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Why is there no low-temperature phase transition in NaOH?

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Although NaOH and NaOD exhibit parallel polymorphism at high temperatures, NaOD exhibits a low-temperature phase transition to a hydrogen-bonded antiferroelectric phase and no comparable transition has been found in NaOH. Measurements of NaOH by dielectric relaxation and adiabatic calorimetry were undertaken to determine if proton disorder becomes frozen in NaOH at low temperatures. No evidence for relaxation in NaOH was found from calorimetry or dielectric measurements. A comparison of the low-temperature heat capacities of NaOH and NaOD showed that NaOH has excess heat capacity, likely due to the existence of tunneling levels, and this was satisfactorily fit to a two-level Schottky anomaly. Thus, hydrogen-atom ordering in NaOH appears to take place through a more gradual process at low temperatures, rather than a low-temperature phase transition as in NaOD. The difference in the behaviour of NaOH and NaOD likely is associated with oxygen-oxygen distances that are slightly longer in NaOH than in NaOD, owing to the different nature of higher-temperature dynamical disorder (classical double-well potential for OD⁻ and tunneling for OH⁻). © 1999 American Institute of Physics. [S0021-9606(99)51108-2]

I. INTRODUCTION

Polymorphism in NaOH and NaOD is extensive and similar above room temperature.¹ On heating, both compounds exhibit phase transitions from the room-temperature orthorhombic structure to a monoclinic structure, and then to a cubic phase before melting. High-temperature polymorphism is a feature common to all of the alkali-metal hydroxides and deuterioxides,¹⁻⁵ with the exceptions of LiOH and LiOD which have only one known phase at atmospheric pressure. In the premelting cubic phases of all the polymorphic alkali-metal hydroxides, the OH⁻ (OD⁻) ions are dynamically disordered, experiencing several different orientations.³⁻⁶ On cooling, the hydroxide ions gradually become more ordered through transitions to phases of lower symmetry. The room-temperature orthorhombic phase of NaOH (NaOD) is made up of layers of Na-O-H (Na-O-D) units that are collinear on the time scale of an x-ray diffraction experiment (see Fig. 1), but the protons have a “radius of action” of 1 Å at room temperature.⁷ Based on this structure, and the low-temperature phase transition of NaOD (*vide infra*), it is likely that the hydroxide/deuterioxide ions experience a symmetric double-well potential, with the two minima canted equally away from the *c* axis. Pressure-dependent Raman experiments indicate that hydrogen bonding is absent in both NaOH and NaOD at ambient conditions.⁸

NaOH and NaOD behave differently at low temperatures: NaOD undergoes a phase transition at $T = 153$ K to a low-temperature monoclinic phase that is not observed in NaOH down to 6 K at atmospheric pressure.⁹⁻¹² This is an example of a deuterium-induced phase transition, an extreme isotope effect whereby the deuterated form of a compound

shows at least one low-temperature phase transition that is absent in the hydrogenated form.¹³ While families of compounds are known to show this phenomenon, NaOH/NaOD appears to be an isolated case in the family of isostructural alkali-metal hydroxides/deuterioxides, and can potentially provide information concerning ordering associated with hydrogen bonding.

Based on structural and nuclear magnetic resonance (NMR) studies,^{3-5,14,15} KOH/KOD, RbOH/RbOD, and CsOH/CsOD, have their hydrogen (deuterium) atoms dynamically disordered between two orientations relative to their parent oxygen atoms (symmetric double-well potential as described above for NaOH and NaOD) in their room-temperature phases. Further configurational ordering of the hydrogen (deuterium) atoms in KOH, KOD, RbOH, RbOD, CsOH, CsOD, and NaOD takes place through a low-temperature phase transition to a more ordered phase.^{3,4,5,11} High-pressure Raman studies indicate the presence of hydrogen bonds in the low-temperature phase of NaOD.⁸ Dielectric and structural studies reveal the low-temperature ordering to be antiferroelectric in NaOD,¹¹ KOH/KOD,^{3,16} and CsOH/CsOD,^{5,17} and ferroelectric in RbOH/RbOD.⁴ Thermal analysis and single-frequency dielectric measurements reported for NaOH and NaOD clearly show a phase transition in NaOD near 153 K, and none in NaOH.¹¹ Furthermore, the heat capacity of NaOH shows no phase transitions between 13 K and room temperature.⁹

High-pressure Raman studies of NaOH and NaOD show⁸ that NaOH undergoes a phase transition to a low-temperature, high-pressure, hydrogen-bonded phase, likely analogous to the low-temperature, ambient-pressure form of NaOD. However, a reasonable explanation for the hydrogen-atom ordering problem in NaOH at atmospheric pressure—viz., why does NaOH not have a low-temperature phase transition?—has not yet been proposed.

One possibility is that NaOH could have residual en-

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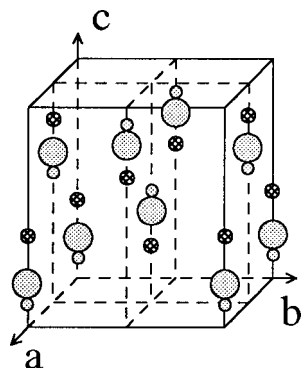


FIG. 1. The crystal structure of NaOH showing Na^+ (darker spheres) and the average positions of hydroxide ions at room temperature.

trophy, i.e., frozen-in disorder at low temperatures. This hypothesis can be tested by looking for enthalpy relaxation (in an adiabatic calorimetric experiment) and dielectric relaxation effects, as these are characteristic of frozen-in disorder.¹⁸ The present article reports detailed calorimetric and dielectric experiments on NaOH and, to a lesser extent, on NaOD, undertaken to gain some insight into the differences in the low-temperature behavior of these materials. The results led to a search for an explanation other than residual entropy for hydrogen-atom ordering in NaOH at low temperatures, as described below.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

All alkali-metal hydroxides and deuterioxides are extremely corrosive, hygroscopic, and air-sensitive, and therefore considerable care must be taken in their preparation and handling.

Powdered NaOH for calorimetric and dielectric measurements was prepared by crushing a quantity of NaOH pellets (Aldrich Chemical Co., semiconductor grade, listed as 99.99% pure) under inert atmosphere conditions. The resulting powder was dried under vacuum at 170 °C for two days. A quantitative analysis for water and carbonate impurities in the sample was performed using a Perkin–Elmer Pyris-1 differential scanning calorimeter, by determining the enthalpies of the corresponding $\text{NaOH}\cdot\text{H}_2\text{O}$ and Na_2CO_3 eutectics. This analysis yielded water and sodium carbonate impurities of 0.7% and 0.8% by mass, respectively, for the calorimetric sample, and 1.2 mass% H_2O and 0.5 mass% Na_2CO_3 for the dielectric sample.

The NaOD sample was prepared by dehydration of a 40 mass% solution of NaOD in D_2O (Aldrich, listed as 99.9 at. % D) in a zirconium crucible under vacuum at 220 °C for several days. The resulting white granular chunks were crushed to a fine powder under inert atmosphere conditions. The sample was again analyzed for water and carbonate impurities using DSC with results of 1.6 mass% water and 0.81 mass% carbonate. The extent of deuteration of the sample was determined using ^1H NMR, by preparing a series of standards of known proton concentration and obtaining a calibration curve of ^1H NMR peak area versus moles of protons. Using the peak area from a ^1H NMR measurement of

the NaOD sample in conjunction with the calibration curve, the isotopic purity of the NaOD sample was found to be 94 ± 6 mol %.

Loadings of the NaOH sample into the calorimeter cell and of the NaOH and NaOD samples into the dielectric measurement cell were performed in a glove box under dry nitrogen.

A 4.1710 g sample of powder NaOH was loaded into a small-sample adiabatic calorimeter, the details of which have been reported previously.¹⁹ Briefly, the apparatus consisted of a sample cell (~ 5 mL) with a centrally located thermometer well containing a platinum resistance thermometer. The cell was surrounded by heater wire and suspended inside an adiabatic shield in a cryostat. The shield, combined with a high vacuum inside the cryostat, maintained the adiabatic conditions. All electrical measurements were made with a HP 3456A digital voltmeter which was interfaced to a computer. Thus, data acquisition and analysis were fully automated.

Pressed powder samples of NaOH and NaOD for the dielectric measurements were obtained by loading a quantity of powder into a cylindrical die and piston setup (under dry nitrogen atmosphere) and applying pressure using an Arbor press to obtain pellets. NaOH and NaOD pressed powders were loaded, in turn, into a dielectric cell, where the sample was sandwiched between two plates of a parallel-plate capacitor. The use of a third ring electrode allowed for the measurement of the dielectric constant of the sample without knowing the sample thickness. The dielectric sample cell was surrounded by heater wire and the temperature was measured with a platinum resistance thermometer attached to the outside of the cell. The cell was suspended in a cryostat in which a high vacuum was maintained. Measurements could be taken over the temperature range from 12 to 360 K, and frequency range 65 Hz to 1 MHz. The capacitance and loss tangent were measured with a HP 4284A precision LCR meter, and the resistance of the platinum resistance thermometer was measured with a HP 34401A multimeter. Automation of the apparatus was achieved by interfacing all of the electronic measuring equipment to a computer. Further details of the dielectric apparatus are reported elsewhere.^{20,21}

III. RESULTS AND DISCUSSION

A. Adiabatic calorimetric measurements of NaOH

The heat capacity of NaOH was determined by adiabatic calorimetry over the temperature range from 35 to 290 K. The present results averaged with the smoothed results of Murch and Giauque⁹ gave uncertainties of less than 1.2% above 100 K, increasing to about 2% at 50 K, confirming that NaOH has no phase transition between 35 K and room temperature.

Although Murch and Giauque⁹ did not mention unusual thermal relaxation effects, and indeed the relationship between relaxation effects and frozen-in disorder was not known until some years after their work was published, we thought it worthwhile to look closely for such effects. After a heat pulse was applied to the sample, the temperature was monitored as a function of time for up to 24 h. However, no

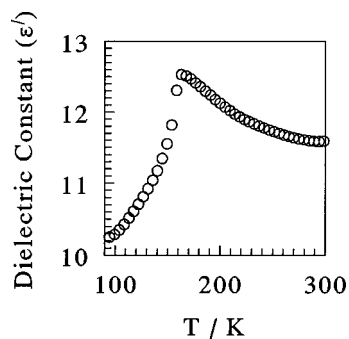


FIG. 2. Low-temperature λ -shaped anomaly in the dielectric constant curve measured for NaOD at a frequency of 10 kHz.

anomalous temperature drifts that would be indicative of enthalpy relaxation in the sample were observed.

B. Dielectric measurements of NaOD

Dielectric measurements of NaOD were performed over the temperature range from 85 to 340 K using twelve measurement frequencies from 80 Hz to 800 kHz. The measured powder dielectric data were converted to data representative of the bulk using Böttcher's formula.^{22–24} Besides the observation of interfacial polarization at high temperatures and low frequencies, the most prominent feature in the dielectric constant data obtained for NaOD was a λ -shaped peak as shown in Fig. 2. (The total uncertainty is within ± 0.30 for all of the dielectric constant values shown.) This anomaly was observed at the same temperature for all frequencies measured, and it is characteristic of a phase transition to a low-temperature antiferroelectric phase at a transition temperature of 160 ± 2 K (temperature at which the maximum dielectric constant occurs). This compares favorably with the transition temperature obtained from adiabatic calorimetry ($T = 153$ K).¹² A similar dielectric anomaly has been reported previously for NaOD.¹¹

The dielectric constant values above a ferroelectric or antiferroelectric phase transition are typically found to obey a Curie–Weiss Law, i.e.,

$$\epsilon' = \epsilon_{\infty} + \frac{C}{T - T_0}, \quad (1)$$

where ϵ_{∞} , C , and T_0 are constants.²⁵ Fitting of the dielectric constant data for NaOD to Eq. (1) at temperatures above the maximum in the λ -shaped anomaly (up to $T = 280$ K) resulted in values of 10.75 ± 0.05 , 176 ± 15 , and 71 ± 6 K for ϵ_{∞} , C , and T_0 , respectively. The value of C found for NaOD is about an order of magnitude smaller than for the $M_3(H,D)(XO_4)_2$ family which also exhibits low-temperature antiferroelectric behavior.^{26–28}

C. Dielectric measurements of NaOH

Several dielectric runs were done for four pressed powder samples of NaOH, most of which covered the temperature range between 80 and 350 K involving measuring frequencies from 80 Hz to 800 kHz. One run was done at lower temperatures, 12 to 90 K.

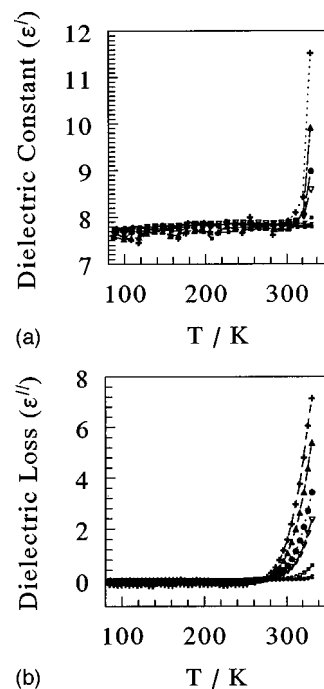


FIG. 3. (a) Dielectric constant and (b) dielectric loss curves measured for NaOH as a function of temperature for several frequencies. The lines are merely for guiding the eye. +, 100 Hz; ▲, 200 Hz; ●, 500 Hz; ▽, 1 kHz; □, 10 kHz; ▼, 100 kHz; ◆, 250 kHz.

Examples of the dielectric constant and dielectric loss results obtained for NaOH are shown as a function of temperature for several frequencies in Fig. 3. (Each data point shown was plotted after conversion of the measured powder data to bulk values using Böttcher's formula.) For all measured temperatures above 80 K, the dielectric constants were within $\pm 8.5\%$ for a measuring frequency of 100 Hz, $\pm 4.2\%$ at 1 kHz, $\pm 2.9\%$ at 10 kHz, $\pm 1.7\%$ at 100 kHz, and $\pm 0.7\%$ at 800 kHz. Between 15 and 100 K, the dielectric constant was independent of frequency and decreased gradually by about 3% with decreasing temperature.²⁰

High dielectric constant and loss values were observed at high temperatures (above 300 K) and low frequencies (below 10 kHz), indicative of increasing conductivity and interfacial polarization.^{29–31} At lower temperatures, where interfacial polarization does not significantly affect the results, the dielectric constant of NaOH is fairly constant at all temperatures, a result that is consistent with a previously reported dielectric study of NaOH.¹¹ The dielectric constant curves shown in Fig. 3 give no gross evidence for anomalous behavior as seen in NaOD (Fig. 2).

However, a closer look (see Fig. 4) reveals a subtle anomaly in the dielectric constant of NaOH. An anomaly is evident in the curve as a broad peak from ~ 90 to 230 K with a maximum in the dielectric constant near $T = 170$ K for a frequency of 100 kHz, and at slightly higher temperatures for lower frequencies. The rising portion of the curve on the low-temperature end looks similar to what would be expected for dielectric behavior due to relaxation of a polarization process, but this cannot be the origin since the rising portions of the curves for different frequencies were essen-

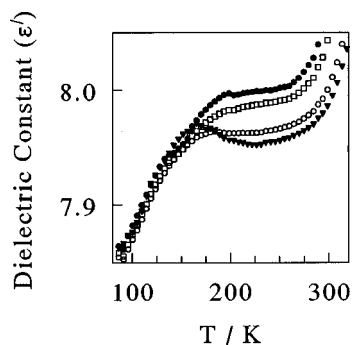


FIG. 4. Dielectric constant measured for NaOH as a function of temperature for various frequencies: ●, 5 kHz; □, 10 kHz; ○, 50 kHz; ▼, 100 kHz. The random uncertainty is within ± 0.02 for each data point.

tially coincident (see Fig. 4), and no appreciable dielectric losses were observed in this temperature region.

While the peak observed in each dielectric curve for NaOH in Fig. 4 is too broad to be due to the occurrence of a phase transition, there is a striking similarity between this anomaly and an anomalous peak, centred at $T = 248$ K, reported in the ambient-pressure dielectric constant curve for the compound $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.³² This was found to be a prelude to a phase transition to a ferroelectric phase that occurred under an applied pressure of ~ 5 kbar.^{33,34} [Interestingly, the deuterated form of this salt, $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$, exhibits a deuterium-induced ferroelectric phase transition at ambient pressure.³⁵ A similar broad peak in the dielectric constant also has been reported for NaK- and NaNH_4 -tartrate mixed crystals containing between 2.5% and 18% NaNH_4 tartrate, which gave rise to a phase transition upon increasing or decreasing the content of NaNH_4 tartrate.³⁶ Thus, it seems that the broad peak observed in the dielectric measurements of NaOH is most probably a prelude to the high-pressure phase transition (analogous to the low-temperature phase transition observed for NaOD at atmospheric pressure) which has been observed in Raman studies of NaOH.⁸

D. Deuteration is equivalent to pressure for NaOH

So-called “geometric effects” can be observed when hydrogen atoms are replaced with deuterium. These effects were first extensively investigated by Ubbelohde and co-workers,^{37–39} and later by others.^{40–42} It has been found that for most short hydrogen bonds (oxygen-oxygen distance in the range of 2.45–2.65 Å), an expansion of the hydrogen bond by as much as 0.03 Å occurs upon deuteration.⁴² Ichikawa and co-workers reintroduced this phenomenon, dubbed the “geometric isotope effect,” as a possible explanation for the large deuterium-induced effects observed for the phase transition temperatures of many hydrogen-bonded solids.^{43–45} Many explanations of the geometric effects associated with deuterium substitution have been offered, most of which involve the quantum-mechanical and vibrational differences of compounds containing hydrogen compared to the more massive deuterium isotope.^{46–50}

The hydrogen-bond distances (oxygen-to-oxygen) in all of the low-temperature phases of the alkali-metal hydroxides and deuterioxides are very long (> 3.2 Å).^{1,3–5,7} From crystal-

lographic measurements of NaOH and NaOD, it has been reported that the interlayer distance in NaOD is smaller than that in NaOH by 0.3% to 0.6%, with the difference increasing with decreasing temperature.¹ For all the alkali-metal hydroxides and deuterioxides, the unit-cell volumes of the deuterated forms, as calculated from reported crystallographic data, are consistently smaller than the volumes of the corresponding hydrogenated forms.^{1,3–5,7,11,16,17,51} While it is known that there can be problems in assessing changes in hydrogen-bond distances from changes in unit cell volumes on deuteration,⁵² it appears that, in this system, deuteration results in shorter oxygen-to-oxygen distances and potential for stronger hydrogen bonds in the low-temperature phases of the deuterated compounds. This is supported by vibrational spectroscopy studies of KOH/KOD, RbOH/RbOD, and CsOH/CsOD,^{53–55} and it implies a geometric effect which, at least on the surface, is opposite to that described by Ubbelohde and by Ichikawa for shorter hydrogen bonds.

It seems likely that the interlayer distance in NaOH (oxygen-oxygen distance between the layers is 3.488 Å at room temperature)⁷ is very close to the upper limit at which a hydrogen-bonded interaction can occur. This could be due to another interaction (*vide infra*) in NaOH that could be more favorable than hydrogen bonding, leading to a longer unit cell parameter along the c axis in NaOH than in NaOD. The shorter interlayer distance in NaOD gives it a distinct advantage towards the possibility of forming a low-temperature hydrogen-bonded phase. Contraction of the interlayer distance in NaOH could be achieved by the application of pressure, and this indeed causes a phase transition analogous to that seen in NaOD at ambient pressure.⁸ Thus, the equivalence of deuteration and pressure observed for NaOH can be accounted for by the contraction of the potential hydrogen-bond distance which occurs with either pressure or deuteration. A similar equivalence between deuteration and application of pressure has been observed for several systems, including $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2/(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$,^{56,57} $\text{NH}_4\text{Cl}/\text{ND}_4\text{Cl}$,^{58,59} $\text{NH}_4\text{Br}/\text{ND}_4\text{Br}$,^{58–60} and CH_4/CD_4 .^{61,62}

E. Low-temperature hydrogen ordering in NaOH

While ordering of the deuterium atoms in NaOD occurs by way of a low-temperature phase transition to a hydrogen-bonded antiferroelectric phase, no such phase transition occurs to order the hydrogen atoms in NaOH at ambient pressure.¹¹ Residual entropy might reasonably be expected for NaOH, but our adiabatic calorimetry and dielectric measurements of NaOH showed no evidence for enthalpy or dielectric relaxation, ruling out the possibility of frozen-in disorder. Ordering in NaOH must take place before absolute zero is reached, but apparently by some mechanism other than a conventional phase transition.

An important clue as to the nature of the entropy-removal mechanism in NaOH is revealed by a comparison of the low-temperature heat capacities of NaOH and NaOD (Fig. 5).^{9,12} It is clearly evident from the figure that at low temperatures the heat capacity of NaOH is significantly greater than that for NaOD. This is the opposite of what would be expected from purely vibrational considerations:

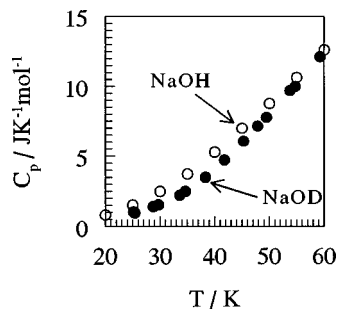


FIG. 5. Low-temperature heat capacities for NaOH and NaOD. \circ NaOH data from Ref. 9, \bullet NaOD data from Ref. 12.

the lower vibrational frequencies associated with some modes in the more massive deuterated compound would give rise to a greater density of vibrational energy levels and, therefore, the deuterated form would normally be expected to have a higher heat capacity. This is the case for NaOH and NaOD at high temperatures,^{9,12} but not at low temperatures, which means that NaOH must have exclusive access to extra low-lying energy levels which cannot be accessed by NaOD. Additional energy levels associated with the greater ability of the lighter hydrogen atoms to undergo quantum-mechanical tunneling are a likely explanation for the additional heat capacity in NaOH, and we now analyze this quantitatively.

The experimentally determined heat capacity is that at constant pressure, C_p , and, for a solid such as NaOH, it should be comprised of several contributions, viz.

$$C_p = (C_p - C_v) + C_v(\text{acoustic}) + C_v(\text{vib}) + \Delta C, \quad (2)$$

where $(C_p - C_v)$ represents the difference between heat capacity at constant pressure and at constant volume, $C_v(\text{acoustic})$ represents the contribution of the acoustic modes to the heat capacity, $C_v(\text{vib})$ represents the contribution of the internal vibrational modes to the heat capacity, and ΔC represents any additional (e.g., anomalous) contributions to the heat capacity. If there were sufficient information, ΔC for NaOH could be calculated directly from Eq. (2). However, the compressibility for NaOH has not been reported [it would be required for the calculation of $(C_p - C_v)$], nor has the Debye temperature [required to calculate $C_v(\text{acoustic})$]. Even more troublesome is uncertainty in the frequencies of the internal vibrations in NaOH;^{8,63,64} for example, $C_v(\text{vib})$ for NaOH from the assignment of Kanaseka *et al.*,⁶³ which does not include $C_v(\text{acoustic})$, exceeds the experimental heat capacity for $T < 45$ K. The most problematic are the lowest frequency modes (below 120 cm^{-1}), which differ by more than 20 cm^{-1} in different investigations.^{8,63}

Nevertheless, the combined heat capacity data for NaOH and NaOD can be used to determine $\Delta C(\text{NaOH})$, as follows. The terms in Eq. (2) representing $(C_p - C_v)$ and $C_v(\text{acoustic})$ should be very similar for NaOH and NaOD.⁶⁵ Furthermore, the contributions to $C_v(\text{vib})$ for the higher-frequency modes appear to be known with good certainty for both NaOH^{8,63} and NaOD⁸ (where, in the latter, splitting of vibrational modes in the low-temperature phase has been

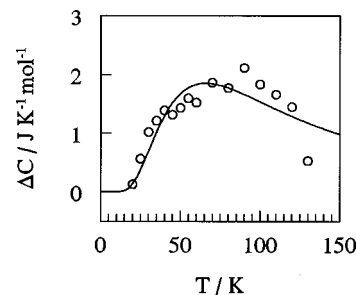


FIG. 6. The excess heat capacity of NaOH at low temperatures (\circ) derived from Eq. (3) as described in the text, along with the fit to the Schottky anomaly, Eq. (4), with $\Delta E/R = 145 \pm 8 \text{ K}$ and $\omega = 0.46 \pm 0.03$.

taken into consideration). Let $C_v^*(\text{vib})$ represent the contribution of all the internal vibrations except for the three lowest frequencies; since the latter represent two Na–O–Na stretches and an NaOX translation, all of which should occur at the same frequency for NaOH and NaOD,⁶³ we can write:

$$\Delta C(\text{NaOH}) = C_p(\text{NaOH}) - C_v^*(\text{vib}, \text{NaOH}) - [C_p(\text{NaOD}) - C_v^*(\text{vib}, \text{NaOD})]. \quad (3)$$

The resulting anomalous heat capacity for NaOH is shown in Fig. 6.

Assuming that the source of the excess heat capacity in NaOH is the thermal population of split tunneling levels, ΔC for NaOH should correspond to a Schottky heat capacity anomaly, which for two energy levels is given by

$$C_v = \frac{R\omega[\Delta E/(RT)]^2 e^{\Delta E/RT}}{(e^{\Delta E/RT} + \omega)^2}, \quad (4)$$

where ΔE is the energy difference between the two levels and ω is their degeneracy ratio (excited state/ground state). A least-squares fit of ΔC to Eq. (4) using $\omega = 1$ and ΔE as the only fitting parameter was unsuccessful. Allowing both ω and ΔE to vary gave a satisfactory fit with optimized parameters $\Delta E/R = 145 \pm 8 \text{ K}$ and $\omega = 0.46 \pm 0.03$. The fitted curve is shown with ΔC in Fig. 6. This fit provides a good representation of the excess heat capacity data over the whole temperature range, and the tunnel splitting is comparable to that for protons in other hydrogen-bonded solids, viz. 52 K in $\text{K}_3\text{H}(\text{SeO}_4)_2$,⁶⁶ 92 K in 5-bromo-9-hydroxyphenalene,⁶⁷ 100 K in $\text{Rb}_3\text{H}(\text{SeO}_4)_2$,⁶⁸ 167 K in $\text{K}_3\text{H}(\text{SO}_4)_2$,⁶⁸ 173 K in $\text{Cs}_3\text{H}(\text{SeO}_4)_2$,⁶⁹ and 194 K in hydrazinium hydrogen oxalate.⁷⁰ Furthermore, tunneling of OH^- ions in doped NaCl has been observed directly by infrared spectroscopy.⁷¹

The entropy change of the deuterium-induced phase transition in NaOD at $T = 153 \text{ K}$ is $0.864 \pm 0.005 \text{ J K}^{-1} \text{ mol}^{-1}$,¹² which is similar to the entropy change associated with the anomalous heat capacity shown in Fig. 6 ($\Delta S \approx 2 \text{ J K}^{-1} \text{ mol}^{-1}$). Therefore, it seems likely that ordering of the deuterium atoms in NaOD occurs by way of a phase transition, while NaOH removes a similar amount of entropy associated with its hydrogen atoms through a more gradual process at low temperatures involving the thermal depopulation of tunneling levels. Besides providing a mechanism for entropy removal in NaOH, hydrogen-atom tunneling also would tend to suppress a low-temperature

phase transition in NaOH through quantum-mechanical delocalization that reduces the effective dipole-dipole ordering interaction between neighboring hydroxide ions. It is likely that the intermolecular interaction in NaOH is insufficient to cause ordering (likely because of the rather long oxygen-oxygen distance), as has been concluded recently for 5-bromo-9-hydroxyphenalenone.⁶⁷

It is interesting to compare the low-temperature behavior of NaOH/NaOD with KOH/KOD. Both KOH and KOD undergo low-temperature phase transitions to a hydrogen-bonded antiferroelectric phase.¹⁶ The transition entropies are nearly identical for both compounds, i.e., $1.0 \text{ J K}^{-1} \text{ mol}^{-1}$.⁷² Thus, it would be expected that excess heat capacity should not exist for KOH at low temperatures. Indeed, the low-temperature heat capacities of KOH and KOD show normal isotopic behavior, with the heat capacity of KOH slightly less than that of KOD.⁷²

The existence of excess heat capacity at low temperatures seems to be a common feature of all substances exhibiting deuterium-induced phase transitions.⁷³ This has been shown for $\text{Rb}_3(\text{H,D})(\text{SO}_4)_2$,⁷⁴ $\text{Rb}_3(\text{H,D})(\text{SeO}_4)_2$,⁷⁵ $[\text{N}(\text{H,D})_4]_2\text{TeCl}_6$,^{76,77} $[\text{N}(\text{H,D})_4]_2\text{PbCl}_6$,^{78,79} and the organic compound 5-bromo-9-hydroxyphenalenone.⁶⁷ A comparison of the published heat capacity data of the hydrogenated and deuterated forms of $[\text{N}(\text{H,D})_4]_2\text{PtCl}_6$ ^{80,81} and $[\text{N}(\text{H,D})_4]_2\text{PdCl}_6$ ^{82,83} also shows excess heat capacity for the hydrogenated form at low temperatures, thus providing a mechanism for entropy removal in lieu of a phase transition. None of these compounds would be expected to possess residual entropy. Although both $(\text{NH}_4)_2\text{SeCl}_6$ and $(\text{ND}_4)_2\text{SeCl}_6$ show low-temperature phase transitions, the transition entropy change for the deuterated compound is ~ 8 times as much as for the hydrogenous compound.⁸⁴ Again, excess heat capacity is observed for the hydrogenous compound at low temperatures which would provide a mechanism for entropy removal.

IV. CONCLUDING REMARKS

The different low-temperature behaviors of NaOH and NaOD can be related to two phenomena. First, geometric changes occur in the alkali-metal hydroxides with deuterium substitution such that the potential hydrogen-bond distance (oxygen-to-oxygen) becomes shorter in the deuterated form. This is likely related to the effects that stabilize the low-temperature form of NaO(H,D): on account of tunneling interactions, the OH^- ion has a greater probability of lying along the c axis than does OD^- which is more classically disordered in a double-well potential, leading to a longer oxygen-oxygen distance in NaOH. The oxygen-oxygen distances in all of the alkali-metal hydroxides and deuterides are very long ($>3.2 \text{ \AA}$), and for NaOH, the potential hydrogen-bond length seems to be located just outside the limit where a hydrogen-bonded interaction can occur. The relevant geometric parameters shrink with deuterium substitution or pressure, allowing phase transitions to a low-temperature hydrogen-bonded phase in NaOD, and a high-pressure hydrogen-bonded phase in NaOH. In this way, deuteration is equivalent to pressure for NaOH.

Second, contrary to normal expectations for the effect of isotopic substitution on heat capacity, at low temperatures the heat capacity of NaOH is greater than that of NaOD. Analysis of the difference in heat capacity is consistent with exclusive access to quantum-mechanical tunneling levels in NaOH that are not present in NaOD. The greater ability of the lighter hydrogen atom to tunnel would tend to prevent a phase transition in NaOH by quantum-mechanical delocalization of the dipolar interaction. Tunneling also provides a mechanism for entropy removal in NaOH so that it has no residual entropy, consistent with the present calorimetric and dielectric relaxation results.

NaOH is a rather simple material, and it should be amenable to molecular dynamics investigations in order to further delineate proton ordering. Additional experimental investigations of NaOH could usefully include a search for tunneling states.

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