Steinberger, 1966) have for this reason not yet been determined.

Comparison of published ZnS polytype layer sequences with those known in SiC immediately demonstrates the fact that the numbers of elements in the Zhdanov symbols of ZnS polytypes are, in general, smaller than those reported in SiC polytypes. In other words, the percentage of hexagonality of ZnS polytypes tends to be lower.

For SiC polytypes, the theory which explains the growth of most observed polytypes is that of Frank (1961) and Mitchell (1957), as modified by Krishna & Verma (1965). This theory is based on the fact that in SiC a thin platelet with (00.1) faces is at first formed. The platelet may have one of the structures $4L$, $6L$ or $15L$ (these being the most frequent SiC structures). As a result of buckling, a step appears. Its height is usually less than the $c$ dimension of the unit cell of the basic structure. A screw dislocation is thus formed which ensures further growth; the Burgers vector of this dislocation is a non-integral multiple of the basic $c$ translation.

It is very unlikely that for polytypism in ZnS the above model is correct in its present form. First, in the initial stages of the growth thin *needles* form with the axis [00·1]; such needles cannot buckle in the way proposed for platelets. Secondly, among the observed ZnS polytypes there are some which have large elements in their Zhdanov sequence [*e.g.* (17 4 2 3)], whereas on the basis of the Mitchell–Verma model such large elements can not be expected.

A modification of the above model, or else a quite different one is, therefore, needed for the explanation of polytypism in ZnS. It seems to be, however, premature to contemplate such a model, since the number of known ZnS polytypes is still too low for meaningful comparison of experiment with theory.

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# The Crystal Structure of Adamantane: An Example of a False Minimum in Least Squares

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A least-squares refinement of the structure of the low temperature form of adamantane, starting with molecules having symmetry $\bar{4}3m$, and tilted 9° about the $c$ axis, refines to a structure not significantly different, and a reduction of the residual from 3·92 to 3·11. On the other hand, if the refinement is started at the published structure, the parameters of which correspond to rather distorted molecules, a structure not significantly different from *this* starting point results, and a reduction of the residual from 15·49 to 14·34.

## Introduction

A recent study of the crystal structure of the low temperature phase of adamantane (Nordman & Schmitkons, 1965, hereinafter referred to as NS) in which it was reported that the molecule departed significantly from $\bar{4}3m$ symmetry by being compressed along one of its $\bar{4}$ axes, prompted us to examine this structure further, partly because NS stated that 'there is no readily apparent interpretation of this effect in terms of close intermolecular contacts', and partly because of current interest in these laboratories in this phase and its relation to the high temperature phase (Dows & Rubenstein, 1965). The low temperature phase, according to NS, is tetragonal, space group $P\bar{4}2_1c$, $a=6{\cdot}60$, $c=8{\cdot}81$ Å, $Z=2$. Precession data (Cu $K\alpha$, 53 visually estimated $F_{\text{obs}}$) were refined by least squares, optimizing seven positional parameters for the carbon atoms, twelve positional parameters for the hydrogen

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atoms, an overall temperature factor, and the scale factor. The resulting molecule had C–C bond distances of 1·475, 1·530, and 1·565 Å, C–H bond distances of 0·91, 1·25, 1·36, and 1·53 Å, and was distorted by being significantly squashed in the **c** direction, *i.e.*, the distance between two opposite methylene carbons was 3·37 Å along the $\bar{4}$ axis as compared with 3·54 Å between those perpendicular to it. No bond angles were presented. The starting point for this refinement was not given explicitly, but it was stated that 'a trial model based on the above symmetry considerations was refined by least squares'; these considerations included mention of the three mutually perpendicular $\bar{4}$ axes of the free molecule, and realization that in the tetragonal crystals one of these is directed along the *c* axis, but that there is a tilt [of 9°] of the molecules about the *c* axis. The final value of *R* was stated to be 8·0%, or quite respectable*.

## Further least-squares refinement

After some preliminary calculations which strongly suggested that the molecule was not significantly distorted, we decided to carry out a refinement with a symmetrical molecule having all C–C = 1·54 Å, C–H = 1·09 Å, and all bond angles 109·5°, allowing variation only of $B$, the angle of tilt, and the scale factor. In this and all subsequent refinements the full-matrix program of Gantzel, Sparks, Long & Trueblood (1965) was used, together with the weighting scheme of Hughes (1941), with $4F_{\min} = 4{\cdot}4$. Furthermore, in all series of least squares, a sufficient number of cycles was calculated until convergence was attained. All form factors were those in Vol. III of *International Tables for X-ray Crystallography*. The best values of the variables resulting from this refinement were $B = 3{\cdot}33$,† tilt = 9°, and $k = 0{\cdot}992$, relative to Table 2 of NS. At this minimum, $R = 4{\cdot}2\%$ and $\Sigma w\Delta^2 = 3{\cdot}92$.

The refinement was then continued, starting from the above minimum, but allowing variation of the scale factor, the 7 carbon positional parameters and the 12 hydrogen positional parameters, but keeping $B$ for all atoms fixed at 3·33. This procedure reduced $R$ to 3·9% and $\Sigma w\Delta^2$ to 3·11. This improvement in $\Sigma w\Delta^2$, according to the tables of Hamilton (1965), is significant at about the 50% level, and the use of the increased number of variables is accordingly not justified.

Of more interest, however, is the fact that these parameters correspond to a molecule which is not significantly distorted from the symmetrical starting point. Pertinent data on this point are included in Tables 1 and 2.

Table 1. *Various sets of positional parameters*

Values for carbon multiplied by $10^4$, for hydrogen by $10^3$. Standard errors in parentheses.

| | | I | II | III | IV |
|---|---|---|---|---|---|
| C(1) | *x* | −0298 | −0296 (14) | −0280 | −0283 (31) |
| | *y* | 1880 | 1870 (13) | 1880 | 1870 (25) |
| | *z* | 1009 | 0999 (9) | 1030 | 1028 (19) |
| C(2) | *x* | 1583 | 1580 (10) | 1580 | 1577 (19) |
| | *y* | 2179 | 2187 (12) | 2170 | 2163 (24) |
| | *z* | 0000 | −0009 (19) | −0050 | −0049 (37) |
| C(3) | *z* | 2017 | 2006 (15) | 1910 | 1890 (29) |
| H(1) | *x* | −051 | −054 (12) | −070 | −068 (26) |
| | *y* | 321 | 317 (12) | 310 | 301 (22) |
| | *z* | 172 | 164 (11) | 140 | 134 (24) |
| H(2) | *x* | 133 | 141 (8) | 120 | 125 (25) |
| | *y* | 021 | 017 (14) | 010 | 006 (26) |
| | *z* | 273 | 267 (8) | 340 | 346 (22) |
| H(3) | *x* | 291 | 290 (13) | 280 | 285 (22) |
| | *y* | 239 | 237 (11) | 250 | 250 (27) |
| | *z* | 071 | 070 (10) | 100 | 100 (27) |
| H(4) | *x* | 137 | 129 (11) | 150 | 154 (15) |
| | *y* | 351 | 354 (12) | 380 | 375 (31) |
| | *z* | −071 | −064 (10) | −100 | −104 (14) |
| $\Sigma w\Delta^2$ | | 3·92 | 3·11 | 15·49 | 14·34 |
| *R* | | 4·2 % | 3·9 % | 8·3 % | 8·7 % |

I Symmetrical molecule, 9° tilt.
II Result of refinement starting at I, $B = 3{\cdot}33$.
III Values of NS.
IV Result of refinement starting at III, $B = 3{\cdot}33$.

Table 2. *Bond distances and angles from various refinements*

Refinements designated as in Table 1. Standard errors in parentheses.

| | I | II | III | IV |
|---|---|---|---|---|
| C–C | 1·540 Å | 1·534 (11) Å | 1·475 Å | 1·461 (22) Å |
| | 1·540 | 1·542 (15) | 1·530 | 1·523 (30) |
| | 1·540 | 1·532 (15) | 1·565 | 1·564 (29) |
| C–C–C | 109·5° | 109·2° (0·9) | 116·6° | 117·4° (1·9) |
| | 109·5 | 110·1 (0·9) | 108·2 | 108·2 (1·8) |
| | 109·5 | 109·7 (0·7) | 108·9 | 108·6 (1·4) |
| | 109·5 | 109·6 (0·7) | 106·8 | 106·9 (1·4) |
| | 109·5 | 108·5 (0·6) | 110·2 | 110·0 (1·2) |
| C–H | 1·09 Å] | 1·05 (8) Å | 0·91Å | 0·84 (17) Å |
| | 1·09 | 1·10 (6) | 1·53 | 1·61 (17) |
| | 1·09 | 1·07 (9) | 1·25 | 1·27 (18) |
| | 1·09 | 1·07 (9) | 1·36 | 1·37 (18) |
| C–C–H | 109·5° | 113° (5) | 126° | 129° (12) |
| | 109·5 | 107 (6) | 110 | 109 (12) |
| | 109·5 | 107 (4) | 94 | 93 (12) |
| | 109·5 | 109 (5) | 119 | 119 (6) |
| | 109·5 | 106 (4) | 115 | 114 (6) |
| | 109·5 | 111 (6) | 94 | 96 (8) |
| | 109·5 | 108 (5) | 119 | 115 (8) |
| | 109·5 | 106 (4) | 116 | 118 (5) |
| | 109·5 | 112 (4) | 108 | 112 (7) |
| H–C–H | 109·5 | 116 (5) | 62 | 62 (8) |
| | 109·5 | 111 (6) | 110 | 110 (10) |

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* The values of $F_o$ and $F_c$ of Table 2 of NS actually correspond to $R = 8{\cdot}2\%$; the difference arises because NS used an entire octant of reciprocal space in their refinement, and based their $R$ on that set of data. Table 2, however, contains *hkl* only for $h \geq k$.

† It is possible that this value of $B$ differs from the value 3·63 obtained by NS because different form factor curves were used in the two studies.

In order to explore just what might have happened in the original investigation, we then used the original NS parameters as a starting point in another refinement, keeping the value of $B$, however, at 3·33. The first cycle of this series gave $R=8{\cdot}3\%$ and $\Sigma w\Delta^2=15{\cdot}49$. This series converged to a set of positional parameters which was not significantly different from the starting point, but, to our great surprise, was quite different from those obtained in our previous refinement. Moreover, the final values of $R$ and $\Sigma w\Delta^2$, *viz.* 8·7% and 14·34, are both startlingly greater than the values of 3·9% and 3·11 obtained above. The parameters and molecular quantities are presented in Tables 1 and 2.

It is thus apparent that when the coordinates I of Table 1 are used as a starting point for least squares, that procedure refines to a different answer than when coordinates III are used as a starting point.

As an after-the-fact analysis as to *how* this could have happened (as opposed to *why*, a very different question) we have examined the $F_{\text{calc}}$ obtained from the two refinements. Of the 53 $F_{\text{calc}}$, 27 are centric and 26 are acentric; among the former, there is one sign change, that of 004, and among the latter there is one significant phase change, caused by a change in the sign of the imaginary part of 134. For the remainder of the acentric $F$'s, the phase changes average about 8°. Moreover, the $\Delta F$'s for what we call the incorrect structure do not, to us, contain a clue which might suggest that something was awry. The average $\Delta F$ is 0·8, with no outstanding discrepancies, the largest value being 4·2. The largest percentage discrepancies occur in the case of 004, 034, and 134, which are 35%, 38%, and 43%, respectively. For the correct structure, the discrepancies are 1%, 22%, and 7%, but there is of course nothing to imply that the sign of 004 is incorrect, or that the sign of 034 is not incorrect. It might be suggested that if, in the final stages of a refinement, there remain $F$'s for which the discrepancies are outside some externally estimated limit, then those $F$'s should be omitted, and the refinement continued. This procedure seems to us a dangerous one, and we do not recommend it.

Meanwhile, we find the occurrence of a false minimum which is quite close to the true minimum rather disturbing.

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# The Crystal Structure of $Y_2BeO_4$*

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The crystal structure of an yttrium beryllium oxide compound has been determined by three-dimensional Patterson and difference Fourier methods and refined by iterative least-squares calculations. The structure analysis showed the composition of the compound to be represented by $Y_2BeO_4$. The unit-cell dimensions are $a_0=3{\cdot}5315\pm0{\cdot}0005$, $b_0=9{\cdot}8989\pm0{\cdot}0010$, and $c_0=10{\cdot}4000\pm0{\cdot}0010$ Å; the cell contains four formula weights of $Y_2BeO_4$ with an X-ray density $\varrho=4{\cdot}582\pm0{\cdot}002$ g.cm$^{-3}$. Within the limits of a linear least-squares refinement of X-ray data the space group is *Pmcn*.

The structure of $Y_2BeO_4$ is described as consisting of ribbons of interconnected octahedra formed from two pseudo-close-packed layers of oxygen atoms between which yttrium atoms occupy octahedral interstices. The ribbons are five oxygen atoms (four octahedra) wide and extend without limit parallel to the **a** direction. The intersection of these ribbons forms channels which contain beryllium atoms trigonally coordinated to oxygen atoms in a coplanar group.

## Introduction

Weir & Van Valkenburg (1960) reported the formation of a compound in the binary system $Y_2O_3$–BeO by arc fusion. The composition of the compound was not determined since it could not be formed by solid state reactions. Potter (1960) also synthesized a compound in the same binary system by quenching a 1:2 molar mixture of $Y_2O_3$ and BeO from the molten state on a platinum strip heater. A comparison of optical and X-ray diffraction data for these two compounds showed them to be identical.

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