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The Solid Phase Transformation in Dimethylacetylene at −119 °C*

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Dimethylacetylene (melting point −32 °C.) undergoes a phase transformation at −119 °C. The high temperature form is stable between −32 and −119 °C.; the space group is $P4_2/mnm$ and there are two molecules per unit cell. Cell dimensions are: $a = 5{\cdot}42 \pm 0{\cdot}02$ and $c = 6{\cdot}89 \pm 0{\cdot}02$ Å (at −50 °C.). The low temperature form is also tetragonal; the space group is $P4_12_12$ with four molecules per unit cell; $a = 5{\cdot}362 \pm 0{\cdot}006$ Å and $c = 13{\cdot}67 \pm 0{\cdot}03$ Å (at −135 °C.). The transformation is of the order–disorder type. In the low temperature structure each molecule is tilted in a specific sense out of the planes perpendicular to the c axis; in the high temperature form each molecule may be tilted in either of two possible directions. The magnitude of the tilt has been determined.

Introduction

Dimethylacetylene ($CH_3\text{–}C{\equiv}C\text{–}CH_3$), hereafter called DMA, is a colorless liquid which melts at −32 °C. and boils at 27 °C. An electron diffraction study of the structure, in the vapor phase (Pauling, Springall & Palmer, 1939), established that the molecule is linear with single and triple bond lengths of $1{\cdot}47 \pm 0{\cdot}02$ and $1{\cdot}20 \pm 0{\cdot}03$ Å, respectively. An X-ray diffraction study of the crystal structure at −50 °C. (Pignataro & Post, 1955) showed that the unit cell is tetragonal at that temperature and contains two molecules; the unit-cell dimensions are $a = 5{\cdot}42$, $c = 6{\cdot}89 \pm 0{\cdot}02$ Å. The space group is $P4_2/mnm$. The arrangement of the molecules in the unit cell at −50 °C. is shown in Fig. 1.

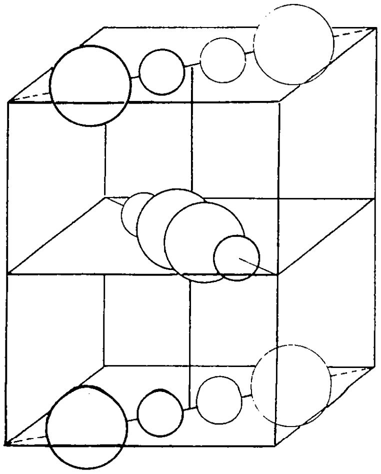

Fig. 1. Arrangement of molecules in high temperature phase.

Measurements of the specific heat of DMA (see Fig. 2) reveal an anomaly near −119 °C. (Yost, Osborne & Garner, 1941). The present investigation was undertaken to determine the nature of the structural changes associated with that anomaly.

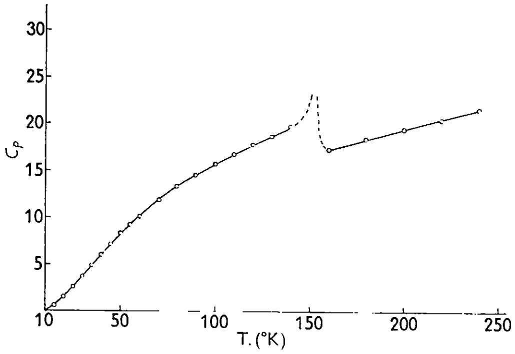

Fig. 2. Specific heat as a function of temperature.

Experimental

A quantity of DMA was distilled twice in vacuum and sealed into thin-walled glass capillaries which were then mounted on the goniometer arcs of precession and Weissenberg cameras. The specimens were cooled by standard methods. They were observed, while being cooled, with the aid of polarizing microscopes mounted on the X-ray cameras. Single crystals of the high temperature form of DMA were grown readily by repeated melting and slowly refreezing the contents of a capillary. The temperature was then generally lowered slowly (at about 10° per hour) through the transition temperature to −128 °C. The specimen was then annealed at this temperature for about half an hour and then cooled further to −150 °C. The optical observations indicated that single crystals of the high temperature form usually transformed into polycrystalline masses as the temperature was lowered through the transition. When the temperature was subsequently raised above the transition region, a

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single crystal of the high temperature phase was often recovered with the original orientation.

In one instance, single crystals of the low temperature form were preserved intact long enough to permit the taking of two oscillation photographs (15° each) at −150 °C. after which the crystal broke into fragments. The photographs, taken with the crystal oscillated about mean positions separated by 90°, were identical in appearance and confirmed that the low temperature form of DMA is tetragonal and that the axis of oscillation was the c axis. The photographs were of poor quality but could be indexed on the basis of a unit cell whose a axis was almost equal in length to that of the high temperature form but whose c axis was twice as long as that of the latter. The intensities and spacings of the ($hk0$) reflections of the two forms of DMA were almost identical, indicating that the c projections of the unit-cell contents of both forms were essentially identical in appearance. For additional crystallographic information, especially about the ($00l$) reflections, it was necessary to resort to powder methods.

For this purpose a Norelco diffractometer was used. The setup is shown in Fig. 3. The sample holder (b), a flat glass slide, was held firmly to the goniometer (d) by a metal spring (c). Temperatures at the specimen (a) as low as −170 °C. were obtained using a cold gas stream (g). The temperature was measured with a chromel p-alumel thermocouple (e). The thermocouple junction was placed on the specimen holder just outside the path of the X-ray beam. The conventional Norelco radiation shield (f) was used. The angular region from 10° to 80° (2θ, Cu K radiation) was repeatedly scanned at −135 °C. At that temperature, $a = 5{\cdot}362 \pm 0{\cdot}006$ Å and $c = 13{\cdot}67 \pm 0{\cdot}03$ Å. The variation of unit-cell dimensions with temperature was measured through the range of transformation (130 to 210 °K.). (See Table 1.) Both c and a increased in length at approximately the same rate as the temperature was raised. A plot of the volume *vs.* temperature is shown in Fig. 4. No anomaly in dV/dT was detected at the transition temperature.

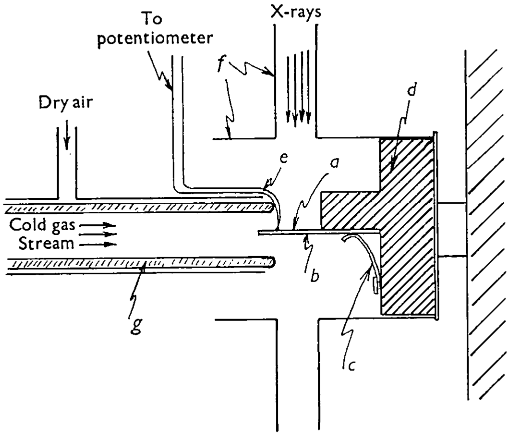

Fig. 3. Experimental arrangement for low temperature measurements with Geiger counter diffractometer (schematic).

Table 1. *Unit-cell dimensions vs. temperature*

(Low temperature phase)

Temperature	a	c
138 °K.	5·364 Å	13·676 Å
144	5·367	13·685
155	5·373	13·701
166	5·379	13·721
175	5·385	13·733
191	5·395	13·752

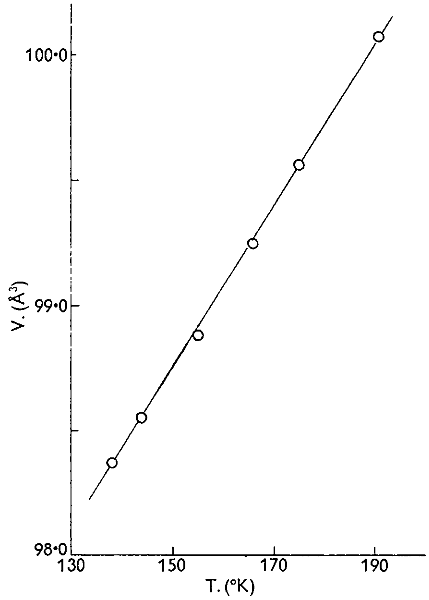

Fig. 4. Volume per molecule as a function of temperature.

Discussion

Reflections of the type ($00l$) with $l \neq 4n$ and of ($h00$) with h odd were systematically absent from all photographs and diffractometer traces of the low temperature form. The space group is therefore $P4_12_12$. There are four molecules in the unit cell (there are two in the high temperature form). The asymmetric unit of structure is half of one molecule.

In addition to the absences noted above, reflections of the type ($h0l$) with $2h+l = 2n$, with n odd, were systematically absent from all diagrams. The *International Tables of X-ray Crystallography*, Vol. 1, p. 182, states that atoms in positions $4a$ of this space group

$$(x,\, x,\, 0),\quad (\tfrac{1}{2}-x,\, \tfrac{1}{2}+x,\, \tfrac{1}{4}),\quad (\bar{x},\, \bar{x},\, \tfrac{1}{2}),\quad (\tfrac{1}{2}+x,\, \tfrac{1}{2}-x,\, \tfrac{3}{4})$$

limit ($h0l$) reflections to $2h+l = n$ odd or $4n$. It is tempting to assume that the converse relation also holds, i.e. that these absences imply the presence of atoms in these four-fold positions. This would be incorrect. It is readily shown by substitution in the expression for the structure factor that these absences result also from the presence of atoms in eight-fold positions of the type:

$$(x, x, z),\ (\bar{x}, \bar{x}, \tfrac{1}{2}+z),\ (\tfrac{1}{2}-x, \tfrac{1}{2}+x, \tfrac{1}{4}+z),\ (\tfrac{1}{2}+x, \tfrac{1}{2}-x, \tfrac{3}{4}+z);$$

$$(x, x, \bar{z}),\ (\bar{x}, \bar{x}, \tfrac{1}{2}-z),\ (\tfrac{1}{2}-x, \tfrac{1}{2}+x, \tfrac{1}{4}-z),\ (\tfrac{1}{2}+x, \tfrac{1}{2}-x, \tfrac{3}{4}-z)\ .$$

The latter permit us to place four molecules of DMA in the unit cell and are apparently the correct positions.

While no effort has been made to tabulate systematically all possible ambiguities of this type in the *International Tables*, it is clear that many such must exist and must be guarded against.

It is of some interest to compare the symmetry elements in the two crystalline forms of DMA. The 4_2 screw axis persists unchanged in the low temperature form but, as a result of the doubling of the c axis, it becomes a 4_1 screw. The n glide of $P4_2/mnm$ also is present in the low temperature cell but, because of the doubling of the c axis, the $c/2$ component of the glide translation becomes a $c/4$ translation.

As a result the systematic absences, which in the high temperature form are characterized by $(h0l)$ with $h+l = n$, n (odd), also occur in the low temperature form in somewhat disguised form. Below the transformation, reflections of the type $h+l/2 = n$ (odd) are absent. This is clearly equal to the condition $2h+l = 2n$ (n odd).

The absence of these reflections, i.e., $2h+l = 2n$ (n odd), indicates clearly the nature of the transformation. Below the transition the molecules are arranged in the positions shown in Fig. 5. The four carbon atoms of each molecule lie in the plane which includes the c axis and the diagonal of the c face. If one molecule is tilted 'up', then the operation of the screw axis will bring the molecule into a 'down' position at a distance of $c/4$ removed, finally repeating the original orientation four molecular layers above the first molecule.

In the high temperature form the molecules appear to be arranged randomly in either the 'up' or 'down' orientation at each molecular site. As a result, position A is effectively equivalent to one at B and the unit-cell dimension, in the c direction, is halved.

It would have been a simple matter to check this picture quantitatively if good single crystal data were available for the low temperature form. However, only a few reflection intensities could be measured with satisfactory precision for a check of this sort. Calculations, based on models did indicate that best agreement with these reflections was achieved when the molecule was tilted by at least 10°—but the error could be as great as 5°.

Excellent data (three-dimensional) were available for the high temperature form. Structure factors were therefore computed as follows: It was assumed that molecules were oriented randomly at each molecular site in either the 'up' or 'down' position. Calculations were based on a half molecule in the 'up' and a half molecule in the 'down' position at each site. Molecular

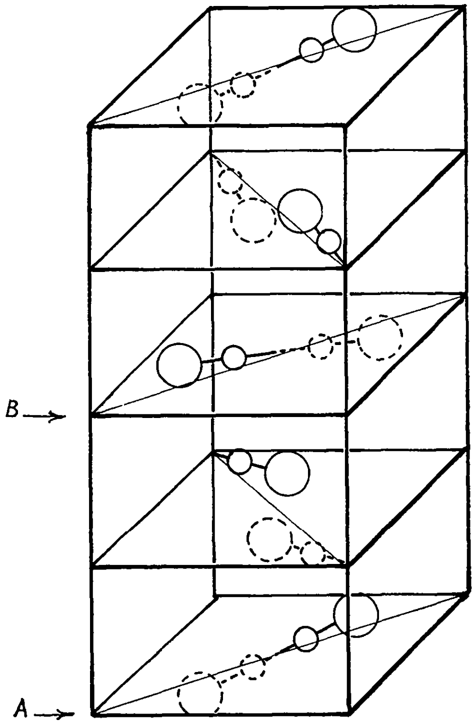

Fig. 5. Arrangement of molecules in the low temperature phase.

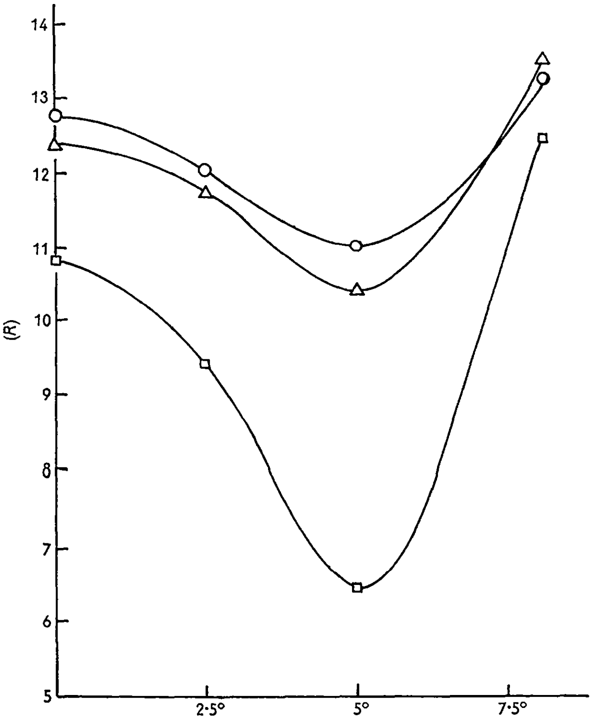

Fig. 6. R factor as a function of molecular tilt.

○: All reflections. △: All reflections, excepting (002) and (201). □: Reflections of type, $l^2/(h^2+k^2+l^2) \geq 0{\cdot}5$ only.

dimensions reported by Pignataro & Post (1955) were used in the calculations. Hydrogen atoms, 1·08 Å from the carbon atoms and assumed rotating freely about the C–C axes, were included in the calculations. Structure factors were computed assuming tilts of 0, 2½, 5 and 7½ degrees with the results shown in Table 2 and in Fig. 6.

Table 2. *R factor as a function of molecular tilt*

R	0	2½	5	7½
All reflections	12·77	12·02	11·02	13·21
All reflections except (002) and (201)	12·39	11·78	10·44	13·53
Reflections of type $l^2/(h^2+k^2+l^2) \geq 0{\cdot}5$ only	10·81	9·42	6·45	12·45

The (002) and (201) reflections were very intense and appeared to suffer strongly from extinction effects. They have therefore been excluded from some of the above calculations. It is clear that there is a distinct minimum in R when the molecular tilt is 5°. As might be expected, the minimum is sharpest when it is computed for reflections whose l index is relatively large.

Although the evidence is scanty for the low temperature form, the 10° tilt indicated for the phase appears physically reasonable and consistent with the high temperature data. The onset of the transition appears to involve a diminution of the angle of tilt above the transition as well as molecular disorder of the type described.

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The Crystal Structure of Mn_3Al_{10}

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The crystal structure of a previously unknown intermetallic compound Mn_3Al_{10}, hereinafter referred to as φ(AlMn), has been determined by X-ray analysis. The cell dimensions and atomic parameters of the structure and the interatomic distances between neighbouring atoms are given. The structure is very similar to that of β(AlMnSi) (Robinson, 1952) and comparisons between the two structures are made.

Introduction

Work by the author has shown the published Al–Mn phase diagram (Hansen, 1958) to be incorrect in the region 33* to 45% Mn. Crystals of the intermetallic compound φ(AlMn) of approximate composition 37% Mn have been grown by suitable heat treatment of aluminium–manganese alloys in alumina crucibles under an argon atmosphere (the phase appeared in approximately single-phase ingots of composition 37% Mn). The manganese and aluminium used were of the highest available purity (both 99·99%), and care was taken to ensure that no contamination occurred during the thermal treatment. Chemical analysis of the ingot from which the crystals used in this work were extracted gave a silicon content of less than 0·05%.

The unit-cell

The hexagonal unit-cell dimensions were measured by the method of Farquhar & Lipson (1946), using Cu $K\alpha$ radiation, and found to be:

$$a = 7{\cdot}543 \pm 0{\cdot}001, \quad c = 7{\cdot}898 \pm 0{\cdot}001 \text{ Å}.$$

The Laue group was determined as $6/mmm$.

The density of φ(AlMn) was measured, by the displacement method, as 3·65±0·05 g.cm.$^{-3}$. The calculated density for Mn_3Al_{10}, assuming two formula units per unit cell, (the number found in the subsequent structure determination) is 3·74 g.cm.$^{-3}$. The agreement between the two density values is satisfactory, the difference between them probably being due to porosity in the material.

Refinement of the structure

The unit-cell dimensions of φ(AlMn) and β(AlMnSi) are very similar, and the Laue groups of the two phases are identical; obviously, therefore, an intimate relationship exists between the two structures. The refinement proceeded on the assumption that the space

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* Weight compositions are used throughout this paper.