Thermochimica Acta, 95 (1985) 447–451
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

A LOW TEMPERATURE PHASE TRANSITION IN NaOD NEAR 150 K

D.T. Amm[1], T.J. Bastow[2], K. Jeffrey[3], R.D. Heyding[4], and S.L. Segel[5]
[1]Northern Telecom, P.O. Box 3511, Station C, Ottawa, K1Y 4H7
[2]CSIRO Div. of Chem. Physics, Clayton 3168, Australia
[3]Physics Dept., University of Guelph, Guelph, Ontario, Canada
[4]Chem. Dept., Queen's University, Kingston, Ontario, Canada, K7L 3N6
[5]Physics Dept., Queen's University, Kingston, Ontario, Canada, K7L 3N6

ABSTRACT

A phase transition in NaOD has been observed calorimetrically near 150 K. The estimated enthalpy of the transition is 200(75) Joules/mole. This phase transition has no corresponding analog in the protonated material, NaOH, down to 10 K. Other physical techniques also reveal the phase transition but give slightly varying values for the transition temperature. These techniques include ^{23}Na nuclear quadrupole resonance, ^{23}Na nuclear magnetic resonance and ^{2}D magnetic resonance. The resonance experiments indicate that the phase transition is a continuous one and that in the lower temperature phase there is one sodium and deuterium crystallographic site per cell. X-ray powder diffraction of the low temperature phase indicates that it is probably monoclinic with $a_m = 3.388(1)$A, $b_m = 11.34(1)$A, $c_m = 3.418(1)$A, $\beta = 90.52^o$ and $V = 131.4$Å^3. The volume of the unit cell is greater at the lower temperature than at the higher temperature. The ^{23}Na pure quadrupole resonance frequency at 77 K is 1.784(2) MHz with an asymmetry parameter of 0.82(5).

Although Busing[1] suggested in 1955 that a phase transition might exist at very low temperatures in NaOD, it was not until recently that we executed the first known calorimetric study of this material. Fig. 1 shows a thermogram taken using a DuPont 990 DTA operating in DSC mode. The enthalpy of the new low temperature transition near 150 K was determined to be 200 (75) J/mole by comparing it with an equally "smooth" transition[2] in CrN at 286 K.

0040-6031/85/$03.30

The phase transition was initially discovered using magnetic resonance techniques[3]. In Fig. 2 A we show the ^{23}Na pure quadrupole resonance frequency (NQR) as a function of temperature and it was our interpretation that the first minimum at 160 K marked the temperature of the phase transition. In Fig. 2 B is plotted the NQR line width vs temperature where the peak in the line width occurs also at 160 K. The resonance intensity is reasonably constant through the phase transition and we conclude that there remains in the low temperature phase a single crystallographic sodium site per cell as is the case for the higher temperature phase. The room temperature phase has been well studied crystallographically[4,5,6,7] and is known to be orthorhombic (pseudotetragonal) with $a = c \neq b$.

Earlier room temperature, and higher, nuclear magnetic resonance studies (NMR) have shown that the pseudo tetragonal structure gives rise to an electric field gradient (EFG) which has axial symmetry (i.e., the asymmetry parameter, η, is zero). In Fig. 3 A we show the broad line ^{23}Na NMR at 23.6 MHz, recorded at 156 K using a *nonadiabatic superfast passage* technique. The absence of shoulders on the peaks in the powder pattern imply that η is less than 0.05. This is the lowest temperature at which this pattern persists. Below this temperature, there is a range of approximately 20 K during which no particularly sharp features occur. The pattern then evolves into one similar to that shown in Fig. 3 B, at 77 K, where the "shoulder features" are well defined and from which we conclude that the asymmetry parameter is 0.82 (5). A value for the pure NQR frequency from the NMR experiment is within experimental error of that shown in Fig. 2 A. Hence, we can conclude that the new low temperature phase possesses "less symmetry" than the higher temperature phase.

Deuteron NMR experiments have also been performed. They show that the low temperature phase is well established at 146 K and the higher temperature phase at 152 K. The changes in the resonance line shape are difficult to quantify, but the value of the deuteron quadrupole coupling is reasonably constant through the phase transition with a value of 270 (20) kHz and a small, but not measurable, value of asymmetry parameter.

X-ray powder diffraction patterns were obtained (at 294 K) using a CSS/STOE diffractometer (which yielded orthorhombic pseudo-tetragonal Cmcm unit cell parameters in excellent agreement with the literature) and below room temperature (RT) (to 123 K) in a Guinier-Lenne camera using silicon as an internal standard. The differences in the room temperature and low temperature patterns are subtle. At 125 K, the (060) reflections of the RT modifications are intact, suggesting that the layer structure persists and

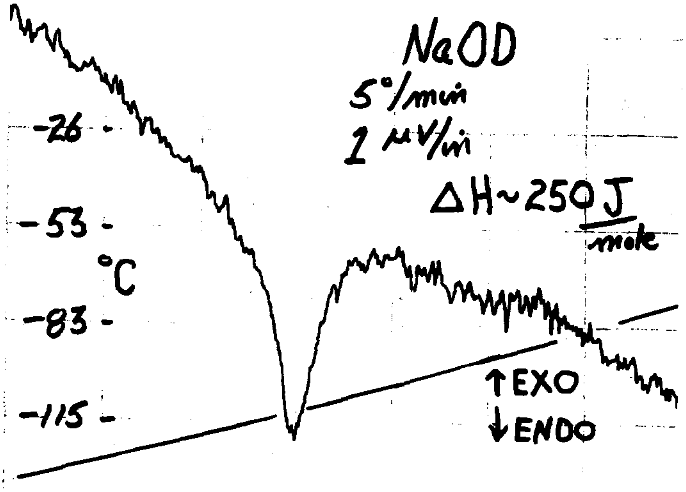

Fig 1 DuPont 990 DSC thermogram of NaOD near 150 K. Increasing temperature.

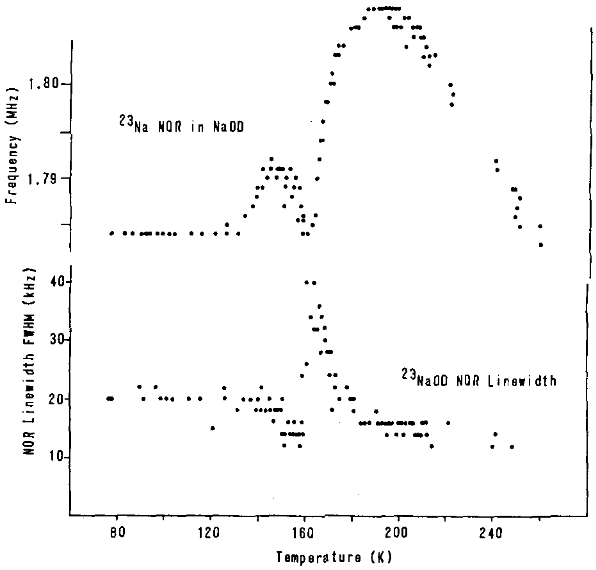

Fig. 2A(upper) ^{23}NaOD pure quadrupole resonance frequency vs temp.
Fig. 2B(lower) ^{23}NaOD NQR line width vs temp.

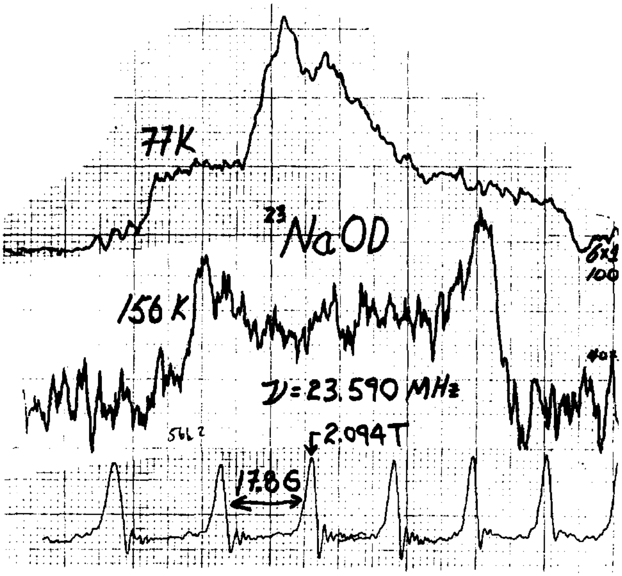

Fig.3A(lower) ^{23}NaOD NMR at 2 Tesla at 23.6 MHz at 156 K.
Fig.3B(upper) as above but at 77 K.

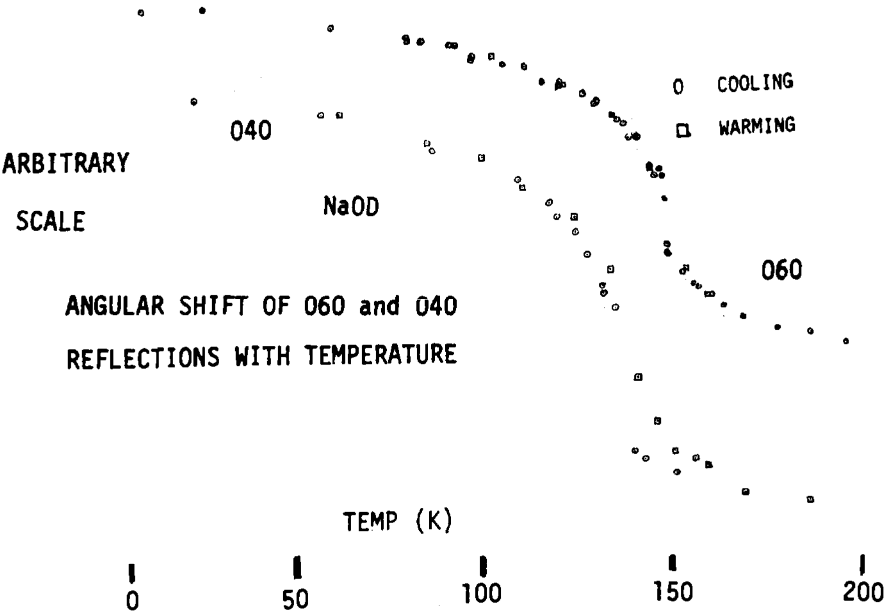

Fig. 4 Angular shift of the (060) and(040) reflections of NaOD vs temp.

that distortion occurs in the layers. The structure has been tentatively assigned monoclinic symmetry. The low temperature monoclinic (RT orthorhombic) dimensions are a = 3.388 (1) (3.4023)Å, b = 11.34 (1) (11.319)Å, c = 3.418 (1) (3.4023)Å, $\beta = 90.52^\circ$. If this cell is correct the molar volume of the low temperature modification is greater than that of the RT modification. These conjectures are based on 11 diffractions lines out of a predicted 50.

CSIRO x-ray diffraction experiments yielded better signal to noise ratios and more lines and, with an Oxford Instruments gas flow system, better temperature variation and resolution, but no satisfactory structure determination could be made. In Fig. 4 we show the variation of the (060) and (040) two theta reflections as a function of temperature.

Earlier phase diagram studies of NaOH by Pistorius[9] indicate that a high pressure modification exists at room temperature. The structure of this modification is unknown at present. It is well known that deuteration[10] mimics an increase in pressure and there is the likelihood that the ambient pressure, low temperature phase of NaOD is identical to that of high pressure, ambient temperature phase of NaOH.

ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Commonwealth Scientific and Industrial Research Organization.

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