Low Temperature Phase of NaOD *

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The existence of a new phase of NaOD below 160 K is reported. NQR, NMR and DTA spectra are given and preliminary X-ray powder diffraction measurements are discussed.

Introduction

The three crystallographically determined phases of NaOH are known to be duplicated in the deuterated analog compound NaOD [1]. At room temperature both compounds are orthorhombic (Bmmb, $Z = 4$). A transition to a monoclinic phase ($P2_1/m$, $Z = 2$) takes place at 514 K for NaOH (500 K for NaOD) then to a cubic plastic phase (Fm3m, $Z = 4$) at 566 K (561 K for NaOD) and finally melting at 592 K (593 for NaOD).

A number of investigations of NaOH by ^{23}Na nuclear resonance have been reported [2–5] which agree on the value of the nuclear quadrupole coupling constant but which offer two alternatives for the value of the asymmetry parameter. [2] and [3] using an NMR NQR double resonance technique report $\eta = 0.4$ while [4] and [5] using high field NMR and direct NQR, respectively, report $\eta = 0$. More recently a detailed high temperature investigation has been made of the orthorhombic to monoclinic transition [6].

As part of a parallel study to those above we have prepared the deuteroxide NaOD and examined inter alia the ^{23}Na coupling constant by continuous wave NQR. At room temperature the ^{23}Na NQR frequency is shifted down by about 1% relative to NaOH. At 77 K the magnitude of this shift had increased dramatically (in the same direction) to 7% and obviously warranted a more detailed study. The pertinent results of this investigation showing the unusual temperature dependence of ν_Q between 120 K and 200 K are given in Fig. 1, and the corresponding resonance linewidths are given in Figure 2. A portion of this sample was investigated over the

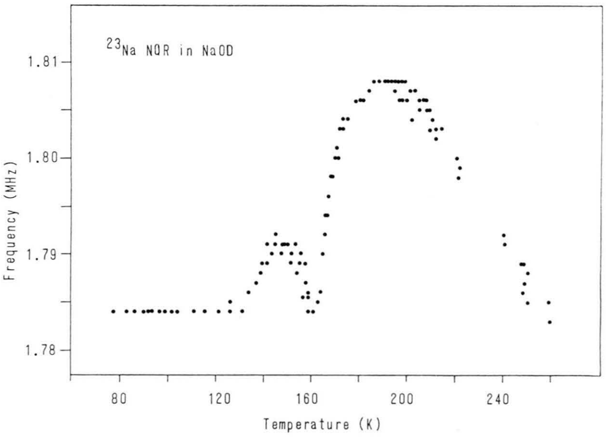

Fig. 1. Dependence of the ^{23}Na NQR frequency ν_Q on temperature in the region near the phase transition.

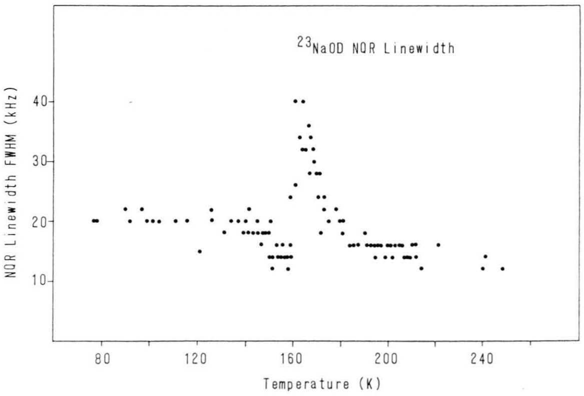

Fig. 2. Linewidth of the ^{23}Na NQR over the temperature region displayed in Fig. 1.

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same temperature range by differential thermal analysis; the results are exhibited in Figure 3. The asymmetry parameter η was determined at a number of temperatures from 77 K to 177 K from the high field quadrupole perturbed ^{23}Na NMR spectrum; the spectra at 177 K and 77 K with the deduced values of η are displayed in Figure 4.

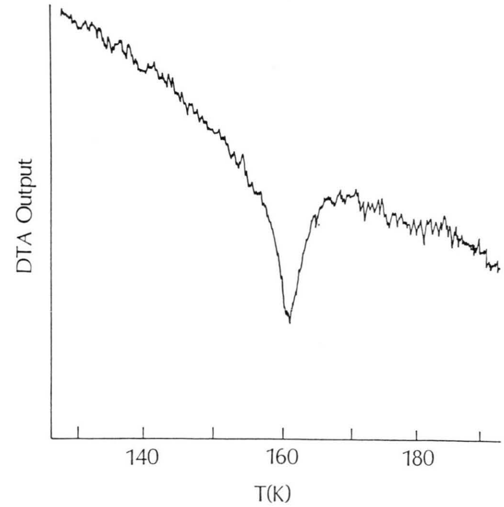

Fig. 3. Differential thermal analysis of NaOD in the temperature region near the phase transition.

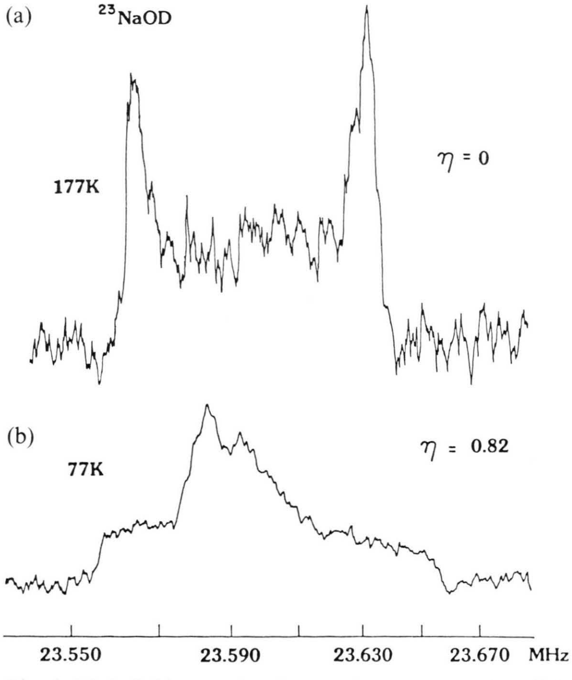

Fig. 4. High field second order quadrupole perturbed ^{23}Na NMR spectra for NaOD at (a) 177 K and (b) 77 K.

Experimental

The continuous wave NQR spectrometer used here was based on a design given by Robinson [7]. Differential thermal analyses were made on a Dupont 990 DTA used in the scanning calorimetry mode. NaOD was prepared by evaporating concentrated NaOD solution (Fisher Scientific) in a silver boat under dry nitrogen. High temperature DTA of the dry material was recorded in order to ensure that the material was low in water and carbonate content. The NMR spectrometer operating in the superfast passage mode has been described previously [4].

Discussion

The behaviour of $\nu_Q(T)$ in the temperature range shown in Fig. 1 indicates that at least one phase transition has taken place although the precise location is not obvious. The resonance linewidths, however, become very broad in a narrow region centred at 160 K which corresponds to the position at which ν_Q dips sharply and which suggests that this temperature is the transition point. The DTA measurements confirm this assignment showing a peak at 157 K and yield an enthalpy for the transition of (200 ± 75) J/mol. A similar study of NaOH showed no such transition above 110 K.

Analysis of the ^{23}Na NMR powder line shape for the $(1/2 \rightleftharpoons 1/2)$ transition at 177 K, where the orthorhombic phase obtains, indicates a value for the asymmetry parameter of $\eta = 0$ (Figure 4a). This is consistent with a similar near zero value of η found for ^{23}NaOH at various temperatures between 77 K and 388 K [4, 5]. As noted previously [4], because of the orthorhombic symmetry the value of η at the ^{23}Na site must be non zero, but its value appears to be principally determined by nearest neighbour contributions which have four fold rotational symmetry about the *c*-axis. At 77 K, well below the transition temperature, the NMR lineshape changes dramatically (Fig. 4b) and analysis yields a value of $\eta = 0.82$, indicating a substantial orientational change in the structure.

A high pressure study of NaOH by means of DTA and volume displacement at temperatures greater than 300 K has been reported by Pistorius [8]. He detected the existence of a new phase of unknown structure (NaOH IV) which was stable at room temperature for pressures above 8 kbar. If the boundary between this phase and the orthorhombic phase intersected the temperature axis below 77 K, a transition to NaOH IV could then occur at atmospheric pressure at sufficiently low temperature. For NaOD the unit cell volume is changing with temperature more rapidly than in NaOH around 300 K [1]. If this trend continues below 300 K, then the transition that occurs at decreased unit cell volume (i.e. increased pressure) could occur in NaOD at higher temperatures than in NaOH. On these grounds it seems likely that the new phase of NaOD reported here has the same structure as NaOH IV.

Our preliminary low temperature X-ray diffraction study on NaOD and NaOH indicates that the principal feature of the structural change taking place in NaOD below T_c is a contraction of the basal plane separation which reaches approximately 5% well below the transition. It is consistent with this speculation that Pistorius reported a volume contraction of 7.5% in NaOH on the transition from the orthorhombic phase II to phase IV. However, in NaOH we observed no further transition from the orthorhombic phase down to 10 K. A neutron diffraction investigation at 77 K is in progress to determine the deuteron positions which appear to hold the clue to the high value of η in the low temperature phase.

It is interesting to note that hints of a structural difference between NaOH and NaOD have appeared in previous investigations by Raman and infra red spectroscopy [9, 10] in the form of small and unexplained spectral differences at low temperatures. However, the same studies also appear to rule out the possibility that hydrogen bonding is responsible for pulling the layers together.

At the time of the VIIIth International Symposium on NQR, the crystal structure of NaOD below 160 K was unknown and no explanation for the anomalous behaviour in the sodium quadrupole coupling was forthcoming. Since that time, work has continued on the study of the transition in NaOD using X-ray and neutron diffraction and dielectric measurements and publication of these results is in progress [11].

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