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Composite Hexabromobenzene Crystals

By E. G. Boonstra and F. H. Herbstein

National Physical Research Laboratory, Council for Scientific and Industrial Research, Pretoria, South Africa

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Weissenberg photographs of hexabromobenzene crystals have shown that many crystals consist of two or more portions. It has been found that two such portions always have their b axes (*i.e.* the needle axes) parallel. The difference in orientation between them is always one of two experimentally determined angles, or a linear combination of these two angles. The phenomenon cannot be termed twinning and its relation to true twinning is discussed. It is suggested that the formation of such composite crystals may be due to oriented overgrowth or oriented agglutination of small crystallites, and results from the pseudo-hexagonal symmetry of the lattice. Preliminary attempts to explain why only two orientation laws are observed, and why true twinning has not been found, have not been successful.

1. Introduction

Hexabromobenzene crystallizes from xylene in long needles showing straight extinction. The cell dimensions were recently measured (Herbstein, 1963) as

$$a = 15{\cdot}3816 \pm 0{\cdot}0010,\ b = 4{\cdot}002 \pm 0{\cdot}003,$$
$$c = 8{\cdot}3768 \pm 0{\cdot}0008\ \text{Å};\ \beta = 92{\cdot}691 \pm 0{\cdot}004^\circ \text{ at } 20\ ^\circ\text{C.},$$

confirming Mark's (1924) original but less accurate results. The space group is $P2_1/n$ with two molecules per unit cell, and the crystals are elongated along b (Gafner & Herbstein, 1960). The pseudo-hexagonal nature of the crystals is clearly shown by the unit cell chosen by Mark ($a = 8{\cdot}44$, $b = 4{\cdot}04$, $c = 17{\cdot}3$ Å and $\beta = 116^\circ\ 30'$, space group incorrectly given as $P2/c$) and by the results of the structure analysis of the isomorphous hexachlorobenzene (Lonsdale, 1931; Tulinsky & White, 1958).

It was noticed here that needle-axis Weissenberg photographs from various crystals in a given crop were not identical. Some photographs could be indexed in terms of the unit cell given above, but others had more complicated patterns. It was later realized that the more complicated photographs consisted of two or more single-crystal patterns shifted with respect to each other along the translation direction of the camera. Thus the crystals used for these photographs are composite, and the portions of which they are composed are rotated relative to each other about the common direction of their b axes. Examination of a number of composite crystals showed that definite and reproducible orientation relationships existed between different portions; only two different orientation relationships were found.

The phenomenon is provisionally ascribed to oriented overgrowth or oriented agglutination, but the details of the nucleation and growth of the portions to form a composite crystal are not clear.

2. Experimental

2·1. *Growth of crystals*

Hexabromobenzene from different sources was used in this work: one batch was synthesized here by the method of Hermion & Anderson (1944) and two other lots were obtained from Dr Th. J. de Boer (University of Amsterdam) and Dow Chemical Co. All three samples gave the same results. Crystals were grown by saturating boiling xylene with hexabromobenzene and cooling slowly. In this way both single and composite crystals were formed. No detailed investigation was made of how the conditions of crystallization affected the formation of composite crystals.

2·2. *Morphology*

The face development of well-formed single crystals is $\{100\}$, $\{101\}$ and $\{10\bar{1}\}$. The measured interfacial angles are given in Table 1 together with the values calculated from the lattice parameters determined by Herbstein. Optical goniometer measurements on composite crystals suggested that in addition to these faces, other small faces of the forms $\{001\}$, $\{301\}$ and $\{30\bar{1}\}$ were sometimes present. In general the face development of the composite crystals was too complicated and imperfect to yield much information. The calculated values of the interfacial angles for the second set of forms are included in Table 1 to illustrate the pronounced pseudo-hexagonal symmetry of the forms in the [010] zone.

Table 1. *Interfacial angles*

Faces	Angle (calc.)	Angle (meas.)
(100), (101)	59° 22′ ± 01′	59° 30′ ± 06′
(100), $(10\bar{1})$	63° 31′ ± 01′	63° 27′ ± 06′
(101), $(10\bar{1})$	57° 07′ ± 01′	57° 03′ ± 06′
(001), (301)	56° 35′ ± 01′	
(001), $(30\bar{1})$	60° 30′ ± 01′	
(301), $(30\bar{1})$	62° 55′ ± 01′	

2·3. *X-ray diffraction*

The [010] spacing was identical on all *b*-axis 15° oscillation photographs, but some crystals gave more densely-populated layer lines than others. Zero-layer Weissenberg photographs also showed this difference in the number of reflexions. The *h0l* Weissenberg photographs of a single crystal (Fig. 1(*a*)) can be indexed in terms of the unit cell given; there is pronounced pseudo-hexagonal symmetry, especially in the intense low-order reflexions. A typical *h0l* photograph of a composite crystal is shown diagrammatically in Fig. 1(*b*). This specimen consists of two portions, and it was found that the two single-crystal patterns could be brought into coincidence by a lateral shift of the one pattern relative to the other along the translation direction of the camera; this corresponds to a relative rotation of about 60° about the oscillation axis. Since the cell dimensions are known, the requirements that the three axes form a right-handed set, and that $\beta > 90°$, enable one to define the $+b$ direction uniquely from such photographs. It follows therefore that the two portions of the composite crystal are so oriented that they have a common $+b$ direction. Their mutual relationship can then be expressed by the relative angular rotation about their common *b* axis required to make the directions of any other given lattice vector in both portions parallel.

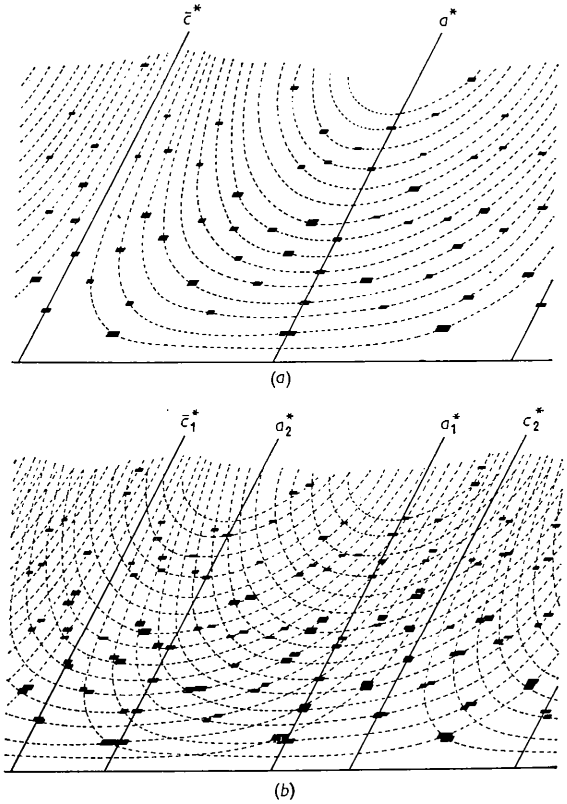

Fig. 1. Diagrammatic representations of *h0l* Weissenberg photographs. (*a*) Single crystal. (*b*) Composite crystal (two portions). For clarity, only the festoons with *h* fixed and *l* variable have been included.

Zero-layer *h0l* Weissenberg photographs were taken of six composite crystals. The number of portions varied from two to six, and the portions differed in size by factors of about 2 to 10. Fairly intense spots were in general obtained for two or three portions only. Measurements of the lateral separation between corresponding spots on the Weissenberg photographs showed that the observed relationship could be expressed in terms of an angle of either about 56 or 63°. These two alternatives seemed to occur with roughly equal frequency. The various portions did not in general have the same length, and consequently the translation measurements are subject to an error of about 1°.

These angles were therefore measured more accurately by the θ-method (Weisz, Cochran & Cole, 1948). Tests on single crystals showed that these could be set sufficiently accurately to give 2θ values which agreed with calculated values to within a few minutes of arc. With a composite crystal, the goniometer angles for the occurrence of a given reflexion from first the one portion, and then from the other portion, were determined. The difference between these values then gave the required angular rotation between the two portions. Two composite crystals, which consisted of two and four portions, were examined and four values were obtained for the angular rotation. An individual measurement on the goniometer circle could be made to about 6 minutes of arc, and it was found that the estimated standard deviation (e.s.d.) of an angular-rotation value was 5 minutes of arc in favourable circumstances. The values obtained in a number of measurements were 56° 17′, 56° 25′, 63° 36′ and 63° 49′. The final weighted-average values (together with e.s.d.) were 56° 20′ ± 06′ and 63° 42′ ± 09′.

It has therefore been established that composite crystals of hexabromobenzene are formed in which the *b* axes of the various portions are in parallel orientation. Two orientation laws have been definitely established in those instances where the crystal consisted of two portions only, the angular orientation difference being 56° 20′ or 63° 42′. In crystals with more than two portions all the observed angular orientation differences could be attributed to these two laws, acting either singly or in combination, *e.g.* an angle of 59° 58′ or 7° 22′ will exist between two portions which are related to a third portion by orientation differences of 56° 20′ and 63° 42′. Such additional angles are not considered further, since they do not seem to occur directly when there are only two portions present in the crystal.

3. Discussion

The facts that the *b* axes of the two portions are parallel, and that the angular rotations needed to achieve the same orientation for the two portions have the above values, show definitely that this phenomenon cannot be true twinning (Cahn, 1954). Instead it is an example of the 'oriented but non-parallel and non-symmetric growth of two similar crystal individuals' which Neuhaus (1951) included in his classification of possible types of epitaxial growth. Other examples are the oriented agglutination of small alum cubes on octahedral alum crystals, with ⟨110⟩ lattice rows parallel (Shaskolsky & Shubnikov, 1933) and the 'Zinnwald' twin law in quartz, in which the close-packed directions in both individuals are parallel (Drugman, 1928). Alternatively, the composite crystals could be described as monoperiodic twins (Friedel, 1933), but the use of 'twin' in this way seems undesirable as it may lead to confusion.

A study of the possible interplanar angles shows that, as a purely formal description, the angle of 56° 35′ will be found when the (001) plane of the one portion is parallel to the (301) plane of the second portion. Similarly 63° 31′ is the angular orientation difference between the two portions, when the planes (100) and $(10\bar{1})$ of the two portions are parallel. It is instructive to consider the relations between the present results and twinning. The face development of composite crystals is more nearly hexagonal than for single crystals. A small interfacial angle of about 6° 30′ is often found on composite crystals, as happens in reticular pseudo-merohedry (Cahn, 1954). The face development may then be so symmetrical that it is impossible to determine the $+b$ direction from the morphological data of only the $(h0l)$ forms; one finds that the data contain an apparent mirror plane in addition to a centre alone. In these macroscopic features the phenomenon resembles true twinning. The difference between this phenomenon and true twinning may be explained in terms of the lattice. If the small deviations of β from 90° and of c/a from $1/\sqrt{3}$ are ignored, then two possible twin laws of interest are those with (101) and (301) as composition planes. Under these assumptions the $+b$ direction is not unique and the twins are related by a rotation of 180° about the normal to the composition plane. The twinning would then be termed reticular merohedry. If the ratio c/a departs slightly from $1/\sqrt{3}$, but β is still 90°, the process is termed twinning by reticular pseudo-merohedry. If, however, β is not exactly 90°, then the $+b$ direction is uniquely determined, and in real twinning the two portions must have their $+b$ axes in anti-parallel orientation. This has not been observed here, but the parallelism of firstly (001) and (301), and secondly of (100) and $(10\bar{1})$ may be related to ideal twinning in the following ways. In the first case, twinning on (101) will correspond to parallelism of (101) and $(10\bar{1})$ but this is closely equivalent to parallelism of (001) and (301) or of (001) and $(30\bar{1})$. This is illustrated in Figs. 2(*a*), (*b*). The closeness of this equivalence will depend on the actual values of β and c/a. Similarly in the second case, twinning on the (301) face corresponds to parallelism of (301) and $(30\bar{1})$, which is in turn closely equivalent to parallelism of (100) and (101) or of (100) and $(10\bar{1})$.

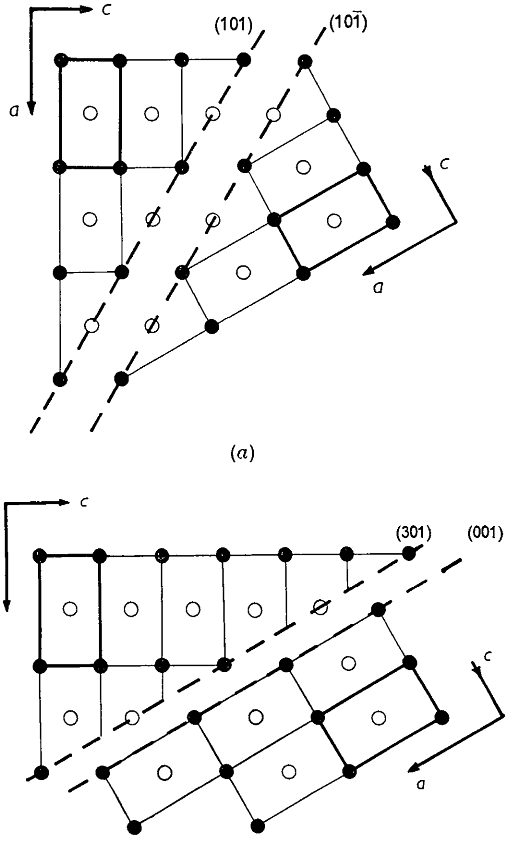

Fig. 2. Correspondence in idealized structure ($c/a = 1/\sqrt{3}$, $\beta = 90°$) between (*a*) parallelism of (101) and $(10\bar{1})$ and (*b*) parallelism of (301) and (001). Full circles at height 0, open circles at height $+\frac{1}{2}b$. Relative difference in height of the two portions unknown.

This description shows that the phenomenon is not true twinning but that it may be attributed to oriented overgrowth or oriented agglutination. This is reasonable since the faces (100), (101), $(10\bar{1})$ occur on the crystals, and the faces (001), (301), $(30\bar{1})$ may be expected to be present in small crystallites. The same growth mode may be postulated to occur as has been suggested for twinning (Buerger, 1945). On a parent crystal a high ledge is supposed to be present on one of the growth faces. A small crystallite may then be deposited on this growing crystal. The chance of retention is highest when it is seated in this re-entrant face. Because of the pronounced pseudo-symmetry an incorrect orientation is also likely to be retained. It is not clear why only two out of the six possibilities of oriented overgrowth or oriented agglutination are observed, and why twinning (*i.e.* with the $+b$ axes anti-parallel) does not seem to occur.

The discussion up to now has been in terms of the lattice. In an attempt to find an answer to the above questions some attention has been given to the molecular arrangement. The set of equivalent positions occupied by the molecular centres form a body-centred array, and the presumably planar molecules are tilted out of the ac plane by about 20°. The assumption is now made that the macrogeometric description of the relation between two portions of a composite crystal may be regarded as a basis for the description of the actual mechanism of formation—either by oriented overgrowth where the second portion grows on the existing single-crystal portion in a definite orientation, or by oriented agglutination where two single crystals stick together in a well-defined orientation relationship. The two portions are joined across a composition plane, but unlike twinning, this plane does not bear the same crystallographic relationship to the two portions. The transition from the one portion across the composition plane to the second is supposed to extend through only a few molecular planes. We have considered in some detail the following aspects: the mismatch in the repeat distance in the composition plane, the molecular arrangement in the possible composition planes and the effects of the disc-like shape of the molecule and its tilt. (The description of the tilt has recently been revised (Strel'tsova & Struchkov, 1961)). None of these lines of attack have produced a clear indication of why the observed effects occur in preference to other possibilities. It seems likely that the reasons for this are tied up with the mechanism of growth of small crystallites and with the faults present in such a crystallite. At present not enough is known about these phenomena to attempt a complete answer.

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Accurate Determination of Cell Dimensions from Single-Crystal X-ray Photographs

By F. H. Herbstein

National Physical Research Laboratory, Council for Scientific and Industrial Research, Pretoria, South Africa

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A front-reflection Weissenberg camera can be easily converted into a back-reflection instrument by adding a simple adaptor and changing the gear ratio on the drive mechanism. Reflections can be obtained at Bragg angles up to 86°. Conventional devices for controlling crystal temperatures over a wide range have been added to the Weissenberg camera used. The errors in cell dimensions due to errors in measured reciprocal-lattice parameters, and in interatomic distances due to errors in cell dimensions, have been derived for triclinic crystals. Measurements on a number of crystals have given standard deviations for reciprocal-lattice parameters of 0·0025–0·01%.

The film mounting described by Mathieson (*Acta Cryst.* (1957), **10**, 351) has been used for normal and inclined-beam rotation photographs. The eccentricity-error extrapolation function for inclined-beam rotation photographs has been derived and tabulated. The standard deviation of identity-period measurements is about 0·1%.

These methods are illustrated by the determination of the cell dimensions of hexabromobenzene at 20 °C.

1. Introduction

Recent advances in the techniques of X-ray crystal-structure analysis make it feasible to reduce the standard deviations of measured bond lengths due to errors in measured intensities to less than 0·2% in favourable circumstances (Cruickshank, 1960). In order that these bond lengths should be on an absolute scale, it is necessary that the errors in cell dimensions should be appreciably smaller. The importance of accurate cell dimensions has recently been demonstrated for orthorhombic sulphur (S_8): revised cell