

Neutron Powder Diffraction Study of Deuterated β -Acetonitrile

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Abstract

The structure of the low-temperature β phase of deuterated acetonitrile, CD_3CN , has been determined by neutron powder diffraction. Experiments were performed using both a triple-axis spectrometer in the elastic mode and a time-of-flight diffractometer with a Fourier chopper. The diffraction patterns obtained have been analysed by Rietveld refinements in which the molecules were constrained to C_{3v} symmetry. A final R_{wp} factor of 7.7% was obtained for an orthorhombic model; space group $Cmc2_1$, cell parameters at 100 K: $a = 6.05$ (4), $b = 5.24$ (4), $c = 7.79$ (6) Å, $Z = 4$. The acetonitrile molecules were found to lie on the mirror planes. The phase transformation $\alpha \rightarrow \beta$ is accompanied by changes in the orientation of permanent dipoles of the molecules, which lead to a structure with a macroscopic polarization in the c direction.

1. Introduction

Acetonitrile, CH_3CN , is interesting because of its large electric dipole moment of 1.31×10^{-29} C m and its significance as an organic solvent. Owing to the comparatively high boiling point of this polar liquid, its microscopic structure is expected to be determined by strong noncentral intermolecular forces arising most likely from the dipole-dipole interactions between pairs of molecules. The liquid state of acetonitrile has been studied by a variety of techniques (for a review, see Michel & Lippert, 1978). All investigations lend support to the hypothesis of antiparallel arrangement of neighbouring molecules.

Acetonitrile exists in two (α and β) solid phases with the transition point at 216.9 K (Putnam, McEachern & Kilpatrick, 1965). Jakobsen & Mikawa (1970) have also postulated the presence of a third (γ) crystalline form appearing only at high pressure. The crystal structure of the high-temperature α phase

has been determined by Barrow (1981) using single-crystal Weissenberg film data. α -Acetonitrile has the monoclinic space group $P2_1/c$ with the lattice parameters $a = 4.11$, $b = 8.27$, $c = 7.98$ Å, $\beta = 100.4^\circ$, and with four molecules in the unit cell. The packing arrangement comprises an antiparallel alignment between neighbouring molecules, and is in reasonable agreement with the structure proposed by Marzocchi & Dobos (1974) on the basis of infrared spectroscopic investigations.

The crystal structure of the low-temperature β phase has been studied previously by Pace & Noe (1968) using X-ray powder methods. They proposed that β -acetonitrile crystallizes in a primitive orthorhombic lattice with the parameters $a = 8.12$, $b = 11.01$, $c = 5.09$ Å, and with eight molecules in the unit cell. Moreover, they concluded from the multiplet structure of infrared absorption bands that the possible space groups are $Pmmm$ and $Pbam$, but no attempt was made to fully determine the low-temperature structure.

The aim of the present neutron powder diffraction study is to obtain information about the structure of the low-temperature β phase and to give an adequate basis for understanding the alignment of the permanent dipole moments and the mechanism of the phase transition. Since it is difficult to get a single crystal of the β form (Barrow, 1981), because of discontinuities in volume at the transition (Landau & Würflinger, 1980), a powder sample has been chosen for the investigation. In the present work we have studied β -acetonitrile by neutron powder diffraction methods so that the hydrogen positions could be determined accurately. Because the scattering of hydrogen is predominantly incoherent, the deuterated acetonitrile, which was assumed to be isostructural with the hydrogenous compound, was used in the diffraction experiments.

2. Experimental

To obtain reliable information about the structure of solid acetonitrile, experiments were carried out using

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Table 1. *Experimental details for CD₃CN measurements*

	TAS4	RTOF
2 θ (°)	10–105	111.3
2 θ step (°)	0.1	—
Wavelength (Å)	2.44	1.54–3.23
(sin θ)/ λ range (Å ⁻¹)	0.04–0.33	0.26–0.54
Sample:		
Temperature (K)	100 (1)	91 (1)
Height (mm)	50	9
Diameter (mm)	14	92

both monochromatic-beam and white-beam diffraction methods as described in Table 1. At Risø the neutron powder diffraction pattern was collected on the TAS4 triple-axis spectrometer operating in the elastic mode with a pyrolytic graphite monochromator, analyser and high-order filter. The results were supplemented by measuring a high-resolution powder spectrum using the time-of-flight diffractometer ASTACUS (Tiitta & Hiismäki, 1979) at the Triga Mk II reactor of the Technical Research Centre of Finland. The high resolution required for this high-order diffraction experiment was obtained by means of the reverse time-of-flight method, RTOF (Pöyry, Hiismäki & Virjo, 1975), with a Fourier chopper and a flight path of 5.998 m. The deuterated acetonitrile samples were of spectroscopic grade purchased from Merck (FRG) and Isocommerz (GDR), and they were used without further purification. The deuterated materials were contained in thin-walled aluminium cans, which were mounted in liquid-nitrogen cryostats. Low-temperature samples containing only β -phase material were obtained with the procedure suggested by Pace & Noe (1968), *i.e.* by supercooling the liquid below the transition temperature, by annealing the crystal at 215 K for one day, and by cooling the sample slowly to the measuring temperature. The tendency of the acetonitrile crystallites to have preferential alignments in the specimen (Bonin, Takeda & Williams, 1969; Sprague, 1979) was reduced at Risø by filling the container with annealing quartz wool (Heraeus RZ 112) and by carrying out experiments with three different sample orientations which gave reasonably concordant results. The specimen investigated by the RTOF method was so large that the addition of four diffraction patterns obtained from different samples was considered to be an adequate precaution against preferred orientation caused by large size crystallites. Preferred orientations resulting from special unit-cell dimensions (flake- or needle-shaped) were not considered to be significant in the present case.

3. Determination of the unit cell

To obtain accurate data for the derivation of cell parameters, the lattice spacings were estimated by

fitting an asymmetric Gaussian profile (Rietveld, 1969) with a linear background to each Bragg peak observed in the TAS4 diffraction pattern depicted in Fig. 1. The unit cell was determined by applying the method proposed by Smith & Kahara (1975) to monoclinic and higher crystal classes. The indexing procedure led to two different choices: monoclinic, $a = 4.00$, $b = 8.03$, $c = 7.80$ Å, $\gamma = 98.2^\circ$; and orthorhombic, $a = 6.06$, $b = 5.26$, $c = 7.80$ Å. The reliability index M (de Wolff, 1968) was 9.2 for the monoclinic solution, while the orthorhombic unit cell yielded a slightly smaller value of 8.7.

The monoclinic solution, however, indicates a relation between the lattice constants a and b or $b = 2a$. This means that a third lattice might exist which gives an equivalent fit. Examination of these three lattices revealed that they are all related to a C -centered orthorhombic lattice with $a = 6.05$, $b = 5.24$ and $c = 7.80$ Å. The reliability index M for this solution is 17.1 or larger than the critical value of 10 which usually guarantees the correctness of the indexing.

It should be noted that the above-mentioned orthorhombic unit cells differ from that proposed previously by Pace & Noe (1968), whereas the monoclinic lattice is closely related to the unit cell of the high-temperature α phase determined by Barrow (1981). Two other interesting properties of the above lattices are that all solutions have a common axis (7.80 Å) and identical volumes (248 Å³). These show that the unit cells contain four molecules as in the high-temperature α phase.

4. Crystal structure analysis

As only a limited number of peaks were observable in the present diffraction patterns, it was necessary to introduce rigid-body constraints (Pawley, 1969) to

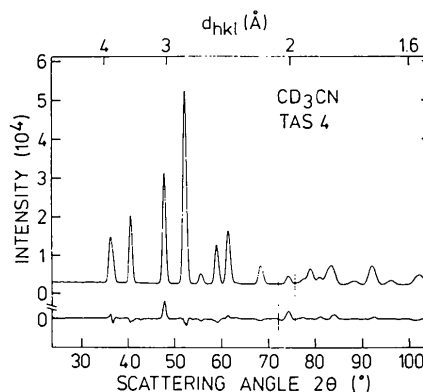


Fig. 1. The neutron diffraction pattern observed with the TAS4 triple-axis spectrometer. The differences between the experimental and calculated patterns are also shown. The calculated profile corresponds to the best fit with the structure $Cmc2_1$. The vertical bars specify the region omitted in the refinement due to the large Al reflection.

reduce the number of variables in the Rietveld refinements (Rietveld, 1969). In the present analysis the powder data is insufficient to support any significant variation of the molecular shape from its ideal C_{3v} symmetry or any differences between the non-equivalent molecules in the unit cell. The molecules were, therefore, constrained to maintain their free-state symmetry and bond angles. The positions of the atoms in the molecule were governed by three atom-atom distances: C(1)–D, C(1)–C(2) and C(1)–N. The position and orientation of each nonequivalent molecule was described by three Euler angles φ , θ , ψ (Goldstein, 1969) and by three crystal coordinates x , y , z , defining the position of the methyl-group carbon C(1). The rest of the structural variables were an overall scale factor, a deuterium level, and three isotropic Debye-Waller factors $B(D)$, $B(C)$, $B(N)$ common to all the D, C and N atoms. The scattering lengths used in the analysis were from Kostorz & Lovesey (1979). In each refinement of the TAS4 powder pattern the usual peak-shape parameters U , V , W , P (Rietveld, 1969) and the unit-cell dimensions were varied together with two parameters defining the background profile or $Y_B = P_1 + P_2(2\theta)$. Because the background was refined simultaneously, the weights for the observations were calculated from counting statistics.

The Rietveld refinement of the RTOF spectrum was carried out using the theory developed especially for the correlated RTOF observations (Tilli, 1982*a, b*). The structural parameters were the same as those in the TAS4 refinements, but the thermal vibration of the atoms was described by one Debye-Waller factor B common to all the atoms. The nonstructural variables adopted for this study included, in addition to the cell dimensions, parameters P_1 , P_2 , P_3 , P_4 for the background and a peak-width parameter P_8 , while the rest of the parameters defining the theoretical profile (Tilli, Tiitta & Pöyry, 1980) were estimated from calibration experiments.

4.1. Orthorhombic models

The constrained rigid-body refinements were started by first analysing the TAS4 diffraction data obtained by omitting two regions from the experimental powder pattern. The range $2\theta < 23^\circ$ was ignored, because no peaks could be observed at very low scattering angles. A separate measurement on the textured Al can revealed a strong 200 reflection in the range $72.4 < 2\theta < 75.3^\circ$ which was removed as well. Other Al reflections (e.g. 111) could not be found.

Examination of systematic absences in the TAS4 powder pattern revealed that the space group cannot be determined uniquely. A few space groups were selected from many possibilities. In the space group $Cmc2_1$ the molecules can be positioned on a mirror

Table 2. Final crystallographic parameters and agreement factors from the best $Cmc2_1$ model refinements on CD_3CN diffraction data

The coordinates of the atoms in the molecular-body system are defined such that the C(2) and N atoms of the molecule lie on the positive z axis. One mirror plane of the molecule coincides with the yz plane. The Euler angles are defined relative to a space reference system formed by the crystal a , b and c axes to establish a right-hand coordinate system. Estimated standard deviations in the last significant digit are given in parentheses.

	TAS4	RTOF
Background		
P_1	1938 (24)	3986 (470)
P_2	-6.89 (40)	1.4×10^6 (2.9)
P_3		9(3)
P_4		9(4)
Peak shape		
U ($^\circ$) ²	4.35 (29)	
V ($^\circ$) ²	-2.45 (31)	
W ($^\circ$) ²	0.872 (83)	$P_8 = 4.15 \times 10^{-6}$ (37)
P	-0.161 (26)	
Peak shift F ($^\circ$)	0.1139 (42)	
Cell parameters (Å)		
a	6.046 (42)	6.009 (4)
b	5.241 (40)	5.211 (3)
c	7.799 (57)	7.750 (5)
Scale factor	7.81 (11)	9.51×10^{-6} (11)
Deuterium occupancy factor (%)	93.48 (90)	89 (3)
Bond lengths (Å)		
C(1)–D	1.1018 (13)	1.06 (5)
C(1)–C(2)	1.311 (11)	1.52 (5)
C(1)–N	2.453 (18)	2.55 (3)
Euler angles ($^\circ$)		
θ	-49.23 (10)	-47.86 (48)
$\varphi = \psi = 0$ by symmetry		
C(1) positions		
y	-0.0762 (24)	-0.0722 (47)
$x = z = 0$ by the choice of origin		
Debye-Waller factors (Å ²)		
$B(D)$	0.36 (19)	Overall
$B(C)$	2.29 (19)	$B = 2.0$ (2)
$B(N)$	2.27 (16)	
Fit quality		
S^2	22.3	1.47
R_{wp} (%)	7.7	
R_p (%)	6.2	

plane thus giving a highly symmetric atomic arrangement. In this model the positions and the orientations of the four molecules in the unit cell can be fixed by one position parameter and by one angular parameter. The result of refinement is depicted in Fig. 1.* The parameters are reported in Table 2 together with the following agreement factors: R_p , R_{wp} (Young, Prince & Sparks, 1982) and S^2 (Abrahams, 1969). The expression S^2 estimates the variance of an observation of unit weight. For a satisfactory model S^2 should have a value of order unity if the observations are correctly weighted in the refinement. For the ordinary

* Lists of numerical data corresponding to the data in Figs. 1 and 2 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43812 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

least-squares fitting, S is simply the ratio of R_{wp} to the expected value for R_{wp} . In the RTOF refinements S^2 was evaluated by means of the statistical theory developed by Tilli (1982*a,b*).

In the present refinements the relatively good quality of fit ($R_{wp} = 7.7\%$ and $R_p = 6.2\%$) was obtained by using a peak-shift parameter F suggested by Cooper & Sayer (1975) and Thomas (1977). The peak shifts δ , arising from the finite aperture of the detector, were calculated using the simplified function $\delta = F \cot 2\theta$, where F is a refinable parameter. With the aid of this expression the peak positions could be fitted satisfactorily as can be observed from the difference profile depicted in Fig. 1. Alternatively, a refinement with the usual parameter Z for the counter zero point (Rietveld, 1969) gave the R factors of $R_{wp} = 11.3\%$ and $R_p = 8.7\%$, and the de Wolff parameter decreased to 11.3 showing the significance of the above correction.

The RTOF diffraction pattern was fitted using the above $Cmc2_1$ structure as a starting model. The result of the refinement is depicted in Fig. 2.* Examination of the values listed in Table 2 shows that the fitting gave an S^2 factor of 1.47, which can be considered to be reasonable. Moreover, the parameters obtained from both refinements are in moderate agreement.

A less symmetric structure is obtained with the space group $Pca2_1$, which allows the molecules to be canted from the mirror plane and the methyl group to be rotated about the C–N axis. In this case five parameters are needed to fix the position and the orientation of the four molecules. The refinement of this structure could not significantly improve the goodness-of-fit although it gave slightly smaller R factors ($R_{wp} = 7.44\%$, $R_p = 5.8\%$, $S^2 = 20.6$). Furthermore, the atomic positions were the same as those given by the $Cmc2_1$ model. In conclusion, the extra flexibility offered by the $Pca2_1$ model is supported neither by the TAS4 nor the RTOF results.

The TAS4 diffraction pattern was also fitted using $Pnma$ structures which can give the optimal packing density for molecules possessing a symmetry plane. The lowest R factors obtained were $R_{wp} = 21.4\%$ and $R_p = 13.5\%$ for the lattice $a = 5.25$ (17), $b = 6.05$ (17) and $c = 7.81$ (22) Å. The fit was unsatisfactory, and thus the $Pnma$ structures were rejected.

4.2. Monoclinic models

In spite of the fact that the orthorhombic solution possesses a de Wolff parameter higher than the critical value of 10 some monoclinic models were also tested. The best model was $P2_1$ with two nonequivalent molecules per unit cell being one of the maximal subgroups of the space group $P2_1/c$ of α phase. In this model, eleven parameters are needed to give the molecular orientations and positions. The structure

of this model and of the $Cmc2_1$ model are again very much alike. The agreement factors do not show any significant difference in comparison with the $Cmc2_1$ model ($R_{wp} = 7.7\%$, $R_p = 6.2\%$, $S^2 = 22.3$). The refinements showed that any reorientation of the molecules from this arrangement will necessarily lead to a significant deterioration of the quality of fit.

5. Discussion and concluding remarks

In this work we have been able to determine the structure of β -acetonitrile using the information obtainable from powder patterns. Examination of the difference profile in Fig. 1 shows clearly that the errors in the fitting originate mainly from incorrect peak intensities, while the model predicts peak positions accurately. The proposed model gives an adequate fitting not only to the TAS4 powder pattern, but also to the RTOF spectrum, thus giving an additional confirmation of the indexing.

The best molecular arrangement model belonging to space group $Cmc2_1$ gave an R_{wp} factor of 7.7%, which is considerably larger than the statistically expected value of 1.6%. It seems, therefore, that either the theoretical model or the weights in the refinement are incorrect. Owing to the limited number of peaks in the powder patterns, fitting was performed using a simple model in which the atomic positions were calculated from the rigid-body molecular model, and the vibrations of the nuclei were evaluated by means of the isotropic temperature factors. In the present case the molecules are probably rigid, so the constrained refinements have yielded meaningful results, but the use of isotropic Debye–Waller factors is clearly unfounded. As stated by Trevino, Prince & Hubbard (1980), in the case of nitromethane the methyl group undergoes libration which leads to a strong anisotropic overall vibration even at 4.2 K. Therefore, it seems most likely that the inclusion of

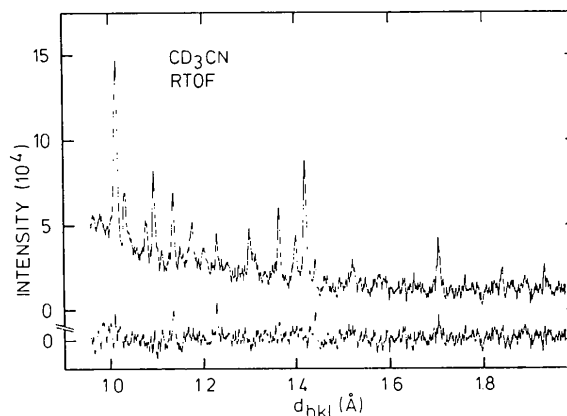


Fig. 2. The neutron diffraction pattern measured using the reverse time-of-flight method (RTOF) (upper curve). The differences between the experimental and the calculated profiles, corresponding to the best fit with the structure $Cmc2_1$, are also shown.

* See deposition footnote.

realistic temperature factors will also improve the fit in this case and remove the small peaks from the difference profiles depicted in Figs. 1 and 2. Moreover, the thermal parameters may have systematic errors because no experimental value of effective absorption was available, and $B(D)$ in particular is strongly correlated to the deuterium occupancy factor.

As a result of the mirror plane of the acetonitrile molecule, the space group $Pnma$ allows optimal packing of the molecules. The efficiency of the packing arrangement can be estimated from the packing coefficient (Dunitz, 1979). The packing coefficient of 0.65 for β -acetonitrile is similar to that observed in molecular crystals (0.65–0.75), which reveals that the molecular arrangement is nearly ideal. The proposed space group $Cmc2_1$ contains the mirror plane and the structure of β -acetonitrile is closely related to the optimal space group $Pnma$, but owing to the symmetry requirements the orientation of the molecules differs in these two space groups. This discrepancy between the ideal and actual packing arrangements most likely results from the anisotropic intermolecular interactions which exist in the acetonitrile crystal.

Information on the arrangement of the molecules in β -acetonitrile has been obtained previously from an investigation of the nuclear quadrupole resonance spectrum (Casabella & Bray, 1958) and from Raman and infrared spectroscopy (Milligan & Jacox, 1962; Pace & Noe, 1968; Marzocchi & Migliorini, 1973). These studies show that the molecules are in nearly axial alignment in the crystal. Moreover, it has been proposed that the molecules are at C_s sites, which suggests that one of the vertical reflection planes of the molecule should coincide with the mirror plane

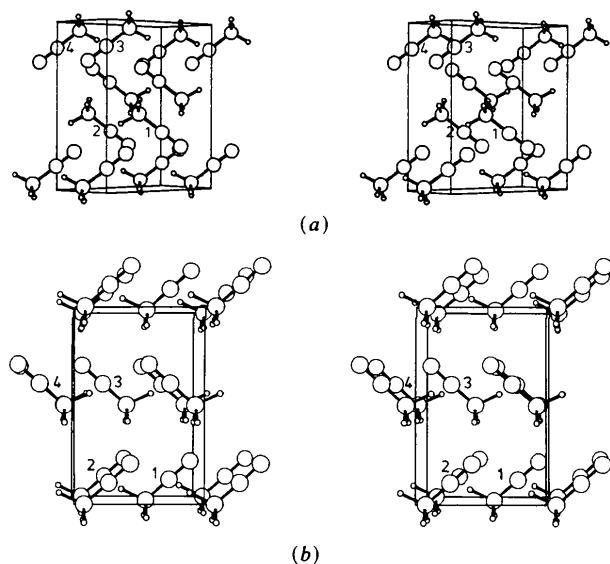


Fig. 3. Stereoscopic views of α -acetonitrile (a) and β -acetonitrile (b). The viewing direction in (a) is along $[10\bar{2}]$, and in (b) along $[100]$.

of the space group. The proposed $Cmc2_1$ structure contains mirror planes thus confirming the latter result. However, the suggestion of a nearly axial alignment of molecules is certainly not supported by the present $Cmc2_1$ structure results.

The phase transition in solid acetonitrile is associated not only with a discontinuous change in volume (Landau & Würflinger, 1980) and entropy (Putnam, McEachern & Kilpatrick, 1965) but also with hysteresis (Putnam, McEachern & Kilpatrick, 1965; Pace & Noe, 1968). All these phenomena belong to a first-order phase transition, which may also exhibit drastic structural changes, because the symmetries of the two phases are not necessarily related.

Information on the mechanism of transformation can be obtained by investigating relations between the structures of the initial and transformed phases. Examination of Figs. 3(a) and 3(b) reveals that the phase transformation $\alpha \rightarrow \beta$ involves a change in the orientation of the C–C axes of the molecules labelled by 1, 2, 3 and 4, which also undergo a 60° rotation of the methyl groups. The labelled molecules form the contents of one orthorhombic unit cell. The reorientation results in a change in the nature of the nearest neighbours, because the first-coordination bonds are broken and reformed. On this basis the phase transition in acetonitrile can be classified as a reconstructive transformation.

The intramolecular atom-atom distances $C(1)-D$ and $C(1)\cdots N$ obtained from the TAS4 and RTOF experiments are in reasonable agreement, but a large discrepancy exists between the C–C bond lengths. The distance $C(1)-D$ and the mean value for the C–C bond differ neither from the gas-phase results determined by electron diffraction (Danford & Livingston, 1955) and microwave spectroscopy (Costain, 1958) nor from the molecular parameters of liquid acetonitrile (Kratochwill, Weidner & Zimmermann, 1973; Bertagnolli, Chieux & Zeidler, 1976a,b; Bertagnolli & Zeidler, 1978). However, the $C(1)\cdots N$

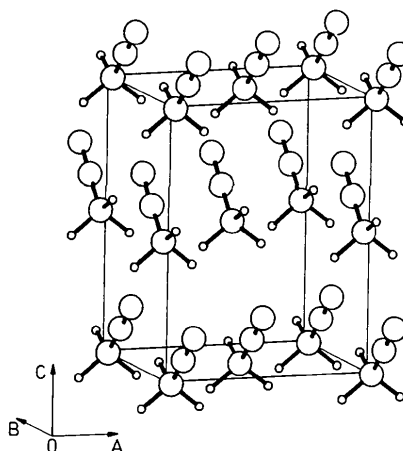


Fig. 4. Arrangement of molecules in β -acetonitrile obtained from refinements within the space group $Cmc2_1$.

distance seems to shorten in the phase transition by about 0.016 Å. The shortening is caused by the improper treatment of thermal motion.

The most important structural change accompanying the phase transition in acetonitrile is the drastic change in the orientation of the molecular dipole moments. The high-temperature α phase possesses a symmetry centre, so the neighbouring molecules have an antiparallel alignment. In the phase transition the symmetry centre disappears and the mirror plane of the molecule coincides with the (10 $\bar{2}$) plane of the α phase. Examination of Fig. 4 shows clearly that the permanent dipoles of the molecules are oriented such that the total polarization is along the c axis. It should be noted that the polarity of the crystal cannot be reversed by application of an electric field, which suggests that β -acetonitrile is probably pyroelectric. Besides the structural changes, the dielectric constant of acetonitrile should also show anomalies at the phase transition. The dielectric behaviour of acetonitrile has been studied by Würflinger (1980). Careful examination of the results has shown that the dielectric constant undergoes a small change at the solid-solid transition. Earlier, the dielectric step was associated with the volume change of the transition, but the present work shows that the phase transition is also accompanied by changes in spontaneous polarization.

The results of the present study should be considered to be preliminary since the difference between the measurement temperatures of the X-ray investigation (Barrow, 1981) and the present neutron diffraction study is large. Therefore, more experiments are needed to reveal the small structural changes accompanying the phase transition in acetonitrile.

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