Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# The Structural Phase Transition in Solid DCN

O. W. Dietrich [a] , G. A. Mackenzie [a b] & G. S. Pawley [a b]

[a] Physics Department, Danish Atomic Energy Commission, Research Establishment Risø, DK-4000, Roskilde, Denmark

[b] Department of Physics, Edinburgh University, The Kings Buildings, Mayfield Road, Edinburgh, EH9 352

Version of record first published: 28 Mar 2007.

To cite this article: O. W. Dietrich , G. A. Mackenzie & G. S. Pawley (1976): The Structural Phase Transition in Solid DCN, Molecular Crystals and Liquid Crystals, 32:1, 21-25

To link to this article: http://dx.doi.org/10.1080/15421407608083616

*Mol. Cryst. Liq. Cryst.*, 1976, Vol. 32, pp. 21–25

Printed in Holland



# The Structural Phase Transition in Solid DCN

O. W. DIETRICH, G. A. MACKENZIE† and G. S. PAWLEY†

*Physics Department, Danish Atomic Energy Commission, Research Establishment Risø, DK-4000 Roskilde, Denmark*

Neutron scattering measurements on deuterated hydrogen cyanide have shown that the structural phase transition from a tetragonal to an orthorhombic form at 160 K is a first order transition. A transverse acoustic phonon mode, which has the symmetry of the transition was observed at very low energies and showed "softening" as the transition was approached from above.

Hydrogen cyanide is a relatively simple molecular crystal which exhibits a phase transition from a high temperature tetragonal to a low temperature orthorhombic form. The transition was first discovered by Giaque and Ruehrwein (1939) who observed a narrow but finite anomaly in the specific heat at 170.4 K indicating a second order phase transition. The molecule is linear and aligned along the *c*-axis of the body centred tetragonal or orthorhombic unit cells, space groups 14 mm and 1 mm respectively (Dulmage and Lipscomb, 1951). The lattice statics and dynamics have been calculated by Rae (1969 and 1972) who found that the acoustic shear mode in the direction of the base diagonal (110) which relates the two structures had an anomalous behaviour giving imaginary frequencies. Rae suggested that the phase change is second order and is associated with an instability of the transverse acoustic mode with wavevector in this direction.

We have undertaken an experimental study using the coherent inelastic neutron scattering technique. The deuterated form DCN was used to avoid the large incoherent scattering of hydrogen. The DCN (melting point −13.8°C boiling point 26°C) was contained in a quartz tube which was mounted in a cryostat so that the bottom and top could be heated or cooled independently in order to grow a single crystal from the melt or from the

† Permanent address: Department of Physics, Edinburgh University, The Kings Buildings, Mayfield Road, Edinburgh EH9 3JZ.

vapour. Unfortunately in a large number of attempts using different designs of sample tube with various temperature gradients and cooling rates we were unable to grow a large enough single crystal to allow a full inelastic neutron study. Only in a few cases could small crystals be selected and oriented with tetragonal plane horizontal, the best of these having a mosaic spread of about 2 degrees. The measurements, limited to small energy transfers and therefore high neutron scattering cross sections, were performed on a triple axis crystal spectrometer at the DR-3 reactor, Risø, operated with pyrolytic graphite monochromator and analyser at an incident wavelength of 2.39 Å.

The twinning of the DCN crystal in the orthorhombic phase is illustrated in Figure 1, which shows the $a^*$–$b^*$ plane in reciprocal space with the tetragonal phase base diagonals marked (110) and ($\bar{1}$10).

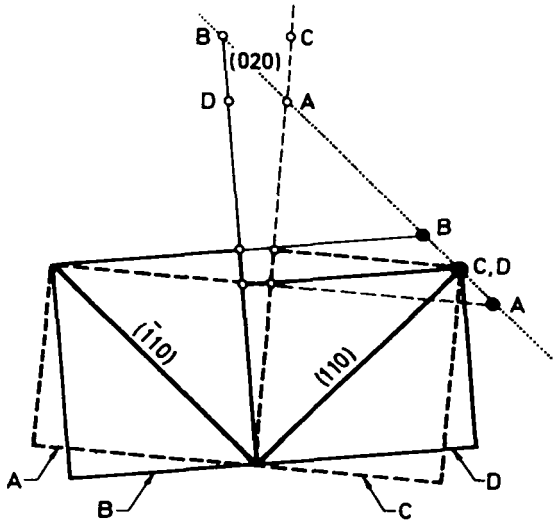


FIGURE 1 Domain structure of the orthorhombic phase.

In the orthorhombic phase one or other of the diagonals retains its direction and approximate length thus giving rise to the 4 possible domain configurations A, B, C and D. This domain structure has been observed by performing elastic scans along the dotted line in Figure 1. Such scans are shown in Figure 2 for temperatures close to the transition. It is evident that the transition is very sharp. The small hump in the centre of the (020) scan at 159.9 K indicates coexistence of the two phases but may be due to a small temperature gradient over the sample.

We have measured the positions of the (110) and (200) reflections over a wide range of temperatures. Figure 3 shows the temperature variation of the

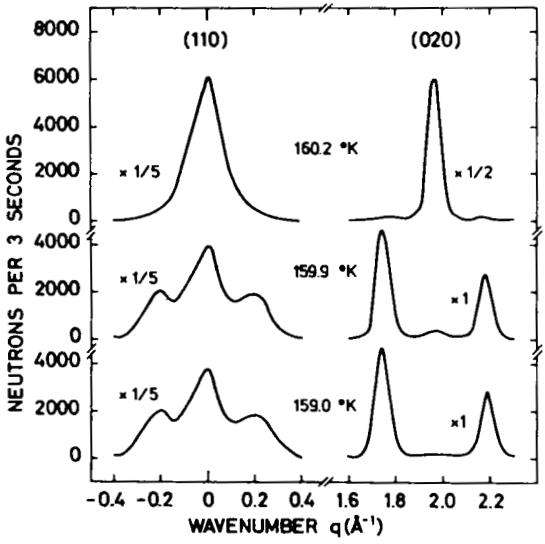


FIGURE 2 Neutron elastic scattering along dotted line in Figure 1.

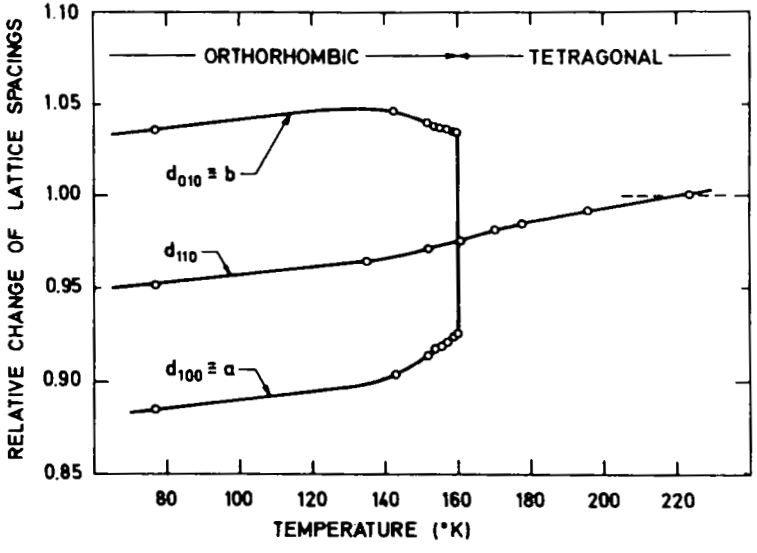


FIGURE 3 Temperature variation of $a$, $b$ and $d_{110}$ relative to their values at 223.5 K.

cell dimensions $a$, $b$ and $d_{110}$ relative to their values at 223.5 K. The quantities $a$ and $b$ show a behaviour characteristic of a first order phase transition at $T_c = 160$ K while $d_{110}$ varies smoothly and almost unaffected through the transition. The transition in DCN occurs 10 K below the transition in HCN. This isotope effect is much smaller and opposite in sign to the shift observed in the hydrogen bonded ferroelectrics, e.g. KDP. We conclude that the hydrogen bond itself plays a minor role in the transition and the decrease in $T_c$ is due to the lowering of some lattice mode frequencies with the increase in molecular mass.

Inelastic scans have been performed along the ($\bar{1}10$) direction in the (110) Brillouin zone following the suggestion of Rae that the phase transition is associated with an instability in a transverse acoustic phonon close to this direction. Some results are shown in Figure 4 where $q_{max}$ refers to the zone boundary in that direction. We observed a 3 peak intensity function as shown for $T = 135$ K at $q/q_{max} = 0.875$. The central peak is believed to arise from incoherent scattering from the whole of the illuminated sample and has been subtracted in all the other scans. The measurements confirm Rae's prediction of a very low energy phonon branch in this direction, the two peaks being due to the creation and annihilation of a phonon. This scattering has also been observed in other zones but the dynamical structure factor is biggest in the 110 zone. In the high temperature tetragonal phase the scans seem to

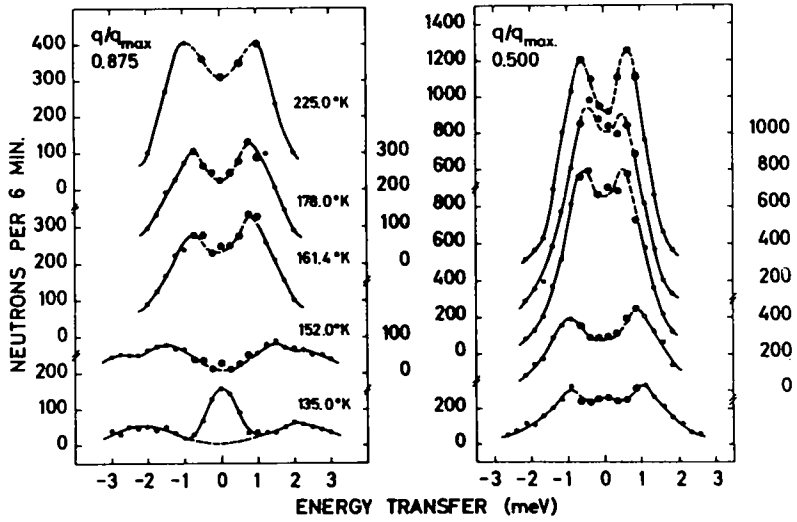


FIGURE 4 Neutron inelastic scattering for two $q$ vectors along the dotted line in Figure 1 in the 110 Brillouin zone. The centre peak (incoherent) in the lower left profile has been subtracted from the other profiles.

indicate a softening of the mode by about 25% between 225 and 178 K but no further softening towards the transition at 160 K.

We plan to grow by other techniques a larger and more perfect single crystal that will enable us to resolve the soft mode at smaller $q$ vectors and to observe if this mode couples to other lattice modes. We are also performing calculations using a computer model of the lattice dynamics to predict the neutron intensities in order to compare theory with experiment.

## References

W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.*, **4**, 330 (1951).
W. F. Giaque and R. A. Ruehrwein, *J. Am. Chem. Soc.*, **61**, 2626 (1939).
A. I. M. Rae, *Molec. Phys.*, **16**, 257 (1969).
A. I. M. Rae, *J. Phys. C: Solid State Phys.*, **5**, 3309 (1972).