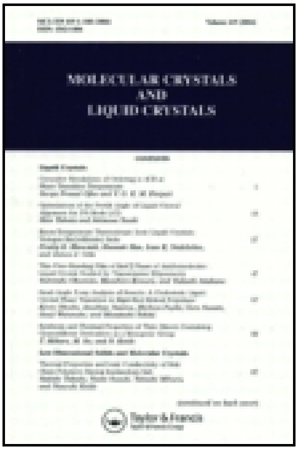

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Phase Transition Boundaries in 1,6-Di(Carbazolyl)-2,4-Hexadiyne

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PHASE TRANSITION BOUNDARIES IN 1,6-DI(CARBAZOLYL)-2,4-HEXADIYNE

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Abstract 1,6-di(N-carbazolyl)-2,4-hexadiyne has a first order phase transition at 142 K at one atmosphere pressure. The boundaries between the high and low temperature phase regions in single crystals have been observed by optical microscopy. Lattice parameters were measured and used to show that the phase boundaries occur on lattice planes for which the mismatch between the two phases is a minimum.

INTRODUCTION

1,6-di(N-carbazolyl)-2,4-hexadiyne, hereafter abbreviated DCH, is one of the many disubstituted diacetylenes that have been studied because solid-state polymerization leads to macroscopic, single-crystal, polymer products.[1-4] In addition to its unusual polymerization behaviour DCH monomer also undergoes a striking first-order phase transition at 142 K at ambient pressure.[4] At this temperature the crystal b-axis contracts by about 8% and the crystal density increases by about 5%. As a consequence of these dramatic changes there is a large thermo-chromic effect.[5]

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This is due to a large shift in the absorption energy of traces of polymer in the crystals in response to the change in their environment at the transition temperature. Because of the large density change the transition temperature is very sensitive to hydrostatic pressure.[6] Under a pressure of approximately 300 MPa the transition temperature is 300 K.

During the optical and pressure studies[5,6] distinct phase transition boundaries were observed. These phase transition boundaries have been studied by optical microscopy and their dynamics recorded using video techniques. In order to aid in the interpretation of these observations the crystal lattice parameters were determined at low temperature.

EXPERIMENTAL METHODS

DCH monomer was prepared using a modification of the method described by Yee.[7] Fine needle-like crystals were grown by slow evaporation of toluene solutions. A Ziess Universal Photomicroscope was used together with an EMI Emicooler cold stage. For dynamic studies a Sony TV camera was mounted above the vertical beam exit of the microscope. Photographic records were obtained either with the integral 35 mm camera or by photographing individual frames of the video recording. Crystal lattice parameters were measured using an Enraf-Nonius CAD-4 automatic four-circle diffractometer.

RESULTS AND DISCUSSION

Phase transition boundaries were observed both on cooling and heating through the phase transition at 142 K. Initially sharp phase boundaries are observed as shown in

Figure 1. Since the crystals are elongated along the b-axis and have prominent (100) facets the orientations of the phase boundaries can be deduced to be along the [031], [03$\bar{1}$], [041] [04$\bar{1}$] directions. Since the boundaries are sharp they must be the (013), (0$\bar{1}$3), (014) and (0$\bar{1}$4) planes respectively. The {013} planes occur much more frequently than the {014} planes.

Using the crystal lattice parameters from the literature[4,8] and measured by us (see Table I) the dimensions of the crystal lattice planes identified as phase boundaries can be determined. The percentage changes in lattice dimension, along the [0n1]

TABLE I. Lattice parameters of DCH as a function of temperature, the standard deviations of the least significant figures are shown in brackets.

Temperature(K)	300[4,8]	300	155	120[4,8]
a(x 10nm)	13.60(4)	13.629(1)	13.529(8)	13.38(1)
b(")	4.55(3)	4.5394(5)	4.527(2)	4.20(5)
c(")	17.60(4)	17.632(2)	17.54(1)	18.44(1)
$\beta(^{o})$	94.0(5)	93.379(6)	93.110(5)	92.0(5)
$\rho(g.cm^{-3})$	1.25	1.246	1.265	1.31
Z	4	4	4	4
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$

direction, and in area of the {01n} planes are listed in Table II. From these figures it can be seen that the (013)

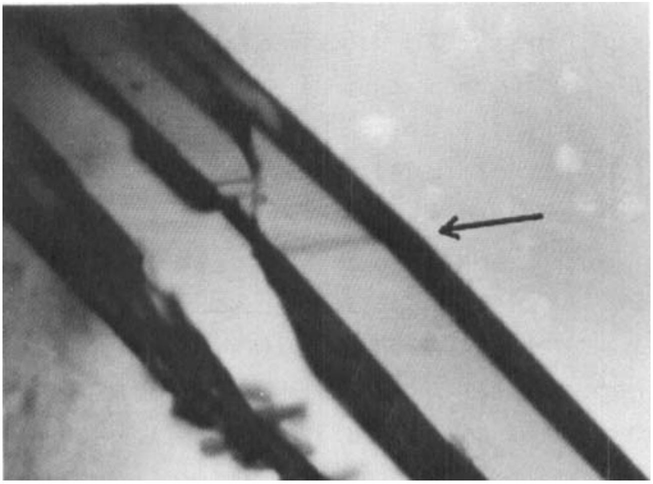

FIGURE 1. Sharp {013} boundary in DCH (arrowed), note bending of the crystal at boundary.

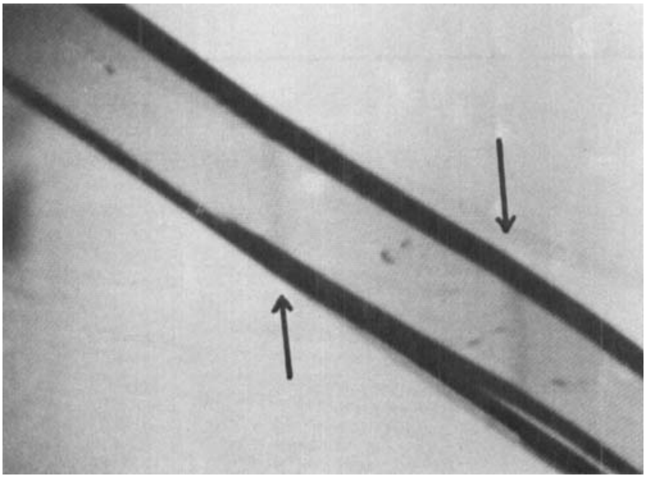

FIGURE 2. Two boundaries formed by local nucleation of the second phase (arrowed).

plane has the smallest change in both quantities. The contraction on the (014) plane is slightly smaller than the expansion on the (012) plane; though a small number of (014) planes occur no (012) planes have been observed. The lattice parameters can also be used to determine the orientations of the phase boundaries and the deviation of the crystal b-axis through the boundary. There is good agreement between the calculated and observed values.

TABLE II. Changes in lattice dimensions of DCH on cooling through the phase transition for the {01n} lattice planes, all values in percent.

n	1	2	3	4	5
$\Delta \ell[0n1]$	+4.4	+2.7	+0.7	-1.0	-2.4
$\Delta A(01n)$	+3.3	+1.6	-0.4	-2.5	-3.6

Repeated cycling through the phase transition leads to a build up of strain. Because the transition temperature is sensitive to strain this leads to local nucleation and pinning of the transition boundaries. Multiple boundaries, which often appear diffuse, are observed as shown in Figures 2 and 3. Single boundaries separating regions in the high and low temperature phases produce an easily detected deviation of the b-axis, multiple boundaries with thin lamellae of alternating phases produce only a lateral displacement in the multiphase region. Samples with many local nucleation sites for the phase transition have been observed to bend through angles approaching 360°. A less dramatic but similar curvature is shown in Figure 4.

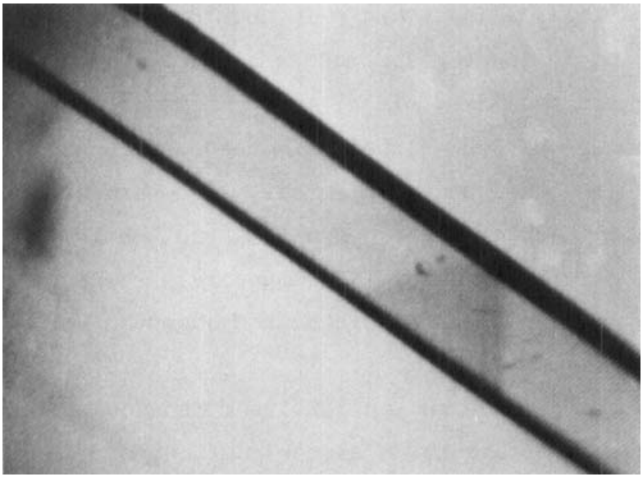

FIGURE 3. Multiple, diffuse boundaries locally nucleated, note absence of bending of the crystal.

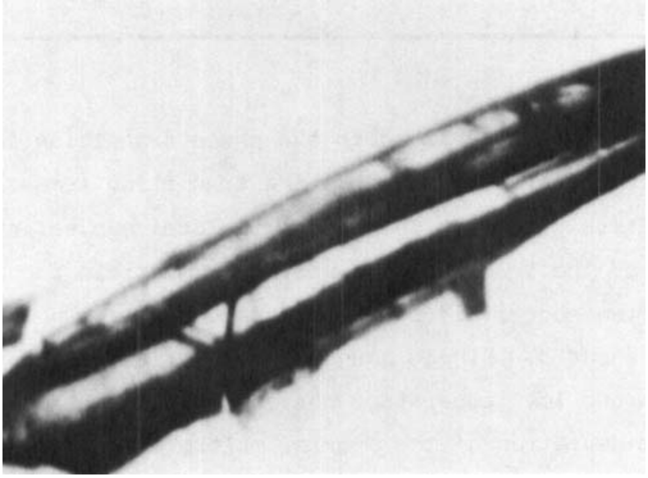

FIGURE 4. Multiply nucleated boundaries producing curvature, particularly of the upper thinner crystal.

Eventually such crystals disintegrate into a microcrystalline powder after many cycles through the phase transition temperature.

CONCLUSIONS

The phase transition boundaries in monomer DCH crystals have been shown to occur on lattice planes for which the mis-match of high and low temperature phases is a minimum. Typical examples of the phase-transition boundary structures observed have been presented. A more detailed account of this work will be published elsewhere.

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