes the a axis, as shown in the right of Fig. A3. In the low-temperature phase the Tl+ ions are located at 2a posi-



Fig. A1. X-ray photograph of the high-temperature phase of TlNO₂.



TINO2 Primitive Cell of the Low-Temperature Phase



Fig. A3. The unit cell and a model of disordered NO_2^{-1} ions in the low-temperature phase of TlNO₂.

unit cell. We assume that O-O axis of the NO2- ion is parallel to [110] based on the crystal packing. When the space group Cmmm is taken for the structure of the lowtemperature phase, the NO_2^- ion must take two different orientations with equal probability in agreement with the site symmetry, as shown in left of Fig. A3. In the case of $C_{2v}^{11} - Cmm^2$, the NO₂⁻ ions can be in an ordered orientation. But even in the latter case the disorder of the NO₂⁻ ion will be able to remain as described in the Discussion.

Fig. A2. X-ray photograph of the low-temperature phase of TINO₂.

tion in both of the possible orthorhombic phases. The NO₂⁻ ions are located at the center of the edge of the orthorhombic