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A calorimetric investigation of the low-temperature phase transition in NaOD^{a)}

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The heat capacity of NaOD from $T = 20$ to 350 K is reported. An anomaly centered at $T = 153.2 \pm 0.1$ K ($\Delta H = 131.1 \pm 0.7$ J mol⁻¹, $\Delta S = 0.864 \pm 0.005$ J K⁻¹ mol⁻¹) corresponds to the onset of a low-temperature antiferroelectric phase. This transformation, which likely involves tunneling of the deuterons, does not appear to have an atmospheric pressure analog in NaOH above $T = 6$ K.

I. INTRODUCTION

Polymorphism in alkali metal hydroxides has long been known to exist, particularly above room temperature. For example, NaOH transforms at 514 K from its room temperature orthorhombic structure ($Bmmb$, $Z = 4$) to a monoclinic structure ($P2_1/m$, $Z = 2$), and then at 566 K to a cubic structure ($Fm3m$, $Z = 4$) with orientationally disordered hydroxide ions, prior to melting at 594 K.^{1,2} The corresponding phase changes in the deuterated analog NaOD occur at 500, 561, and 593 K, respectively.¹

In addition, there is evidence for a low-temperature phase in NaOD that appears not to exist in NaOH. The first suggestion of this low-temperature phase was based on an early infrared study,³ which remained uncited for almost 30 years. However, recent NMR, NQR, and DTA studies,⁴⁻⁷ as well as x-ray and neutron diffraction and dielectric measurements,⁸ now show this transition clearly to occur in NaOD and not in NaOH, at least not at atmospheric pressure and temperature greater than 6 K. The source of this transition is the transformation to a monoclinic low-temperature phase ($P2_1/a$, $Z = 4$) in which the deuterioxide ions are canted with respect to the orthorhombic c axis, as shown in Fig. 1. This canting is equally abundant in each of two senses with respect to the orthorhombic ac plane, and the structure is

antiferroelectric. The transformation to this phase, which appears to be driven by the softening of a transverse optic mode, is accompanied by a 4.6% contraction of the c axis (most of which occurs gradually, but part of the volume change is discontinuous), and the transition is therefore first order.

Although there was a considerable amount of experimental information concerning the low-temperature phase transition in NaOD, including an estimate of the transition enthalpy (200 ± 75 J mol⁻¹) from DTA experiments,⁴⁻⁶ measurement of the heat capacity of NaOD could reveal more about this transformation. A precise value of the entropy of the transition, as determined from heat capacity measurements, will help delineate the nature of the transition. In addition, the transition entropy will be a sensitive test for simulation calculations of the phase transformations in alkali metal hydroxides and deuterioxides, which themselves could reveal the subtle effects of slight changes in lattice parameters on phase stability.

II. EXPERIMENTAL

NaOD was prepared by the dehydration of 40 mass % NaOD in D₂O (gold label, >99% D, Aldrich Chemicals),

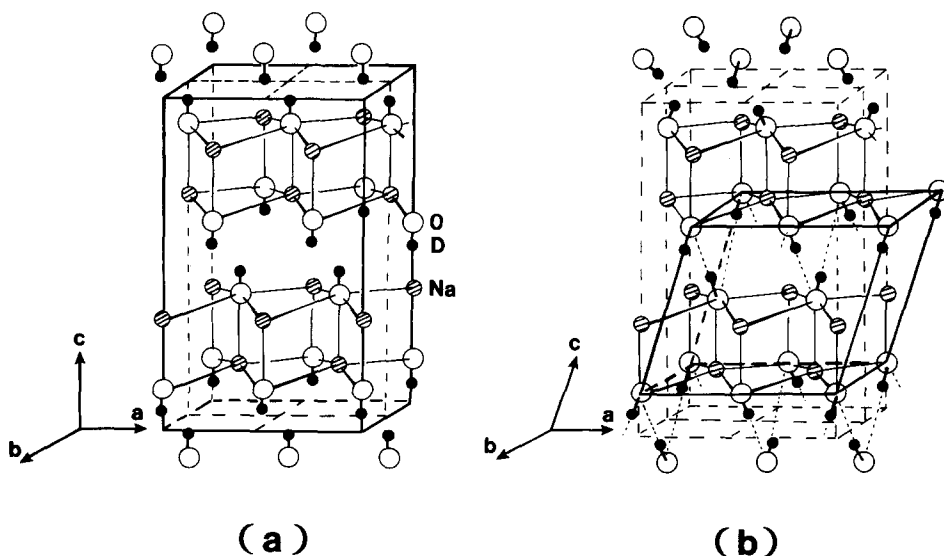


FIG. 1. The structure of NaOD, (a) at room temperature, (b) at 77 K.

^{a)} Dedicated to Professor James A. Morrison, on the occasion of his retirement.

carried out in a zirconium crucible under vacuum at 160 °C in an Abderhalden drying apparatus.⁹ All manipulations were carried out in a glove box under a dry nitrogen atmosphere.

The sample was analyzed for the following potential impurities: D₂O (<0.2 mass %, as determined by the undetected NaOD·D₂O eutectic at 337 K^{2,4} in the heat capacity measurements); ¹H (4 ± 2 mol %, as determined by the H₂O ¹H NMR signal of a D₂O solution of NaOD relative to a series of standards); Na₂CO₃ (2.5 mass %, as determined by x-ray powder diffraction¹⁰).

The heat capacity of 15.768 g of finely powdered NaOD was measured from $T = 20$ to 350 K in a heat-pulse adiabatic calorimeter with a known accuracy of ± 1%.^{11,12} The

sample was sealed in an atmosphere of about 1 Torr of helium exchange gas, in the cylindrical copper calorimeter vessel, and the calorimeter was surrounded by an adiabatic shield, all contained within a vacuum chamber ($P < 10^{-6}$ Torr). The temperature (resistance of the Pt thermometer) and heat input were measured with a Hewlett-Packard 3456A digital multimeter, interfaced with a Hewlett-Packard HP87A personal computer.

III. RESULTS AND DISCUSSION

The heat capacities of NaOD as a function of temperature are given in Table I. The values are given in order of increasing temperature since no thermal history effects were

TABLE I. Experimental values of the heat capacity of NaOD.

T/K	$C_p/[J/(K \text{ mol})]$	T/K	$C_p/[J/(K \text{ mol})]$	T/K	$C_p/[J/(K \text{ mol})]$
21.56	0.919	80.00	20.18	118.25	34.91
25.13	1.040	80.27	20.27	120.26	35.69
25.36	0.965	81.86	21.37	122.39	36.44
28.76	1.416	84.67	22.54	125.13	37.34
29.70	1.538	85.08	22.54	129.35	39.01
33.59	2.224	85.22	22.37	129.97	39.42
34.65	2.497	88.49	24.09	130.79	39.70
38.30	3.503	90.22	24.40	135.12	41.38
41.78	4.727	90.25	24.81	135.89	41.87
45.27	6.060	91.31	25.34	136.36	41.71
47.86	7.147	95.16	26.74	139.33	42.98
49.46	7.777	95.22	26.27	142.12	44.68
53.75	9.705	95.41	26.29	143.36	45.15
54.71	9.990	97.97	27.72	143.39	45.26
59.25	12.13	100.43	28.55	143.42	45.22
60.08	12.36	101.87	29.27	143.77	45.17
64.57	14.23	104.65	30.39	147.31	47.88
65.23	14.53	106.98	31.02	147.34	48.20
69.75	16.35	108.64	31.72	148.48	49.97
70.29	16.57	111.43	32.69	149.02	51.27
74.89	18.27	113.59	33.41	149.63	52.19
75.29	18.42	115.48	34.13	150.75	54.15
151.84	58.33	173.06	49.30	238.41	57.63
152.42	63.53	173.25	49.16	239.06	57.79
152.70	65.43	176.72	49.79	239.26	58.04
152.98	67.78	179.32	50.08	246.55	58.67
153.24	73.05	182.44	50.52	246.70	58.61
153.88	59.00	184.08	51.03	250.48	59.20
154.97	52.93	186.66	51.18	254.36	59.52
156.10	50.37	190.31	51.76	254.78	59.66
157.24	49.16	194.04	52.20	261.75	60.22
158.40	48.24	195.03	52.58	262.08	60.20
159.54	48.16	198.21	53.05	269.84	60.91
160.71	47.99	201.46	53.26	273.06	61.24
161.75	48.38	206.03	54.06	277.63	61.63
161.85	48.28	206.19	54.10	284.43	62.17
161.95	48.24	208.91	54.37	285.43	62.55
162.44	48.93	214.16	55.30	293.30	62.88
163.02	48.21	216.39	55.44	295.84	63.00
164.16	48.76	217.02	55.15	296.32	62.97
164.78	48.37	223.92	56.29	298.51	63.84
165.68	48.33	228.09	56.61	304.73	63.70
169.40	48.66	230.30	56.97	307.27	63.89
172.03	49.10	231.48	57.05	307.93	64.87
313.12	64.59				
317.41	64.60				
326.88	65.86				
336.43	66.45				
346.09	67.09				

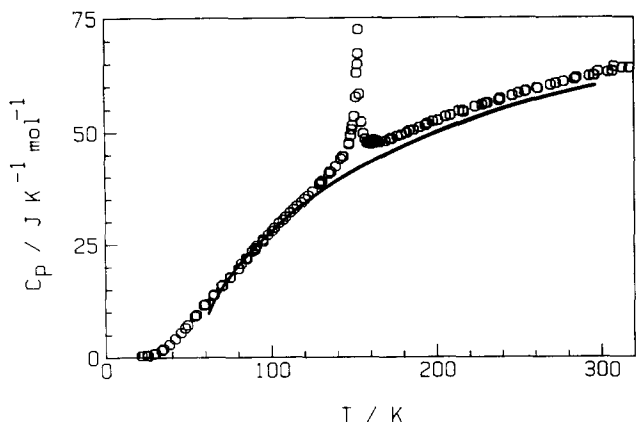


FIG. 2. The heat capacity of NaOD (O), in comparison with that of NaOH (—) (Ref. 15).

observed. In fact, the sample was thermally well-behaved, and showed relaxation times of only about 5 min after the introduction of a heat pulse, compared with about 10 min for other inorganic salts that have been examined in this same calorimeter.^{13,14}

The heat capacity of NaOD is illustrated in Fig. 2 in comparison with literature values for NaOH.¹⁵ The thermal anomaly that exists in NaOD at $T = 153.2 \pm 0.1$ K does not appear to have an analog in NaOH at atmospheric pressure in the temperature range of the NaOH measurements (60–300 K).

It is important to note that no attempt will be made here to fit the C_p data with critical exponents, as the transition is known⁸ to be first order. Although it is still relatively common to see critical exponents analysis applied to such transitions, this approach has been shown to be misleading.¹⁶

The enthalpy of the phase transition in NaOD was determined by measuring the heat required to take the sample from below the transformation to above it, and correcting for the heat that would have been required had there been no transformation. Similarly, the entropy of the transition was derived from the integration of the quotient of the excess heat capacity and the temperature, from just below the transition to just above it. The results are $\Delta H_{\text{trs}} = 131.1 \pm 0.7$ J mol⁻¹ and $\Delta S_{\text{trs}} = 0.864 \pm 0.005$ J K⁻¹ mol⁻¹.

The enthalpy result is just at the limit of the cited error from the DTA experiment on NaOD [$\Delta H_{\text{trs}}(\text{DTA}) = 200 \pm 75$ J mol⁻¹], which is not surprising considering the relatively small value of the transition enthalpy and the inherent error involved in DTA measurements.¹¹

The value of the entropy change is of considerable interest. It is close to the value of the transition entropy in squaric acid (\equiv acetylenedicarboxylic acid, HOCCCCOOH), 0.93 J K⁻¹ mol⁻¹.¹⁷ (There the low-temperature phase of the layered structure is ferroelectrically ordered in the plane and antiferroelectrically ordered from plane to plane.) In neither NaOD nor squaric acid is the transition entropy sufficient to account for independent ordering of dipole moments in the low-temperature phase, as this would amount to $R \ln 2$ ($= 5.76$ J K⁻¹ mol⁻¹) for NaOD and twice that value for squaric acid. It therefore seems more likely that the transition is related to the low-entropy transitions in antiferroelectrics such as NH₄H₂PO₄ (ADP) and NH₄H₂AsO₄

(ADA) and their deuterated analogs¹⁸; these transitions have been attributed to a tunneling of the protons (deuterons). Further evidence for this mechanism for ADP and ADA comes from the very large shift of the transition temperature on deuteration, from 148 to 238 K in ADP and 216 to 299 K in ADA. The isotope effect can most easily be understood in terms of tunneling between two minima in a double-well potential; the energy levels of the deuterated compound are lower in the wells and hence the heavier isotope effectively has a wider barrier through which to tunnel. In the case of NaOH and NaOD, the isotopic shift appears to be sufficient to move the transition temperature to below 6 K in the protonated form⁸ (if it appears at all), at ambient pressure. However, it would not be surprising to see this transformation in NaOH under applied pressure, as the substitution with a heavier isotope is often equivalent to application of pressure.¹⁹ Indeed, a high pressure phase of NaOH has been detected,²⁰ and it is possible that this phase corresponds to the low-temperature form of NaOD.

In summary, we have reported the measurement of the heat capacity of NaOD, and the thermodynamic characteristics of a small entropy (0.864 J K⁻¹ mol⁻¹) phase transformation at 153.2 K. This transition does not appear to occur in NaOH, at least not at ambient pressure and temperatures above 6 K. It is hoped that these results, and the relative simplicity of the hydroxide system, will prompt simulation experiments on alkali metal hydroxides. In turn, these calculations may shed light on the mechanism of the phase transformations in other antiferroelectric systems.

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¹H.-J. Blief and H. Dachs, *Acta Crystallogr. Sect. A* **38**, 470 (1982).

²A.-P. Rollet and R. Cohen-Adad, *Rev. Chim. Miner.* **1**, 451 (1964).

³W. R. Busing, *J. Chem. Phys.* **23**, 933 (1955).

⁴D. T. Amm, Ph.D. thesis, Department of Physics, Queen's University, Kingston, Canada (1985).

⁵D. T. Amm, T. J. Bastow, K. Jeffrey, R. D. Heyding, and S. L. Segel, *Thermochim. Acta* **95**, 447 (1985).

⁶T. J. Bastow, D. T. Amm, S. L. Segel, and R. D. Heyding, *Z. Naturforsch. Teil A* **41**, 283 (1986).

⁷S. Elschner and T. J. Bastow (to be published).

⁸T. J. Bastow, M. M. Elcombe, and C. J. Howard, *Solid State Commun.* **57**, 339 (1986).

⁹Arthur I. Vogel, *Textbook of Practical Organic Chemistry*, 4th ed. (Longman, London, 1978), p. 121.

¹⁰*Powder Diffraction File Search Manual, Hanawalt Method, Inorganic*, edited by L. G. Berry (Joint Committee on Powder Diffraction Standards, Swarthmore, PA, 1976).

- ¹¹M. A. White, *Thermochim. Acta* **74**, 55 (1984).
- ¹²M. J. M. Van Oort and M. A. White, *J. Chem. Soc. Faraday Trans. 1* **81**, 3059 (1985).
- ¹³M. A. White and K. Nightingale, *J. Phys. Chem. Solids* **46**, 321 (1985).
- ¹⁴M. A. White (unpublished results).
- ¹⁵J. C. R. Kelly and P. E. Snyder, *J. Am. Chem. Soc.* **73**, 4114 (1951).
- ¹⁶A. Hüller and W. Press, in *The Plastically Crystalline State* (Wiley, London, 1978).
- ¹⁷E. Barth, J. Helwig, H.-D. Maier, H. E. Müser, and J. Petersson, *Z. Phys. B* **34**, 393 (1979).
- ¹⁸N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Clarendon, Oxford, 1978), and references cited therein.
- ¹⁹A. Hüller, *Faraday Discuss. Chem. Soc.* **69**, 66 (1980).
- ²⁰C. W. F. T. Pistorius, *Z. Phys. Chem. (NF)* **65**, 51 (1969).