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Pressure-induced phase transition in adamantane. By T. ITO, *Faculty of Industrial Arts, Kyoto University of Industrial Arts and Textile Fibers, Matsugasaki, Kyoto, Japan 606*

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An X-ray study of adamantane under hydrostatic pressures up to 8000 kg cm^{-2} at room-temperature has confirmed that the pressure-induced phase transition from the face-centered cubic structure to a tetragonal structure takes place at 4800 kg cm^{-2} . The observed spacings and intensities strongly support that the pressure-induced structure of adamantane is the same as the temperature-induced structure reported by Nordman & Schmitkons [*Acta Cryst.* (1965). 18, 764–767].

Introduction

The phase transition of adamantane at 208.62°K at normal pressure has been studied from widely different viewpoints. Nordman & Schmitkons (1965) have shown that the transition involves change in molecular arrangements from a disordered face-centered cubic room-temperature structure to an ordered tetragonal low-temperature structure, with an increase in density from 1.08 g cm^{-3} at room-temperature to 1.18 g cm^{-3} at -110°C . Very recently, Breitling, Jones & Boyd (1971) have reported the pressure-induced phase transition in adamantane at room-temperature, suggesting that the pressure transition takes place by the same structural change as the temperature transition. In this paper some X-ray results which strongly support their report will be given.

Experiments

Adamantane (Aldrich Chemical Co.) was purified by recrystallization from light petroleum solution. It melted at $269\text{--}270.5^\circ\text{C}$. The X-ray diffraction photographs of the sample under high pressure were obtained with high-pressure X-ray diffraction apparatus of a piston-cylinder type which can be used up to 8 kbar (Kabalkina & Vereshchagin, 1962; Ito & Marui, 1971). The sample holder is a small tapered block of beryllium metal, with a drilled central hole 1 mm in diameter and 6 mm deep located in a heavy Maraging steel cylinder of 10 mm inside diameter and 100 mm outside diameter. The cylinder has apertures reaching the sample holder and can be coaxially mounted on a semicylindrical multiple exposure camera whose radius is $100 \pm 0.02 \text{ mm}$ through all the exposure positions (Ito & Marui, 1971). The powder sample was packed into the hole in the sample holder and placed under the pressure medium (water) in the cylinder, a portion of the medium being introduced through a pinhole into a high-pressure gauge of a strain-gauge type. The high-pressure gauge was calibrated against a lever-type controlled-clearance piston gauge with an estimated limit of uncertainty of less than $\pm 0.015\%$ up to 10000 kg cm^{-2} (Yasunami, 1968).

Results and Discussion

Fig. 1 shows 11 exposures at 20°C on the same film, where Ni-filtered $\text{Cu K}\alpha$ radiation was used with each exposure time 120 min. The pressures applied (expressed in kg cm^{-2}) are, from bottom to top, 1 (normal pressure), 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 1 and 277. The last is a residual pressure due to the friction between the Bridgman seal and the wall of the cylinder when the pressure was released from 8000 kg cm^{-2} . The exposures were carried out in order of increasing pressure. The pressure was raised

over a period of 3 min and a further 20 min was allowed for equilibration of the pressure before each X-ray exposure. From Fig. 1 it is evident that the pressure-induced phase transition in the crystal of adamantane takes place at a pressure p_r given by $4000 < p_r \leq 5000 \text{ kg cm}^{-2}$. The diffraction lines at normal pressure can be interpreted, as shown in Table 1, by a face-centered cubic lattice with $a = 9.42 \text{ \AA}$, in reasonable agreement with the previously reported values, e.g. $a = 9.45 \text{ \AA}$ (Nordman & Schmitkons, 1965). The diffraction lines at 5000 kg cm^{-2} , on the other hand, can be interpreted by a tetragonal lattice with $a = 6.54$ and $c = 8.82 \text{ \AA}$ (Table 1). These a and c values as well as the intensities determined by visual inspection are qualitatively in agreement with the results obtained by Nordman & Schmitkons (1965) for the low-temperature ordered structure of adamantane at -110°C ($a = 6.60$ and $c = 8.81 \text{ \AA}$). Thus our existing data indicate strongly that the room-temperature tetragonal structure of adamantane induced by pressure p_r is the same as the structure proposed by Nordman & Schmitkons (1965) for the low-temperature ordered structure in which the molecules rotate 9° about the c axis. As seen from Fig. 1, the pressure-induced transition of adamantane is reversible on releasing the pressure.

Table 1. Powder pattern data for adamantane at 20°C

Pressure (kg cm^{-2})	Intensity	hkl	d (\AA)	
			Observed	Calculated
1	rs	111	5.44	5.44
	s	200	4.71	4.71
	vw	220	—	3.33
	w	113	2.84	2.84
	m	222	2.72	2.72
	vw	400	—	2.36
	w	331	2.16	2.16
	5000	rs	011	5.25
s		110	4.63	4.62
m		002	4.41	4.41
w		012	3.65	3.66
w		112	3.19	3.19
m		021	3.07	3.07
w		121	2.78	2.78
s		022	2.63	2.63
w		122	2.44	2.44
w		004	2.19	2.21

In order to clarify the detail of the phase transition of adamantane under pressure, multiple exposures were taken with increasing pressure at intervals of 100 kg cm^{-2} from 4500 up to 5200 kg cm^{-2} . The results are shown in Fig. 2, which clearly shows that $4700 < p_r \leq 4800 \text{ kg cm}^{-2}$. This is in agreement with the results obtained by Breitling, Jones

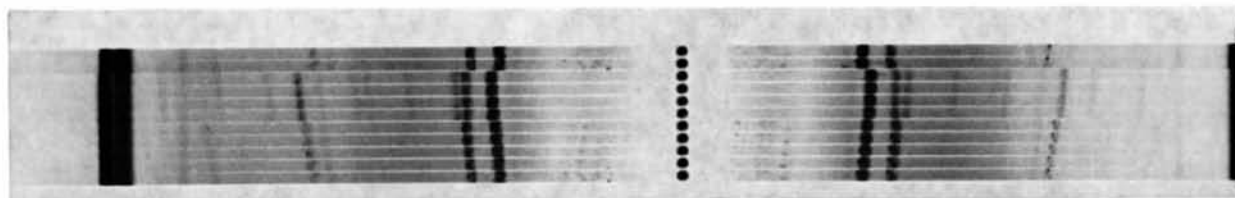


Fig. 1. Multiple-exposure powder patterns of adamantane under various hydrostatic pressures up to 8000 kg cm^{-2} . The values of the pressure are given in the text. Camera radius 100.05 mm ; $\text{Cu } K\alpha$ radiation; $20 \pm 1^\circ\text{C}$.



Fig. 2. Multiple-exposure powder patterns of adamantane under hydrostatic pressures around p_T ($p_T = 4800 \text{ kg cm}^{-2}$). Pressures (kg cm^{-2}): (from bottom) 1, 4500, 4600, 4700, 4800, 4900, 5000, 5100, 5200, 1 and 298 (released from 5200 kg cm^{-2}). Exposure time is 160 min for each exposed zone.

& Boyd (1971). Further inspection of Fig. 2 suggests that the structure initially induced by the transition at 4800 kg cm⁻² is not stable within the time scale of the X-ray exposure. For example the spacing of the (110) plane of the tetragonal structure at 4800 kg cm⁻² still shows a little expansion with a further increase in pressure of 100 kg cm⁻², as compared with Fig. 1, where steady reduction of the (110) spacing is seen above 5000 kg cm⁻². In all these pressure regions, the (011) and (002) planes show steady decrease in spacing with increasing pressure and are more compressible than the (110) plane. Thus the crystal of adamantane after the transition is fairly anisotropic in the strains induced by hydrostatic pressures, being more compressible in the *c* direction than in the directions perpendicular to it. The strains are, however, isotropic before the transition, as shown by the cubic structure sustained under pressure (Fig. 1). The unit-cell dimension of the cubic structure just before the pressure transition is $a = 9.20 \text{ \AA}$ (at 4600 kg cm⁻²) and the calculated volumetric strain of the crystal at this stage is 6.9%.

It is worth while to note that at *p*, and 20°C, the crystal transition in adamantane arises in such a way that one of

the original cubic axes shrinks 4.2% and becomes parallel to the tetragonal *c* axis, while both of the other two axes expand 0.5% in the tetragonal [110] and $[\bar{1}10]$ directions (numerical values were calculated at two pressures, 4600 and 5000 kg cm⁻²). The net effect is an abrupt volumetric contraction of 3.1%, which corresponds to abrupt molecular rearrangements toward denser packing.

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The crystal structure of α -D-glucose monohydrate. By E. HOUGH,* S. NEIDLE,† D. ROGERS and P. G. H. TROUGHTON, *Chemical Crystallography Laboratory, Imperial College, London, SW7 2AY, England*

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The crystal structure of α -D-glucose monohydrate has been refined with intensity data measured diffractometrically, using the coordinates from the photographic study of Killean, Ferrier & Young [*Acta Cryst.* (1962). **15**, 911]. The final *R* index is 0.0301 for 906 statistically significant reflexions.

Introduction

The determination of the crystal structure of α -D-glucose monohydrate has been previously reported by Killean, Ferrier & Young (1962). Their study was based on visual estimation of Weissenberg photographs, and their model refined to an *R* of 0.17. This communication reports an accurate re-refinement using intensities estimated diffractometrically.

Experimental

A single crystal kindly supplied by Dr R. C. G. Killean was used. Data were collected on an off-line Siemens automatic diffractometer, with the crystal mounted about the *a* axis. The compound crystallizes in the space group $P2_1$, with lattice constants $a = 8.803$ (1), $b = 5.085$ (1), $c = 9.708$ (2) Å, and $\beta = 97.67$ (1)°. Intensity data were collected using a five-value measuring technique (Allen, Rogers & Troughton, 1971), to a limit of 70° in θ , using Cu $K\alpha$ radiation. 915 independent reflexions were recorded, of which 906 had intensities significantly greater than background [$I > 2.58\sigma(I)$].

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Structure refinement

Least-squares refinement was started with the coordinates of Killean *et al.* for the carbon and oxygen atoms, which were refined anisotropically. The positions of the hydrogen atoms were deduced from difference maps, and refined with isotropic temperature factors. The scattering factors used for carbon and oxygen were those published by Cromer & Waber (1965), and for hydrogen those given by Stewart,

Table 1. *Final positional parameters for the non-hydrogen atoms ($\times 10^4$), as fractions of the unit-cell edges*

	Standard deviations are in parentheses.		
	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	1891 (3)	1372	700 (3)
C(2)	1088 (3)	14 (6)	1783 (3)
C(3)	1942 (3)	308 (7)	3245 (2)
C(4)	3611 (3)	-458 (6)	3235 (3)
C(5)	4322 (3)	1058 (6)	2142 (3)
C(6)	5959 (3)	296 (8)	2033 (3)
O(1)	1814 (2)	4128 (5)	858 (2)
O(2)	-467 (2)	833 (5)	1686 (2)
O(3)	1227 (2)	-1425 (5)	4112 (2)
O(4)	4442 (2)	96 (5)	4578 (2)
O(5)	3450 (2)	544 (5)	792 (2)
O(6)	6133 (2)	-2493 (5)	1870 (2)
O(7)	-1179 (2)	-4750 (5)	3217 (2)