

Table 1. *Refined atomic parameters*

Positional parameters and thermal parameters, B_i , where
 $T_i = \exp(-B_i \sin^2 \theta / \lambda^2)$,
 from the final least-squares analysis

No.	Type	x	σ_x	y	σ_y	z	σ_z	B
1	C	0.071	(5)	-0.140	(6)	0.028	(2)	1.0
2	C	0.056	(7)	-0.024	(5)	0.093	(3)	1.0
3	C	-0.011	(6)	0.124	(5)	0.063	(3)	1.0
4	Cl	-0.024	(2)	0.260	(2)	0.142	(1)	5.5
5	Cl	0.141	(2)	-0.335	(2)	0.071	(1)	5.5
6	O	0.095	(4)	-0.058	(4)	0.181	(2)	3.4
7	C	0.576	(6)	-0.132	(6)	0.057	(3)	1.9
8	C	0.542	(8)	0.007	(5)	0.098	(3)	1.9
9	C	0.479	(6)	0.130	(6)	0.037	(3)	1.9
10	CH ₃	0.446	(6)	0.302	(7)	0.086	(3)	6.0
11	CH ₃	0.654	(6)	-0.265	(8)	0.116	(4)	6.0
12	CH ₃	0.590	(7)	0.034	(8)	0.202	(4)	6.0

deviations are listed in Table 1; the standard deviations are about 0.06 Å for the positions of the light atoms and 0.02 Å for the chlorine atoms. (These values are in approximately the expected ratio whereas, as Donohue & Trueblood point out, the standard deviations given by HW are greater for the chlorine atoms than for the lighter atoms.) The standard deviations in the temperature factors B are about 2.0 for the light atoms and 0.7 for the chlorine atoms. In the last least-squares refinement cycle no coordinate shift was as much as 1/3 of its standard deviation. The final R factor was 0.14 compared with the value 0.27 we obtained with the parameters of HW.

Our results indicate that, within the large experimental errors, both the chloranil and the hexamethylbenzene

molecules are planar. The maximum deviation from the least-squares plane of the chloranil molecule, calculated with weights proportional to the atomic numbers,* is 0.087 Å for two of the carbon atoms; the maximum deviation from the best plane of the hexamethylbenzene molecule is 0.045 Å. The two planes are closely parallel, the calculated dihedral angle being 2.1°. Similarly, the bond distances show no significant deviations from the expected values, the extreme value 1.71 Å calculated for a pair of C-CH₃ bonds being only two standard deviations from the normal distance of 1.54 Å.

Accordingly, we reach the conclusion that the experimental data are compatible with planar molecules having normal dimensions and that it is not necessary to postulate, as HW have done, a zigzag arrangement of polarization bonds to explain the structure.

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References

- DONOHUE, J. & TRUEBLOOD, K. N. (1956). *Acta Cryst.* **9**, 965.
 HARDING, T. T. & WALLWORK, S. C. (1955). *Acta Cryst.* **8**, 787.
 NYBURG, S. C. (1961). *X-ray Analysis of Organic Structures*, p. 287. New York: Academic Press.

* It is clearly more appropriate to include all twelve atoms of the chloranil molecule in the calculation of the best plane than (as HW did) to consider only the six carbon atoms.

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The crystal structure of the chloranil-hexamethylbenzene complex. By S. C. WALLWORK, *Department of Chemistry, University of Nottingham, England* and T. T. HARDING, *Imperial Chemical Industries, Ltd., Billingham Division, Billingham, Co. Durham, England*

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The refinement of the crystal structure of the chloranil-hexamethylbenzene complex by Jones & Marsh (1962) confirms the suggestion already made (Wallwork, 1961) that the molecular distortions originally reported (Harding & Wallwork, 1955) are probably not significant. They were mistakenly interpreted as being significant in the original work because the standard deviations of atomic positions were incorrectly calculated. In spite of the improvements in R and molecular planarity brought about by the recent refinement it is clear that the present X-ray data are not sufficient to establish accurate atomic

positions. New and more extensive data are now being obtained at about -100 °C. and these will be used in a further refinement of the structure.

References

- HARDING, T. T. & WALLWORK, S. C. (1955). *Acta Cryst.* **8**, 787.
 JONES, N. D. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 809.
 WALLWORK, S. C. (1961). *J. Chem. Soc.*, p. 494.

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Some observations on growing crystals of argon. By L. H. BOLZ, H. P. BROIDA and H. S. PEISER, *National Bureau of Standards, Washington D.C., U.S.A.*

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There is considerable interest in the measurement of the properties of single crystals of the rare gases [Kyoto

Conference on Magnetism and Crystallography (1961), Cook (1961), Jones (1958), and Dobbs & Jones (1957)].

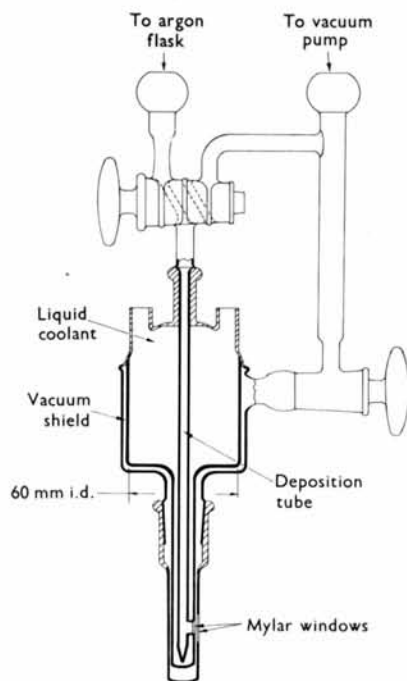


Fig. 1. Crystal growth Dewar.

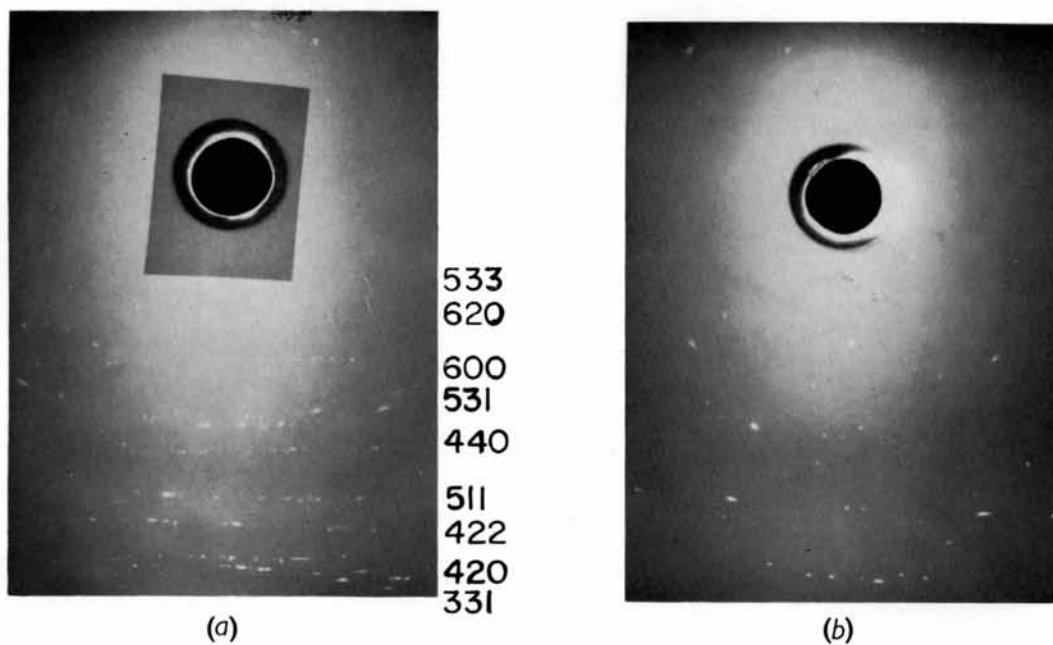


Fig. 2. X-ray glancing-angle diffraction photographs of argon grown at the following rates: (a) 4 mm./min., (b) 1 mm./min.

To the best of our knowledge, no one has yet made a large single crystal of any of the rare gases. Argon is close-packed cubic and its crystal growth has been studied to some extent [Dobbs & Jones (1957)].

In compact, transparent, optically isotropic solids grain boundaries may not constitute optical discontinuities; therefore, transparency can not be used as evidence against polycrystalline character.

Barker, Dobbs & Jones (1953) obtained compact solids by slow cooling from vapor. X-ray pictures of these solids showed them to be polycrystalline with a grain size of around 0.1 mm. Stansfield (1956) grew similar solids by a modified Bridgman method. He progressively froze argon from a melt by lowering a tube into liquid oxygen near 70 °K. at a rate of 1 mm./min. By a thermal etch technique, he estimated the grain size to be up to 4 mm. Barker & Dobbs (1955) observed a rapid increase of absorption of 1-mm. ultrasonic waves when compact argon was annealed above 75 °K. This increased absorption may be indicative of grain growth to dimensions comparable with the ultrasonic wave-length.

There are other methods for obtaining compact solid argon. Stewart (1955) compacted loosely packed crystal aggregates in a 1-cm.³ steel cavity at 4000 atm. at 65 °K. White & Woods (1956) filled a 0.5 × 3" Inconel tube at 78 °K. above the triple point pressure (516 mm. of Hg) and obtained a transparent solid grown from the bottom and sides. The grain size in these studies was not measured.

Our experimental arrangement (see Fig. 1) like Stansfield's (1956) follows Bridgman's method and consists essentially of a glass inner tube (ca. 10 mm. O.D.) connected to an argon-containing flask at room temperature. This tube is surrounded by two other tubes—all of unsilvered glass for ease of observation. The outermost tube is a vacuum jacket, the middle one serves to hold the liquid coolant. Usually the coolant was at temperatures nearer to the melting point of argon, 83.6 °K., than in Stansfield's (1956) experiments. Provision is made for the coolant level to be raised very gradually at rates from about 0.2 to 2 mm./min. They are fast compared with the rates commonly used for the crystallization of metals by Bridgman techniques [Lawson & Nielsen (1958)]. As the sample tube is cooled, argon condenses to a liquid, which then freezes to a clear solid. In most experiments, the argon gas supply was turned off at the stopcock when the desired quantity of liquid had collected. By rapid cooling such that a solid crust is formed on the liquid argon surface, it is possible to obtain vapor snakes [Verschlingel & Schiff (1954) and Stansfield (1956)].

In some of our experiments, the cold cell described above was modified for entry and exit (over a cone of 55° semi-vertex angle) of X-rays (Fig. 1) by addition of Mylar windows. This apparatus fits onto the sample holder platform of a G.E.XRD5 X-ray goniometer adapted for the taking of glancing-angle photographs, with sample oscillation arbitrarily set at 15°. The number of spots per Debye-Scherrer ring is then inversely proportional to the grain size. Knowing the multiplicity of the diffracting planes, the proportion of the Debye-Scherrer 'ring' recorded and the area of sample (about 5 mm.² in our experiments) irradiated, grain-size estimates (Peiser,

Rooksby & Wilson, 1955) of up to 4 mm. have been obtained. Two diffraction photographs (Fig. 2) show by inspection that larger grains are produced by slower cooling rates. Thus, our results encourage the view that large crystals of argon can be grown.

We have also grown transparent solid argon films by quenching argon vapor onto a copper cold finger at about 4 °K. The argon was introduced slowly through a flow gage. The X-ray diffraction record, using the cold cell described by Black *et al.* (1958), shows these argon films to be polycrystalline with appreciable line-broadening, indicating a grain size of the order of a few hundred Ångström units.

When the quenching becomes less efficient by increasing the film thickness or the flow rate, the appearance of the argon film becomes 'snowy', that is, opalescent. This indicates that the films are no longer compact. The X-ray diffraction maxima sharpen, but remain continuous. We believe that there are dendritic crystals, elongated along the [111] direction, growing perpendicularly to the deposition surface. The principal evidence for this hypothesis was obtained in collaboration with F. A. Mauer. It is based on X-ray diffractometer traces of argon depositing during gradual warm-up well below the triple-point temperature. The deposits are initially characterized by strongly preferred orientation (111) parallel to the substrate surface. Later, approximately random orientation is observed such as could be caused by dendrite branching or bending. Eventually, when surface evaporation becomes rapid, just before loss of the entire argon film, well oriented (111) layers are re-exposed to the X-ray beam.

References

- BARKER, J. R. & DOBBS, E. R. (1955). *Phil. Mag.* **46**, 1069.
 BARKER, J. R., DOBBS, E. R. & JONES, G. O. (1953). *Phil. Mag.* [7], **44**, 1182.
 BLACK, I. A., BOLZ, L. H., BROOKS, F. P., MAUER, F. A. & PEISER, H. S. (1958). *J. Res. Nat. Bur. Stand., Wash.* **61**, 367.
 COOK, G. A. (1961). *Argon, Helium and the Rare Gases*, Vol. 1. *History, Occurrence and Properties*. (See especially chapter 9 by A. C. Hollis Hallett 'Liquid and Solid-State Properties'). New York and London: Interscience Publishers.
 DOBBS, E. R. & JONES, G. O. (1957). *Rep. Phys. Soc. Progr. Phys.* **20**, 516.
 JONES, G. O. (1958). *Z. phys. Chem.* **16**, 267. *Kyoto Conference on Magnetism and Crystallography*. (1961). Science Council of Japan proceedings in press.
 LAWSON, W. D. & NIELSON, S. (1958). *Preparation of Single Crystals*. London: Butterworths.
 PEISER, H. S., ROOKSBY, H. R. & WILSON, A. J. C. (1955). *X-Ray Diffraction by Polycrystalline Materials*. London: The Institute of Physics.
 STANSFIELD, D. (1956). *Phil. Mag.* [8], **1**, 934.
 STEWART, J. W. (1955). *J. Phys. Chem. Solids*, **1**, 146.
 VERSCHLINGEL, R. & SCHIFF, H. I. (1954). *J. Chem. Phys.* **22**, 723.
 WHITE, G. K. & WOODS, S. B. (1956). *Nature, Lond.* **177**, 851.