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Phase Transitions in Solid Methanol

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Neutron powder diffraction patterns were measured for the ordered α-phase and the disordered β-phase of deuterated methanol. The structure of the α-phase at 160 K is in agreement with that found earlier at 15 K. A complete refinement of the structure of the β-phase at 170 K was also carried out. The space groups are α-$P2_12_12_1$ and β-Cmcm. For the disordered phase, the thermal parameters indicate that the molecules are localized rather than being in free rotation. A transformation matrix was found that relates the unit cells of the two phases. The transition involves mainly the large-angle rotation of molecules in a plane. In a second experiment, the α- to β-phase transition in both deuterated and undeuterated solid methanol was examined using Raman spectroscopy and a metastable phase was produced, for the undeutered sample, by rapid quenching through the phase transition. Only two modes of the methyl groups in this metastable phase differ from the internal modes of the stable α-phase. © 2002 Elsevier Science (USA)

Key Words: **phase transition; methanol; Raman; powder neutron diffraction.**

INTRODUCTION

Methanol has been extensively studied, both experimentally and theoretically, to test theories of hydrogen bonding and of chain formation. When cooled, methanol freezes at 175.37 K and then undergoes what was originally thought to be second-order transition (1) from a high-temperature β-phase to a low-temperature α-phase at 157.4 K (2). Later measurements with a dilatometer (3) showed that there are actually two transitions, a first-order transition at 159 K and a second-order transition at 156 K. An amorphous phase is obtained by vapor deposition at low temperatures and this phase transforms to the α-phase on warming to 130 K (4). Yet another crystalline phase is obtained when the pressure is increased beyond 3.5 GPa at ambient temperatures (5).

In our earlier studies using Raman spectroscopy (6) and powder neutron diffraction (7), there was no evidence of the phase between 156 and 159 K, but a metastable phase was discovered by quenching the β-phase to low temperatures. The current study was undertaken to determine the details of the disordered β-phase and the nature of this metastable phase.

EXPERIMENTAL DETAILS

Neutron Powder Diffraction

The deuterated methanol, CD_3OD, was supplied by MSD Isotopes and had an isotopic purity of at least 99%. To prepare a polycrystalline sample, a thin-walled vanadium can measuring 5 cm long by 5 mm in diameter was immersed in liquid nitrogen. Cooled liquid methanol was dripped into the can, and the solid formed was mechanically ground into a fine powder before more liquid was added. The filled can was mounted in a top loading helium cryostat precooled to 77 K.

Diffraction measurements were made at the NRU reactor at Chalk River on the Dualspec powder diffractometer, which has an 800 wire BF_3 detector covering a range of 80°, with wire separation of 0.1°. During data collection the detector was shifted 0.05° to give a total of 1600 data points per profile. Measurements were made at two wavelengths of 1.3289 and 2.3709 Å to cover a wide range of *d*-spacings and to give good resolution. Data were recorded in the ranges 4–84° and 38–118° in 2θ using the short wavelength and in the range 24–104° using the long wavelength.

The sample was initially in the α-phase and preferred orientation was checked by recording the diffraction pattern at 20° intervals of sample rotation at a sample temperature of 120 K. Preferred orientation was not a problem at this stage and the diffraction pattern was recorded at 160 K (above the transition temperature mentioned in the Introduction but just below the phase

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transition as determined from direct observation of the diffraction pattern) using both short and long wavelengths. The temperature was raised to 170 K to convert the sample to the β-phase as verified by the diffraction pattern. Again patterns were recorded at the two wavelengths. At the end of these runs, there was a second check on preferred orientation, which showed that significant preferred orientation had developed. Our standard practice is to rotate the sample continuously about a vertical axis during a run to minimize the effects of preferred orientation, but there is evidence, as discussed later, that the problem is not eliminated.

In an attempt to produce the metastable phase, the sample was removed from the cryostat at 170 K, was rapidly cooled in liquid nitrogen, and then was replaced in the cryostat at a temperature near 100 K. The resulting diffraction pattern recorded at 100 K was characteristic of the α-phase except for some extra peaks that rapidly disappeared before they could be scanned. New samples were formed and two more attempts were made to produce the metastable phase, without success. A diffraction pattern was recorded at 5 K for comparison with our earlier work (7). The best results at four temperatures are shown in Fig. 1. Best in this case means lacking in preferred orientation for the α-phase but there was always significant preferred orientation in the β-phase.

Raman

Samples of CH_3OH and CD_3OD were sealed in glass tubes mounted on the tail of a closed-cycle refrigerator and Raman spectra were recorded using a standard system with a Spex 1401 double monochromator. The samples were cooled, until the solid formed, and then warmed until the Raman spectra indicated that the transformation from the α- to β-phases was complete. Next, the samples were cooled at the maximum rate allowed by the closed-cycle refrigerator in an attempt to produce the metastable phase. Raman spectra in the internal mode regions were recorded at various stages of this process. Methanol is a weak scatterer, so spectra of the lattice region can only be obtained with difficulty (6).

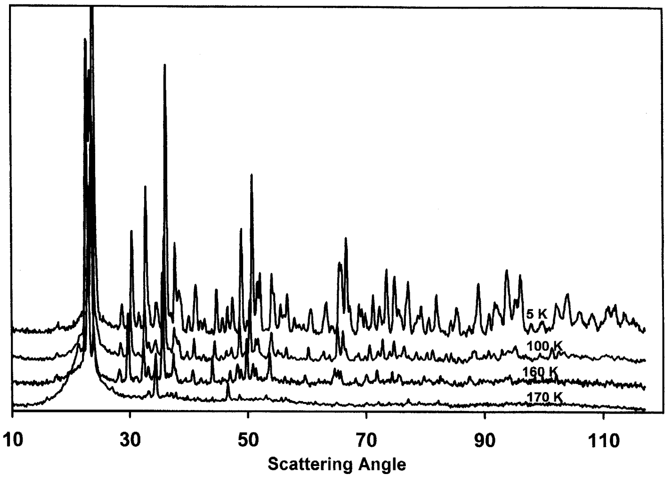

FIG. 1. Neutron powder diffraction pattern of methanol in the α-phase (lower three temperatures) and in the β-phase (highest temperature).

Analysis — Neutron Powder Diffraction

The structure of the α-phase at 15 K is known from our previous work (7), so it was a straightforward process to use the fitting program GSAS (8) to obtain new parameters for the new run at 5 K. These parameters were used to generate a rigid body representing the molecule, and this rigid body was used in the analysis of the α-phase runs at 100 and 160 K and the β-phase run at 170 K, just above the transition. The space group and suggested positions for the carbon and oxygen atoms in the β-phase were known from the earlier X-ray work (9) and these were used in the present analysis. There are a limited number of Bragg reflections in this phase, so it was necessary to retain the rigid body rather than refining the parameters of each atom separately. Rigid-body thermal parameters were refined for both phases. The pronounced diffuse background in the β-phase was fitted with 20 parameters using the radial distribution function provided in GSAS.

RESULTS AND DISCUSSION

Neutron Powder Diffraction

Emphasis here is on the measurements made on either side of the phase transition since the results for 15 K were presented earlier (7) and are consistent with the new results at 5 K. Measured, calculated and difference profiles are shown for methanol at 160 K (Fig. 2) and at 170 K (Fig. 3), and the final structural parameters for the two phases are listed in Table 1. The contents of the unit cell are shown in Figs. 4 and 5, which include a depiction of the rigid body anisotropic thermal motions with ellipsoids at the 0.50 probability level. For the α-phase, the fit is good, as indicated by the factors R and the difference curves, but for the β-phase, the fit to the Bragg peaks is only fair. This is to be expected since there is significant preferred orientation and the simple harmonic model used to represent the thermal motions of the molecules is not adequate at the relevant temperatures particularly with light atoms and a disordered phase.

The rigid-body analysis showed that the molecule rotates by 3.2° (X), 5.3° (Y) and $-1.4°$ (Z) between 5 and 160 K, but these changes are not obvious precursors of the phase transition. The rotations during the phase transition are

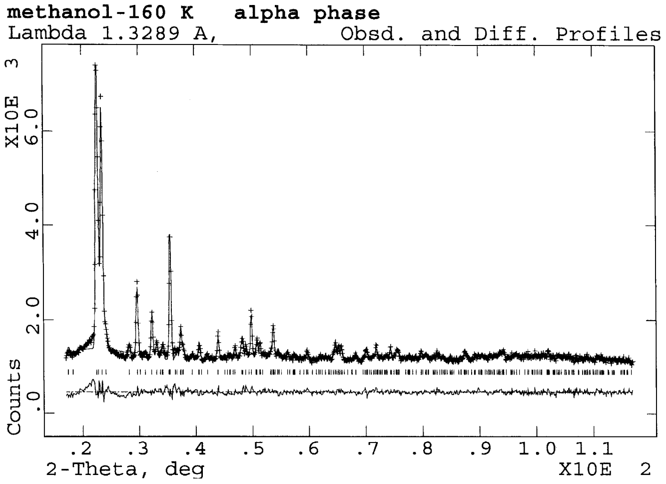

FIG. 2. Observed, calculated and difference profiles for methanol in the α-phase at 160 K.

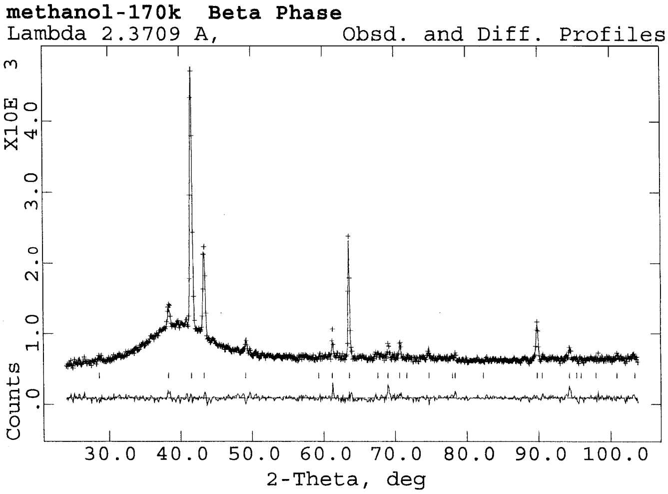

FIG. 3. Observed, calculated and difference profiles for methanol in the β-phase at 170 K.

much larger and are not the same for all molecules since the symmetry relations among molecules are different for the two phases. Angles *X*, *Y* and *Z* are defined in Table 1.

Phase Transition in Methanol. The structural parameters for methanol at 160 K, below the phase transition in the α-phase, and above the phase transition at 170 K in the β-phase are given in Table 1. In both phases, the C–O bond is close to or exactly in the plane perpendicular to the shortest axis, so the phase transition likely takes place as a result of a reorientation of the molecules within this plane. It appears that the length of the *c*-axis of the α-phase is cut in half as a result of reorientation of the molecules, breaking of the H bonds and disordering of the hydrogens.

TABLE 1
Structural Parameters for Methanol

Space group	$P2_12_12_1$ (160 K)	*Cmcm* (170 K)					
Z	4	4					
Lattice parameters (Å), thermal parameters (Å^2) and agreement factors							
	160 K	170 K					
a	4.9434(7)	6.4090(13)					
b	4.6547(8)	7.1993(7)					
c	9.1148(19)	4.6490(10)					
Vol.	209.73(8)	214.51(10)					
R_{ex}	2.67%	3.63%					
R_{wp}	3.60%	4.14%					
R_p	2.70%	3.03%					
Rigid body parameters (Å)^a				Molecular geometry at 5 K (Å and °)			
C	0.000	0.000	0.0000	*OC*	1.410(4)	$\angle COD_1$	106.5(5)
O	0.000	0.000	1.4104	OD_1	0.959(6)	$\angle D_2CD_3$	108.4(7)
D_1	0.920	0.000	1.6833	CD_2	1.091(7)	$\angle D_2CD_4$	108.3(4)
D_2	−1.033	0.000	−0.310	CD_3	1.084(5)	$\angle D_3CD_4$	108.7(7)
D_3	0.333	0.951	−0.399	CD_4	1.068(7)		
$D_4{}^b$	0.601	−0.777	−0.419				
Rotation angles	*R*1(*X*)	*R*2(*Y*)	*R*3(*Z*)	Origin *x*	*y*	*z*	
$P2_12_12_1$ (160 K)	−9.7(9)	−58.8(4)	−101.8(10)	0.1947(11)	0.5017(25)	0.1082(8)	
Cmcm (170 K)	90.0	0.0	90.0	0.0	0.2236(15)	0.0	

[a] C–O bond is along the *Z*-direction to start and rotations are applied in the order *Z*, *Y* and *X* about orthogonal axes. The molecule is then translated so that the C atom moves from the origin of the coordinate system to the position labelled origin above.

[b] Produced by mirror plane in *Cmcm*.

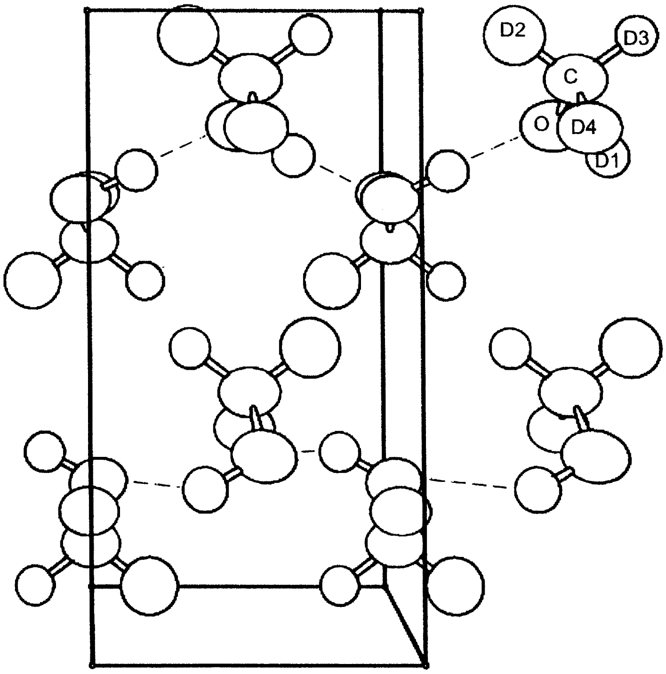

FIG. 4. Unit cell of methanol in the α-phase at 160 K. $Y \Rightarrow Z \Downarrow$.

An approximate transformation matrix between the two phases $\alpha \rightarrow \beta$ is

$$\begin{vmatrix} 1 & 0 & .5 \\ -1 & 0 & .5 \\ 0 & 1 & 0 \end{vmatrix}$$

giving a length of 6.7236 Å for the a- and b-axis of the β-phase, which is intermediate between the measured values, and an angle between these axes of close to 90°. The centers of mass of the molecules are close to the positions required for the structure of β-phase with a face-centerd arrangement in the $x-y$ plane and an interleaving face centerd arrangement in a second $x-y$ plane separated from the first by $z = 0.5$. As the influence of the H bonds decreases with increasing temperature, the dipole–dipole interactions tend to align adjacent molecules in an anti-parallel fashion as observed in the β-phase. This requires a major change in the orientations of the molecules in the $x-y$ planes.

Diffuse Scattering. The strong diffuse scattering from the β-phase is evidence of the disorder in the phase.

Implicit in the choice of *Cmcm* as the space group and *m*2*m* as the site symmetry is disorder of all of the hydrogens. The integrated intensity of the diffuse peak is comparable to the sum of the integrated intensities of the Bragg peaks, so most of the atoms must be involved in the disorder, as expected. There is steric interference and electrostatic repulsion between the hydroxy hydrogens of adjacent molecules when the hydrogens are in their positions of closest approach; so, there will be short-range ordering of the molecules to minimize these effects. Since there are only a small number of Bragg peaks, the thermal parameters are not particularly reliable, but the thermal ellipsoids for all the atoms including the hydrogens are close to spherical so the molecules likely spend most of their time with the O–D bond in the mirror plane rather than being in free or nearly free rotation.

An attempt was made to model the diffuse scattering using DISCUS (10). Molecules with the two orientations at 180° to each other were randomly distributed throughout a model crystal and provision was made for large-amplitude rotational motions about the C–O bond and for short-range order. With this simple model, the calculated diffuse scattering is too weak and the maximum of the diffuse peak is at too low an angle. Future work with single crystals may be necessary to develop a complete understanding of the diffuse scattering.

At all recorded temperatures below the transition temperature, there is some diffuse scattering around the strong peaks that occur near a scattering angle of 25° (see Fig. 1). This is taken as a measure of the disorder in the

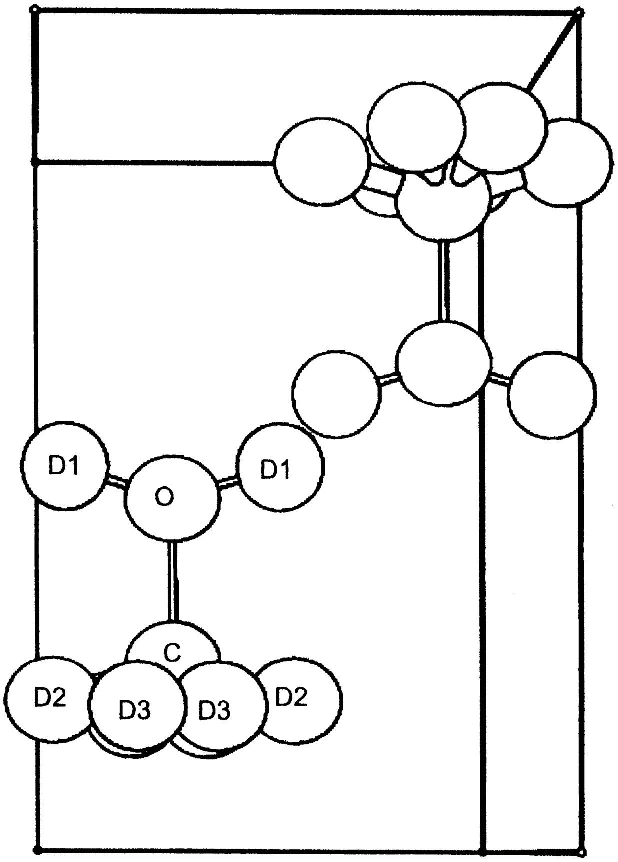

FIG. 5. Unit cell of methanol in the β-phase at 170 K. $Z \Rightarrow Y \Uparrow$.

sample. Our earlier results (7) did not show this effect, so the degree of disorder must depend on the thermal history. The earlier sample was annealed for 1.5 h below the phase transition whereas the current samples were cooled directly from above the phase transition.

Raman Spectra

In the Raman experiments, only the α- and β-phases were observed with the deuterated samples. A metastable phase was observed with the rapidly cooled undeuterated samples, but not in every cycle of rapid cooling. This is consistent with the neutron diffraction experiments, in which the metastable phase was not observed in deuterated methanol. The transition between the α- and β-phases, as determined from the Raman spectra, has a very large hysteresis, and takes place between 125 and 135 K with decreasing temperature, and between 155 and 165 K with increasing temperature. The results from the undeuterated sample are shown in Figs. 6 and 7 for two different regions of the spectra with a range of temperatures. The runs at 40 K are for three successive quenches and illustrate the point that not all quenches gave the metastable phase rather than the α-phase (middle spectra). The remaining spectra show the effect of warming the metastable phase through the α- to β-phase transition temperature.

Evidence of the metastable phase is clearly seen in the current Raman runs on the undeuterated sample but only in the rocking and bending modes, at 1160 and 1460 cm^{-1}, respectively, involving the methyl groups. In both cases, the splitting of the most prominent mode disappears and the merged peak is slightly lower in frequency than the average of the split peaks.

The structure of the metastable phase can only be determined by a careful X-ray study. Careful because of the difficulty of finding the H atoms with X-rays, and with X-rays rather than neutrons because of the large incoherent scattering of neutrons from hydrogen. In the absence of such a study we are left to speculate based on our knowledge of the other phases of methanol. In the β-phase the C–O bonds in adjacent chains are almost parallel (see Fig. 5). The transition to the α-phase involves a puckering of the individual chains so that the C–O bonds in adjacent chains make an angle ϕ of approximately 50^0 to each other as shown in Fig. 5. One likely form of disorder on quenching is that the hydrogen bonding of the α-phase is maintained but the molecules are oriented about the hydrogen bonds with an angle $+\phi$ or $-\phi$ in a random or nearly random fashion that gives rise to broad peaks characteristic of a disordered sample as we observed.

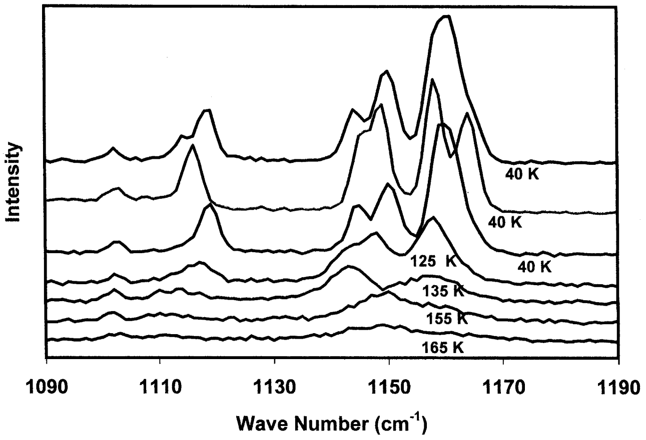

FIG. 6. Raman spectra of methanol—region 1.

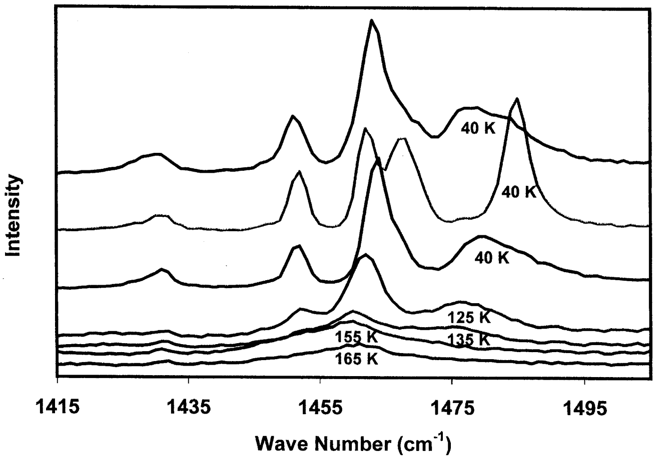

FIG. 7. Raman spectra of methanol—region 2.

CONCLUSIONS

The structure of the α-phase at 160 K is in agreement with that found earlier at 15 K. There are small rotations of the molecules between the two temperatures but these cannot be related in any simple way to the large rotations that take place during the transition to the β-phase. A transformation matrix was found which relates the unit cells of the two phases. The transition involves mainly the reorientation of the molecules in a plane. For the disordered phase, the thermal parameters indicate that the molecules are localized rather than being in free rotation.

A metastable phase can be produced by rapidly quenching a sample of undeuterated methanol through the α- to β-phase transition. No equivalent phase was observed with deuterated methanol in the current experiments except on a very short time scale. The rocking and bending modes of the methyl groups distinguish the metastable phase from the stable α-phase.

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REFERENCES

1. K. K. Kelley, *J. Am. Chem. Soc.* **51,** 180 (1929).
2. G. S. Parkes, *J. Am. Chem. Soc.* **47,** 338 (1925).
3. L. A. K. Staveley and M. A. P. Hogg, *J. Chem Soc.* **1954,** 1013 (1954).
4. A. B. Dempster and G. Zerbi, *J. Chem. Phys.* **54,** 3600 (1971).
5. D. R. Allan, S. J. Clark, M. J. P. Brugmans, G. J. Ackland, and W. L. Vos, *Phys. Rev. B* **58,** 809 (1998).
6. A. Anderson, B. Andrew, E. M. Meiering, and B. H. Torrie, *J. Raman Spectrosc.* **19,** 85 (1988).
7. B. H. Torrie, S.-X. Weng, and B. M. Powell, *Mol. Phys.* **67,** 575 (1989).
8. A. C. Larson and R. B. Von Dreele, Report No. Laur, The Regents of the University of California, pp. 86–748, 1989.
9. K. J. Tauer and W. N. Lipscomb, *Acta Crystallogr.* **5,** 606 (1952).
10. Th. Proffen and R. B. Neder, *J. Appl. Crystallogr.* **30,** 171 (1997).