from those calculated may be due to a slight distortion of the molecule. However, the unreliability of the observed carbon positions does not justify a further speculation into the nature of this distortion.

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The Structure of $TiBe_{12}$†

BY R. F. RAEUCHLE‡ AND R. E. RUNDLE

Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa, U.S.A.

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$TiBe_{12}$ is hexagonal with $a_0=29{\cdot}44$, $c_0=7{\cdot}33$ Å, $Z=48$. There is a pseudo-cell, however, with $A_0=4{\cdot}23$, $C_0=7{\cdot}33$ Å, $Z=1$, one Ti per pseudo unit at 0, 0, 0 or 0, 0, $\frac{1}{2}$, and it is the alternation between these two positions which leads to the larger cell. Idealized beryllium positions have been found for the pseudo-cell.

The structure is disordered, and though the general reason for the disorder is apparent, the particular type of disorder observed has not been explained. The structure leads to an unusual set of absences.

1. Introduction

The structures of a number of alloys of high beryllium content have recently been determined. Most of these proved to be MBe_{13} compounds, and were found by Baenziger & Rundle (1949) to have the cubic $NaZn_{13}$ structure (Ketelaar, 1937; also Zintl & Haucke, 1937). A titanium compound, orginally thought to be $TiBe_{13}$, was found by Baenziger (1947) to have a hexagonal lattice. Zero- and third-layer Weissenberg diagrams, which are representative of the even and odd hexagonal reciprocal-lattice nets of $TiBe_{12}$, are shown in Fig. 1. The reflections appearing in the even-layer lines correspond to the centers of the hexagons in the odd-layer lines. The absences seemed sufficiently unusual to warrant an attempt at a complete structural determination.

2. Experimental procedure

Samples of $TiBe_{12}$ were obtained by heating titanium–beryllium mixtures of approximately 1:15 atomic ratio to about 1400° C. in an induction furnace. One sample obtained in this way had a small cavity in the center into which hexagonal needles extended. There seemed to be only small amounts of a second phase present, so presumably the compound contains only a little less beryllium than $TiBe_{13}$. A satisfactory chemical analysis of the compound has not been obtained because of the difficulty in obtaining adequate samples known to be of one phase.

Needles from the central cavity were easily separated from the matrix, and several, about 1 mm. in length and 0·05–0·1 mm. in diameter, were chosen for examination by X-ray diffraction. The face development on the needles proved to be (100), with end-face generally unobservable.

The following Weissenberg and precession photographs were made:

Cu $K\alpha$ radiation:	Weissenberg ($hk0$) to ($hk5$) and ($h0l$).
Mo $K\alpha$ radiation:	Weissenberg ($hk0$) to ($h, k, 10$), precession ($hk0$), ($h0l$), (hhl).
Ag $K\alpha$ radiation:	Weissenberg ($h0l$).

The Cu $K\alpha$ pictures were taken by the multiple-film technique. The Mo $K\alpha$ Weissenberg with even l indices and the Ag $K\alpha$ pictures were taken as a series of timed exposures at doubled intervals of from $\frac{1}{4}$ to 16 hr.

The intensities of all reflections on the Cu $K\alpha$ films, the Mo $K\alpha$ Weissenberg films of even l index, and the ($00l$) reflections from the Ag $K\alpha$ film were estimated by visual comparison of five multiple films (Robertson, 1943) or of six timed exposures. Squares of the structure factors were calculated in the usual fashion. Adsorbtion was quite small for all data, and the temperature corrections were small for the reflections used in the structural determination. Several photographs

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‡ Present address: Metallurgy Department, Naval Research Laboratory, Washington 20, D.C., U.S.A.

were considerably over-exposed to check the systematic absences.

Towards the end of the structural work, when a disordered structure was suspected, a number of Laue pictures were made with filtered and unfiltered molybdenum radiation. A streaking was obtained in the (*hk*0) reciprocal-lattice plane in several directions, but no streaking was found perpendicular to that plane. The Laue diagrams showed considerable evidence of diffuse scattering, but this could not be measured with the facilities available.

3. The unit cell and space group

All of the diffraction patterns obtained could be accounted for by a hexagonal lattice with lattice constants $a_0 = 29{\cdot}44 \pm 0{\cdot}01, \quad c_0 = 7{\cdot}33 \pm 0{\cdot}01$ Å,

as determined from (*hhl*) precession diagrams (Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å). The Weissenberg diffraction patterns obtained with the crystal rotated around the c_0 axis show the diffraction symmetry C_{6l} in all levels. This fixes the point symmetry as D_{6h}, C_{6v}, D_6 or D_{3h}. A great many extinctions occur; indeed, only $\frac{1}{48}$ of the possible reflections occur on the even-layer lines, and $\frac{11}{48}$ on the odd-layer lines. The only extinction of possible significance in the determination of the space group is, however, (00*l*) when *l* is odd. In the odd-layer lines only those reflections occur which lie along the edges of the series of hexagons which are shown in the Weissenberg diagrams of Fig. 1. The reflections (00*l*) (*l* odd) occur at the centers of such hexagons, and are thus equivalent to (441), etc., which are also absent. The possible space groups are the following:

$$D_{6h}^1\text{–}C6/mmm, \quad D_6^1\text{–}C62, \quad D_6^6\text{–}C6_32,$$
$$C_{6v}^1\text{–}C6mm, \quad D_{3h}^1\text{–}C\bar{6}m2, \quad D_{3h}^3\text{–}C\bar{6}2m.$$

From the observed density of 2·30 g.cm.$^{-3}$ and a cell volume of 111·5 Å^3, the weight of the unit pseudo-cell in molecular-weight units is 154. This is compatible with the formulae Ti_2Be_5 or $TiBe_{12}$. The former is incompatible with the approximate composition of the phase. Although the accuracy of the density determination probably does not preclude $TiBe_{11}$ or $TiBe_{13}$, the calculated formula is much closer to $TiBe_{12}$. The volume of the pseudo-cell calculated from the atomic volumes of titanium and beryllium is 110 Å^3 for $TiBe_{12}$, and would differ by 7·5 Å^3 for $TiBe_{11}$ and $TiBe_{13}$.

4. Division of the problem

The even-layer-line Weissenberg and precession diagrams, considered independently of the odd layer, may be indexed on the basis of a smaller hexagonal pseudo-cell. The C_0 axis of the pseudo-cell is identical with the c_0 axis of the true cell, while the A_0 pseudo-cell axis is perpendicular to the real cell axis, a_0. The pseudo-cell lattice constants are

$$A_0 = 4{\cdot}23, \quad C_0 = 7{\cdot}33 \text{ Å},$$

with one $TiBe_{12}$ per pseudo-unit.

A pseudo-cell structure may be determined from the intensities of the reflections with even *l* index using standard methods. This pseudo-cell structure may be interpreted in terms of the real cell structure by means of the concept of hypothetical disorder due to Harker (1948). The formulae which apply in the present case are readily derived.

The electron-density functions at the points *x*, *y*, *z* and *x*, *y*, $z+\frac{1}{2}$ are given by

$$\rho(x,y,z) = \frac{1}{V}\sum\sum_{-\infty}^{+\infty}\sum F(hkl)\exp\left[-2\pi i(hx+ky+lz)\right],$$

and

$$\rho(x,y,z+\tfrac{1}{2}) = \frac{1}{V}\sum\sum_{-\infty}^{+\infty}\sum \exp\left[-2\pi i\frac{l}{2}\right]F(hkl)$$
$$\times\exp\left[-2\pi i(hx+ky+lz)\right].$$

Therefore

$$\rho(x,y,z)+\rho(x,y,z+\tfrac{1}{2}) = \frac{1}{V}\sum\sum_{-\infty}^{+\infty}\sum\left\{1-\exp\left[-2\pi i\frac{l}{2}\right]\right\}$$
$$\times F(hkl)\exp\left[-2\pi i(hx+ky+lz)\right],$$

and

$$\tfrac{1}{2}\{\rho(x,y,z)+\rho(x,y,z+\tfrac{1}{2})\} = \frac{1}{V}\sum\sum_{-\infty}^{+\infty}\sum F(hkl)$$
$$\times\exp\left[-2\pi i(hx+ky+lz)\right] \quad (l \text{ even}).$$

Thus, if within the real cell the electron-density function $\rho(x,y,z)$ is replaced by the average of $\rho(x,y,z)$ and $\rho(x,y,z+\frac{1}{2})$ at every point of the cell, the result will be a structure whose reflections with even *l* index have the same intensity as those of the real structure and whose reflection with odd *l* index are absent. Reciprocally, the structure obtained from the reflections of even *l* index is just this average structure. In $TiBe_{12}$, because of the absences in the even layers, the averaged structure obtained in this way is not primitive, and if a primitive cell be chosen in the average structure, the pseudo-cell described above is obtained.

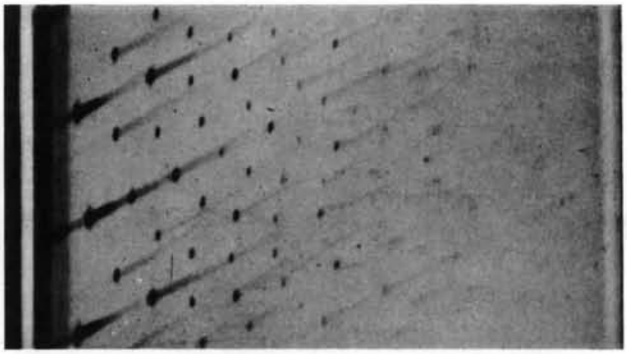
It is obvious from this that once a structure is found for the pseudo-cell (and in this half atoms may be used) the real structure may be found by resolving any ambiguities that may exist between the points $z=0$ and $z=\frac{1}{2}$. In this resolution the intensities of reflections with odd *l* index must be used.

5. The structure of the pseudo-cell

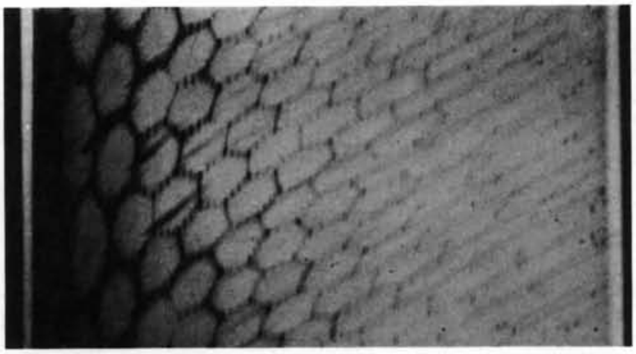
The Patterson function projected on to (001), using the Cu $K\alpha$ (*hk*0) Weissenberg data, shows three different peaks with the peak heights listed in Table 1. The Patterson projection can be interpreted by means of the following positions in the plane group, C_6^{I}:

Ti in (*a*) 0, 0.
2 Be in 2(*a*) 0, 0.
6 Be in 2(*c*) $\frac{1}{2}, 0; 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}$.
4 Be in 2(*b*) $\frac{1}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}$.

These positions are in accord with the probable chemical composition, $TiBe_{12}$. While $TiBe_{11}$ and $TiBe_{13}$ are not impossible, the only change in the



(*a*)



(*b*)

Fig. 1. (*a*) (*hk*0) and (*b*) (*hk*3) Weissenberg photographs of $TiBe_{12}$.

beryllium positions which is compatible with the Patterson projection is the subtraction or addition of a beryllium at 0, 0. There seems to be hardly enough room along the c_0 axis for one titanium atom and three beryllium atoms, while a single beryllium atom at (0, 0) would leave a hole in the structure. Consequently, we favor the composition $TiBe_{12}$, but do not absolutely exclude $TiBe_{13}$.

Table 1. *Peak heights from Patterson projection of pseudo-cell on to* (001)

x	y	Height
0	0	690
$\frac{1}{3}$	$\frac{2}{3}$	200
$\frac{1}{2}$	0	300

The positions above are also possible in C^{I}_{3i} and C^{II}_{3i}, and the only possible variation is the displacement of the origin to $\frac{1}{3}$, $\frac{2}{3}$ in C^{I}_{3i}. This makes no difference in the pseudo-cell but must be considered in the transition to the real cell.

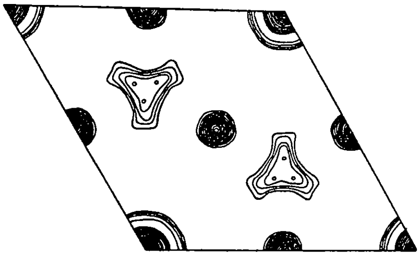


Fig. 2. Fourier projection of pseudo-cell on to (001).

The Fourier projection on to (001) gives further evidence that these positions are approximately correct. This projection (Fig. 2) was calculated from (*hk*0) Mo *Kα* Weissenberg diffraction data with signs assigned from the structure factors calculated from the above positions. The integrated peak heights on an arbitrary scale are given in Table 2. These peak heights agree very well with those expected for the postulated x and y positions. It will be noticed that the peak at $\frac{1}{3}$, $\frac{2}{3}$ is partially resolved into three peaks. Since there are only two beryllium atoms at that position, this separation must represent a small deviation from the ideal pseudo-structure, and indicates that the position $\frac{1}{3}$, $\frac{2}{3}$ of the pseudo-structure is the average of positions in the real structure. Such a deviation may be large enough to influence the intensities of the observed reflections of the *hk*0 planes, but not large enough in itself to cause other reflections to appear. This is true because the intensity of a reflection is proportional to the square of the structure factor, F. Since

Table 2. *Integrated peak heights from Fourier projection of pseudo-cell on to* (001)

x	y	Height
0	0	87,141
$\frac{1}{3}$	$\frac{2}{3}$	17,806
$\frac{1}{2}$	0	15,793

$$(F+\delta)^2=F^2+2F\delta+\delta^2,$$

a small change in parameters which changes F to $F+\delta$ will change the intensity by $2F\delta+\delta^2$. For a reflection where $F=0$ for the 'ideal' structure the intensity will now be only δ^2 for the deformed structure.

Weissenberg and rotation pictures around c_0 show that the (*hk*0), (*hk*4) and (*hk*8) intensities are quite similar, and that (*hk*2), (*hk*6) and (*h*,*k*,10) are also similar but different from the other set. Thus we are led to postulate a layer structure for the pseudo-cell, with atoms lying $\frac{1}{4}$ apart in z. Packing considerations then lead to the following pseudo-cell structure in D^{1}_{6h}:

1 Ti in (*a*) $0, 0, 0$; or (*b*) $0, 0, \frac{1}{2}$.
2 Be in (*e*) $0, 0, z_1$; $0, 0, \bar{z}_1$; z_1 near $\frac{1}{4}$.
6 Be in (*i*) $\frac{1}{2}, 0, z_2$; $0, \frac{1}{2}, z_2$; $\frac{1}{2}, \frac{1}{2}, z_2$; $\frac{1}{2}, 0, \bar{z}_2$; $0, \frac{1}{2}, \bar{z}_2$; $\frac{1}{2}, \frac{1}{2}, \bar{z}_2$; with z_2 near $\frac{1}{4}$.
2 Be in (*c*) $\frac{1}{3}, \frac{2}{3}, 0$; $\frac{2}{3}, \frac{1}{2}, 0$.
2 Be in (*c*) $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$.

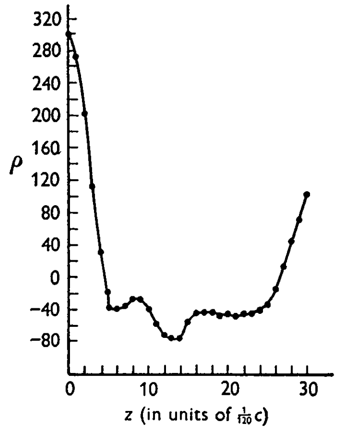


Fig. 3. One-dimensional projection on to c.

Each of the parameterless sets can be given x and y parameters in some one of the other possible space groups, but except for such deformations the above sets are the only ones which explain all the data. The one-dimensional Fourier projection along c calculated from Ag *Kα* data shows that most of the atoms near $\frac{1}{4}$ are in fact precisely at $\frac{1}{4}$, so $z_2=\frac{1}{4}$ (Fig. 3). There are small peaks near $z=\frac{1}{4}$, at 0·22 and 0·28. Because (*hk*3) reflections appear to be the strongest of the reflections with l odd, and because of the size of the titanium atom, we take z_1 as 0·28 when Ti is at 0, 0, 0 and at 0·22 when Ti is at $0, 0, \frac{1}{2}$. In Table 3, observed (00*l*) structure

Table 3. *Comparison of calculated and observed structure factors for* (00*l*) *reflections*

		F_c			
Index	F_o	$z_1=0{\cdot}25$	$z_1=0{\cdot}26$	$z_1=0{\cdot}28$	$z_1=0{\cdot}03$
002	11·6	7·8	7·9	8·2	8·8
004	25·0	34·6	34·5	33·7	32·2
006	9·8	4·4	4·7	6·3	8·6
008	15·2	24·7	24·3	22·3	20·0
0,0,10	4·6	2·8	3·2	5·8	7·4
0,0,12	10·0	16·5	16·1	13·7	13·4
0,0,14	5·6	2·7	3·1	5·1	4·4

factors are compared with those calculated for the above structure, and also with those calculated with z_1 at 0·26 and 30. It is seen that these intensities are not very sensitive to this z parameter, and that agreement is in every case quite good if we except (004), which is the strongest reflection appearing in the entire reciprocal lattice. We presume that extinction causes the discrepancy in F (004).

In Table 4, observed and calculated structure factors for reflections (hkl) with l even are compared for reflections observed with Cu $K\alpha$ radiation. The ($hk4$) reflections are somewhat sensitive to z_1, and 0·28 seems to give the best fit.

Table 4. *Calculated and observed structure factors for the pseudo-cell*

Pseudo-cell index	True index	F_o	F_c
100	440	15·0	12·6
110	12,0,0	20·9	21·6
200	880	23·2	23·6
210	16,4,0	10·8	8·2
300	12,12,0	15·3	17·1
220	24,0,0	25·9	26·5
310	20,8,0	7·1	6·8
400	16,16,0	17·9	16·6
320	28,4,0	7·8	5·8
410	24,12,0	9·1	14·3
102	442	15·2	13·1
112	12,0,2	21·5	20·8
202	882	3·3	−4·1
212	16,4,2	12·7	8·4
302	12,12,2	16·7	16·9
222	24,0,2	6·2	4·6
312	20,8,2	11·3	12·4
402	16,16,2	3·5	−3·8
322	28,4,2	10·6	6·2
412	24,12,2	9·7	12·5
104	444	7·3	7·3
114	12,0,4	15·8	16·3
204	884	17·5	19·0
214	16,4,4	7·6	6·2
304	12,12,4	11·3	13·6
224	24,0,4	19·1	21·0
314	20,8,4	5·7	5·4
404	16,16,4	14·4	13·1

6. The structure of the real cell

The determination of the structure of the pseudo-cell in the preceding section has left an ambiguity in the z parameter of the titanium and beryllium atoms at $x=0$, $y=0$. The titanium atom may occur at $z=0$ or $z=\frac{1}{2}$, the two berylliums lying 0·28 × 7·36 Å away along the z axis. It is natural, then, to assume that in the true unit cell this ambiguity will be completely removed, and that each of the forty-eight titanium atoms in the unit cell will have a z parameter of either 0 or $\frac{1}{2}$. As will be shown later, it is impossible to explain the structure on this basis. While it is certainly true that each titanium has a z parameter of 0 or $\frac{1}{2}$, an individual titanium set at, say, ($\frac{1}{2}$,0) is not always at $z=\frac{1}{2}$, but possesses definite probabilities for lying in one or the other of these positions. It is necessary to use reflections with l odd to obtain information about this distribution.

The absence of ($00l$) reflections with l odd is conclusive evidence that there are equal numbers of titanium at $z=0$ and $z=\frac{1}{2}$. Indeed, as will be seen later, a reflection whose structure factor is $1f_{\mathrm{Ti}}$ should be seen clearly at small $\sin\theta$, and a separation of titanium between $z=0$ and $z=\frac{1}{2}$ in the ratio of 23 : 25 would give rise to a structure factor of $2f_{\mathrm{Ti}}$ for all ($00l$) reflections with l odd. There must, therefore, be twenty-four titaniums at each level.

The pseudo-cell net picks our forty-eight points within the real cell which are equivalent except for the ambiguity in the c_0 direction. The two possible positions for the titanium atom within the pseudo-cell correspond to two possible sets of positions in the real cell. The point positions $\frac{1}{3}$, $\frac{2}{3}$ occur in the pseudo-cell in the space group D_{3h}^1, but when these positions are referred to the axes of the real cell, they are found to occupy the positions of D_{3h}^3. This happens because the two space groups differ only in the angle the vertical mirror plane makes with a_0 and b_0. In D_{3h}^3 each of the symmetry-connected atomic sets has a zero contribution to F (401), and it is therefore impossible to explain the appearance of (401) with titanium in these pseudo-cell positions.

There remains, therefore, only the possibility that the titanium atoms occur at 0, 0 in the pseudo-cell, and atoms may be placed over the pseudo-cell origins in all of the possible space groups.

All of the possible space groups possess in common a three-fold axis. It will, therefore, be convenient to list the various atomic positions of the titanium atoms in terms of the three-fold sets, and they are so listed in Table 5. The set A (0,0; $\frac{1}{3}$,$\frac{2}{3}$; $\frac{2}{3}$,$\frac{1}{3}$) is not a three-fold position because of symmetry. But, since all of the other sets are true three-fold sets, these atoms must occur together at $z=0$ or $z=\frac{1}{2}$ if the atoms are to be arranged with twenty-four atoms at $z=0$, and twenty-four at $z=\frac{1}{2}$.

Table 5. *The xy parameters of the three-fold titanium sets*

Set	Positions
A	$0, 0;\ \frac{1}{3}, \frac{2}{3};\ \frac{2}{3}, \frac{1}{3}$
B	$\frac{1}{4}, 0;\ 0, \frac{1}{4};\ \frac{3}{4}, \frac{3}{4}$
C	$\frac{3}{4}, 0;\ 0, \frac{3}{4};\ \frac{1}{4}, \frac{1}{4}$
D	$\frac{1}{2}, 0;\ 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}$
E	$\frac{1}{12}, \frac{2}{12};\ \frac{1}{12}, \frac{11}{12};\ \frac{10}{12}, \frac{11}{12}$
F	$\frac{2}{12}, \frac{1}{12};\ \frac{11}{12}, \frac{1}{12};\ \frac{11}{12}, \frac{10}{12}$
G	$\frac{4}{12}, \frac{2}{12};\ \frac{10}{12}, \frac{8}{12};\ \frac{10}{12}, \frac{2}{12}$
H	$\frac{2}{12}, \frac{4}{12};\ \frac{8}{12}, \frac{10}{12};\ \frac{2}{12}, \frac{10}{12}$
I	$\frac{1}{2}, \frac{1}{4};\ \frac{3}{4}, \frac{1}{2};\ \frac{3}{4}, \frac{1}{4}$
J	$\frac{1}{4}, \frac{1}{2};\ \frac{1}{2}, \frac{3}{4};\ \frac{1}{4}, \frac{3}{4}$
K	$\frac{5}{12}, \frac{1}{12};\ \frac{11}{12}, \frac{4}{12};\ \frac{8}{12}, \frac{7}{12}$
L	$\frac{1}{12}, \frac{5}{12};\ \frac{4}{12}, \frac{11}{12};\ \frac{7}{12}, \frac{8}{12}$
M	$\frac{7}{12}, \frac{2}{12};\ \frac{10}{12}, \frac{5}{12};\ \frac{7}{12}, \frac{5}{12}$
N	$\frac{2}{12}, \frac{7}{12};\ \frac{5}{12}, \frac{10}{12};\ \frac{5}{12}, \frac{7}{12}$
O	$\frac{8}{12}, \frac{1}{12};\ \frac{11}{12}, \frac{7}{12};\ \frac{5}{12}, \frac{4}{12}$
P	$\frac{1}{12}, \frac{8}{12};\ \frac{7}{12}, \frac{11}{12};\ \frac{4}{12}, \frac{5}{12}$

Elimination of ordered structures

It is now necessary to seek an arrangement of titanium atom in two layers which will explain the absences in the odd reciprocal-lattice layers. A comparison of reflections which were present on even- and odd-layer films showed that a reflection whose structure factor is $0{\cdot}5f_{\mathrm{Ti}}$ to $1{\cdot}0f_{\mathrm{Ti}}$ would certainly appear. This then was used as a criterion, and the structure factors for all the possible ordered arrangements of titanium atoms were considered. There are 6435 possible ordered structures consistent with twenty-four titanium atoms at both $z=0$ and $z=\frac{1}{2}$ arranged in three-fold sets. A systematic method of handling this number of possibilities has been devised, and it has been shown that for every ordered structure the structure factor for at least one of the absent reflections was larger than the maximum value for extinction. Since the absences on the odd layers are periodic ones, it is not possible that the observed absences could be caused by the canceling of the titanium contribution by a beryllium contribution. For this reason all of the possible ordered structures must be eliminated as not compatible with the observed data.

A disordered structure

There are several pieces of evidence which lend support to the idea of a disordered structure. The original Weissenberg patterns themselves led to an early suspicion that the structure was not wholly ordered, since, as can be seen from Fig. 1, certain of the spots on the odd-layer pictures appear to be diffuse. The Laue diffraction patterns, taken with molybdenum radiation, also give evidence of disorder (cf. § 2). The streaking observed in these photographs indicates a streaking in the reciprocal lattice in planes perpendicular to c^*. This streaking is characteristic of a two-dimensional disorder (Zachariasen, 1945).

Nature of the disorder

It has been found possible to explain the over-all intensity patterns quite satisfactorily on the basis of a partially disordered structure in D^1_{6h}. No reasonable method could be found by which the remaining possible space groups could be investigated with respect to disordering, and little attempt was made to find a disordered structure in other groups. It can hardly be expected that any such structure could explain the observed data any more satisfactorily than does the present postulated structure.

Since the diffuse, non-Bragg scattering has not been studied, and, consequently, the correlation among the disorder sites is not known, each of the atomic sets of titanium in D^1_{6h} must be treated as independent. It is assumed that for each set, X, there is a definite probability, p_X, that the set occur at $z=0$, and a probability of $1-p_X$ that it occur at $z=\frac{1}{2}$. Since the disorder is probably a two-dimensional one, the Be–Ti–Be —Be–Ti–Be chains in the c_0 direction are probably completely ordered along their length, but each chain may start with a titanium atom at either $z=0$ or $z=\frac{1}{2}$ with a probability that depends on its position in the (001) plane.

Fourier synthesis

Since information concerning the z parameters of the titanium atoms is to be found in reciprocal-lattice layers with odd l index, the problem of the meaning of Fourier syntheses of reciprocal-lattice layers other than the equatorial layer was considered. A rather simple interpretation of such syntheses has been obtained and used in the further clarification of the structure.

A plane in reciprocal space, of interest in the present problem, is defined by the equation $l=l_1$ (constant). The structure factors for points on this plane are given by

$$F(hkl_1)=V\int_0^1\int_0^1\int_0^1\rho(x,y,z)\times\exp\left[2\pi i(hx+ky+l_1z)\right]dx\,dy\,dz.$$

Therefore

$$\int_0^1\rho(x,y,z)\exp\left[2\pi il_1z\right]dy=\frac{1}{V}\sum_{-\infty}^{+\infty}\sum F(hkl_1)\exp\left[-2\pi i(hx+ky)\right],$$

where use has been made of the usual Fourier inversion.

Real and imaginary parts may be separated to give

$$\int_0^1\rho(x,y,z)\cos 2\pi l_1z\,dz=\frac{1}{V}\sum_{-\infty}^{+\infty}\sum F(hkl_1)\cos 2\pi(hx+ky),$$

$$\int_0^1\rho(x,y,z)\sin 2\pi l_1z\,dz=\frac{1}{V}\sum_{-\infty}^{+\infty}\sum F(hkl_1)\sin 2\pi(hx-ky),\dagger$$

respectively.

Since the titanium x, y parameters are all multiples of one-twelfth, the contributions of the titanium atom to $F(hkl)$ is periodic in h and k for all possible titanium combinations, and this allows only eight independent structure-factor contributions in D^1_{6h}.

If the eight reflections (401), (501), (221), (101), (201), (301), (111) and (441) are chosen as representative of the independent structure factors, it is found that only the first three, (401), (501) and (221), are present. An observation of the first-layer photograph (Fig. 1) shows that the periodicity which has been postulated on the basis of the titanium positions is also apparent in the total intensities. This is to be expected, since the beryllium atoms are displaced very little from their pseudo-cell positions.

Normally, it is not possible to carry out a series of Fourier syntheses with all of the possible permutations of the signs of the structure factors because the number of permutations is far too great. In the present case, however, this is possible since only three independent

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† Similar formulae have been derived in a somewhat different form by Clews & Cochran (1949). These authors, however, used such syntheses for a somewhat different purpose.

sign assignments need be applied to the first-layer data. This procedure necessitates the assumption that any deviations of beryllium atoms from their idealized positions will not affect the assignment of signs. It is difficult to see how the small possible displacements of beryllium atoms from their pseudo-cell positions could cause the sign of the structure factor to be different from the titanium contribution to the structure factor. There will therefore be only four possible variations in the signs of the structure factors of the reflections appearing in the first layer. Changing all the signs of the first-layer structure factors will have the effect of adding $\frac{1}{2}$ to all of the z parameters in the structure and will yield the same structure with the origin displaced by $\frac{1}{2}$ in the z direction. Therefore, the sign of (401) may arbitrarily be taken as positive, and the various combinations of positive and negative signs be taken for (501) and (221). These sign combinations may be represented schematically by

	(401)	(501)	(221)
I	+	−	−
II	+	+	−
III	+	−	+
IV	+	+	+

The various possible structure-factor combinations represented above will be referred to by the Roman numeral which precedes it. Sign combination and structures derived from this sign assignment will be referred to by the same Roman numeral. Thus, structures I will have the structure factor of (401) and related structure factors positive, and the structure factors of (501) and (601), and the structure factors related to them, negative.

First-layer Fourier syntheses were made with each of the possible sign combinations. The sums were carried out by increasing the frequencies of the International Business Machine card set to thirty in order to include a majority of the reflections obtained with Cu $K\alpha$ X-rays. The following formula was used:

$$R(x,y)=\sum_0^\infty\sum_0^\infty\{F'(h\bar{k}l)+F'(hkl)\}\cos 2\pi hx\cos 2\pi ky$$
$$\times\{F'(h\bar{k}l)-F'(hkl)\}\sin 2\pi hx\sin 2\pi ky$$

with $F'(h\bar{k}l)=0$ if h or $k=0$.

The values of the peak heights for the four summations are given in Table 6. The sums of all of the peak heights for each of the structures is also included, for reasons discussed below.

The interpretation of the first-layer transforms is particularly simple in this case. Earlier, the formula

$$R(x,y)=\int_0^1\rho(x,y,z)\cos 2\pi l_1 z\,dz$$

has been derived, where l_1 is the l index of the layer for which the synthesis is made. In the present structure the problem is to distinguish between titanium atoms at $z=0$ and titanium atoms at $z=\frac{1}{2}$. If, in the above integral, the function $\rho(x,y,z)$ is shifted by $z=\frac{1}{2}$ (i.e. if $\rho(x,y,z)$ is replaced by $\rho(x,y,z+\frac{1}{2})$), the integral becomes

$$\begin{aligned}R'(x,y)&=\int_0^1\rho(x,y,z+\tfrac{1}{2})\cos 2\pi l_1 z\,dz\\&=\int_{\frac{1}{2}}^{\frac{3}{2}}\rho(x,y,z)\cos 2\pi(l_1 z+\tfrac{1}{2})\,dz\\&=-R(x,y)\quad\text{if } l_1 \text{ is odd.}\end{aligned}$$

If the structure were perfectly ordered, one would expect peaks of only two kinds at titanium sites, equal to each other in absolute magnitude but the one the negative of the other. It is readily apparent from Table 6 that this is not the case.

Although the structure is not entirely ordered, it still must be true that there are as many titanium atoms at $z=0$ as at $z=\frac{1}{2}$. For this reason the sum of $R(x,y)$ over all the titanium sites must be zero. This consideration eliminates the sign assignments III and IV. In the two remaining syntheses, probabilities may be assigned to each titanium set which will explain the observed peak heights. The probabilities have been assigned by making use of the fact that the peak heights are proportional to $2p_{xy}-1$. These probabilities are also listed in Table 6. In both cases the maximum peak has been assigned a probability of unity, and the probabilities have been rounded off to give a set of small rational fractions.

In Table 7 the pertinent structure factors are evaluated for the two cases. It is obvious that the first set,

Table 6. *Peak heights from the $F(hk1)$ Fourier syntheses and the probabilities deduced therefrom*

		Structure I		Structure II			
Sets	Atomic position	Peak heights	Probability that set is at $z=0$	Peak heights	Probability that set is at $z=0$	Structure III† peak heights	Structure IV† peak heights
A	0, 0	− 531	$\frac{1}{4}$	531	$\frac{8}{12}$	1687	2761
B, C	$\frac{1}{4}$, 0	919	$\frac{3}{4}$	581	$\frac{8}{12}$	1637	1299
D	$\frac{1}{2}$, 0	937	$\frac{3}{4}$	2011	1	207	1281
I, J	$\frac{1}{2}$, $\frac{1}{4}$	1650	1	1312	$\frac{10}{12}$	906	568
M, N	$\frac{7}{12}$, $\frac{2}{12}$	−1180	$\frac{1}{8}$	−1618	$\frac{1}{12}$	666	228
K, L, O, P	$\frac{5}{12}$, $\frac{1}{12}$	− 175	$\frac{1}{2}$	− 695	$\frac{3}{12}$	− 257	− 695
E, F	$\frac{1}{12}$, $\frac{2}{12}$	72	$\frac{1}{2}$	− 366	$\frac{5}{12}$	− 586	−1024
G, H	$\frac{4}{12}$, $\frac{2}{12}$	1284	$\frac{1}{8}$	332	$\frac{7}{12}$	−1284	− 210
	Weighted sum	180		732		10596	8952

† No probabilities have been determined for these structures.

obtained from the p's derived from the sign combination $F(401)$ positive, $F(501)$ negative and $F(221)$ negative, gives the better correlation with the observed data. Not only do most of the structure factors of the absent reflections vanish but the structure factors of the reflections which are present are put in the observed order.

Table 7. *Comparison of the relative structure factors for the two disordered structure, I and II*

	Structure I	Structure II	Observation
$R(101)$	$-0{\cdot}2$	$1{\cdot}30$	Absent
$R(201)$	0	$-0{\cdot}75$	Absent
$R(301)$	0	$-0{\cdot}5$	Absent
$R(401)$	7	$7{\cdot}25$	Present
$R(501)$	$-1{\cdot}72$	$-0{\cdot}26$	Present
$R(111)$	$-0{\cdot}5$	$0{\cdot}16$	Absent
$R(221)$	$-1{\cdot}75$	$3{\cdot}5$	Present
$R(441)$	0	0	Absent

Since the Fourier synthesis of the first-layer data is a new method, a three-dimensional Fourier summation, $\rho(x, y, 0)$, was made as a check using all of the Cu $K\alpha$ data with the sign assignment I, which gave the best fit above. The peak heights from this summation are given in Table 8. The probabilities obtained from the $F(hkl)$ synthesis are also included, and they will be seen to parallel the peak heights. They are not proportional to them, as might have been expected. This is due partly to an incorrect background in the three-dimensional synthesis. This lack of correlation arises because the streaking of the odd-layer reflections appears to be different on the $(h0l)$ films, used for correlation, and the (hkl_1) films. The agreement between the probabilities and the peak heights seems to be good enough, however, to confirm the postulated probabilities.

Table 8. *Three-dimensional Fourier section* $(x, y, 0)$ *for the sign assignment I*

Sets	Atomic position	Peak heights	Probability that set is at $z=0$
A	$0, 0$	6500	$\frac{1}{4}$
	$\frac{1}{3}, \frac{2}{3}$	4500	$\frac{1}{4}$
B, C	$\frac{1}{4}, 0$	9000	$\frac{3}{4}$
D	$\frac{1}{2}, 0$	8960	$\frac{3}{4}$
I, J	$\frac{1}{2}, \frac{1}{4}$	10000	1
M, N	$\frac{7}{12}, \frac{2}{12}$	4500	$\frac{1}{8}$
K, L, O, P	$\frac{5}{12}, \frac{1}{12}$	7100	$\frac{1}{2}$
E, F	$\frac{1}{12}, \frac{2}{12}$	6600	$\frac{1}{2}$
G, H	$\frac{4}{12}, \frac{2}{12}$	4200	$\frac{1}{8}$

Structure I, then, seems to satisfy all of the requirements of the observed data. That the agreement is fairly good, in spite of the lack of refinements, is shown by the comparisons in Table 9, where calculated and observed structure factors are recorded for three of the odd layers. Adjacent reflections are, in most cases, placed in the observed order with approximately the correct intensity ratios. It could not be expected that reflections farther apart would exhibit agreement between the observed and calculated structure factors, and they do not. Because the extent of the variation of the observed structure factor from the calculated value within each layer seems to depend on l more strongly than might be expected, some minor adjustment of the z parameters of the beryllium atoms at $z=0$ and $\frac{1}{2}$ or $\frac{1}{4}$ and $\frac{3}{4}$ might be indicated.

7. Discussion

The pseudo-cell structure indicates that there are linear Be–Ti–Be groups arranged parallel to c_0 with a Be–Ti distance of 2·13 Å. About each such group there are eighteen beryllium atoms arranged hexagonally in three layers, six at the level of titanium, and six at approximately the level of each of the two beryllium atoms (Fig. 4). Distances are given in Table 10. The beryllium atoms not involved in the $TiBe_2$ groups form two types of hexagonal nets, one type at $z=0$ and $\frac{1}{2}$, consisting of hexagons with shared edges, and the other at $z=\frac{1}{4}$ and $\frac{3}{4}$, consisting of smaller hexagons with shared corners. Centers of the hexagons coincide in the (001) plane. The $TiBe_2$ groups are placed within these hexagons so that a titanium atom occurs at the center of a hexagon at $z=0$ or $\frac{1}{2}$, and beryllium atoms occur near $z=\frac{1}{4}$ or $\frac{3}{4}$. The fit is apparently close enough, so that if a titanium atom is at $z=0$ in the pseudo-cell, it lowers the probability that neighboring titanium atoms will be at $z=0$.

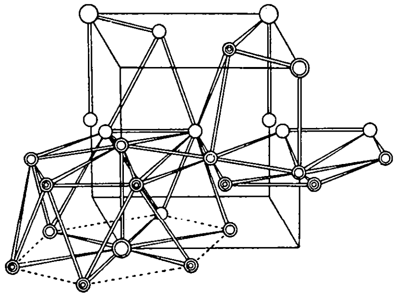

Fig. 4. Part of an ordered pseudo-cell for $TiBe_{12}$. Half the polyhedron of 18 beryllium atoms surrounding a $TiBe_2$ group can be seen in the lower left-hand corner. Large circles are titanium, small are beryllium.

By making assumptions as to the nature of the restrictions on neighboring titanium atoms being at the same level, it is quite easy to arrive at ordered structures which have the same repeat as that observed for the real structure. These ordered structures do not have hexagonal symmetry, and we have not succeeded in finding a way of introducing a randomness in the structures which will account for the probabilities and hexagonal symmetry observed.

If the disordered structure which has been postulated is correct, there is little immediate hope of refining the beryllium positions. It was seen from the pseudo-cell Fourier projection (Fig. 2) that certain of the beryllium atoms must show small displacements from their ideal pseudo-cell positions. These displacements certainly depend on the relative positions of adjacent titanium atoms. If the titanium atoms were perfectly ordered, size considerations alone might make it possible to find accurately the beryllium displacement. As matters stand now, the magnitude of this displacement can be found from the Fourier projection, but the direction of an individual displacement cannot be found and could not unless the correlation among the titanium probabilities were known, or unless three-dimensional Fourier syntheses were made using all reflections obtainable with molybdenum radiation. This is far beyond the capacity of our present punched-card equipment, and appears impractical.

Table 9. *Calculated and observed structure factors for structure I*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
221	62	−100	313	47	− 93	23,9,3	105	− 55
311	62	− 93	403	232	249	24,8,3	174	144
401	192	249	503	108	− 92	20,13,3	30	− 54
501	83	− 90	603	126	− 98	28,0,3	21	150
601	89	− 94	703	137	− 89	225	54	− 54
701	101	− 85	803	372	234	315	57	− 50
801	261	222	813	86	− 86	405	192	135
811	66	− 81	823	92	− 93	505	83	− 50
821	67	− 85	833	93	− 85	605	83	− 53
831	70	− 78	663	58	− 88	705	81	− 50
661	66	− 82	753	58	− 82	805	171	132
751	66	− 76	843	239	218	815	52	− 49
841	237	201	943	60	− 80	825	57	− 52
941	73	− 73	10,4,3	51	− 84	835	57	− 48
10,4,1	75	− 76	11,4,3	38	− 77	665	58	− 50
11,4,1	81	− 68	12,4,3	179	204	755	58	− 47
12,4,1	81	176	13,3,3	36	− 76	845	267	126
13,3,1	0	− 63	14,2,3	36	− 81	945	74	− 46
14,2,1	0	− 67	12,5,3	36	− 76	10,4,5	69	− 48
12,5,1	84	− 62	15,1,3	36	− 75	11,4,5	61	− 44
15,1,1	0	− 62	12,6,3	47	204	12,4,5	201	117
12,6,1	87	− 65	16,0,3	179	198	13,3,5	0	− 44
16,0,1	73	163	12,7,3	43	− 73	14,2,5	0	− 47
12,7,1	94	− 60	17,0,3	37	− 73	12,5,5	65	− 43
17,0,1	73	− 60	10,10,3	43	− 77	15,1,5	0	− 43
10,10,1	83	− 63	11,9,3	43	− 72	12,6,5	71	− 45
11,9,1	83	− 59	12,8,3	209	190	16,0,5	37	112
12,8,1	209	158	18,0,3	37	− 75	12,7,5	77	− 41
18,0,1	78	− 62	13,8,3	43	− 69	17,0,5	29	− 41
13,8,1	78	− 57	19,0,3	37	− 69	10,10,5	87	− 43
19,0,1	83	− 56	14,8,3	43	− 72	11·9,5	87	− 40
14,8,1	83	− 60	20,0,3	202	182	12,8,5	275	108
20,0,1	207	147	15,8,3	43	− 67	18,0,5	32	− 43
15,8,1	84	− 54	20,1,3	43	− 67	13,8,5	68	− 40
20,1,1	76	− 54	20,2,3	43	− 71	19,0,5	37	− 40
20,2,1	76	− 56	16,8,3	204	177	14,8,5	48	− 42
16,8,1	156	141	17,7,3	43	− 66	20,0,5	300	103
17,7,1	76	− 53	18,6,3	43	− 70	15,8,5	0	− 39
18,6,1	76	− 56	20,3,3	43	− 66	20,1,5	77	− 38
20,3,1	76	− 52	19,5,3	43	− 65	20,2,5	71	− 41
19,5,1	76	− 52	16,9,3	43	− 65	16,8,5	153	103
16,9,1	0	− 52	20,4,3	204	173	17,7,5	24	− 38
20,4,1	222	137	16,10,3	30	− 70	18,6,5	32	− 40
16,10,1	0	− 54	21,4,3	0	− 62	20,3,5	65	− 38
21,4,1	81	− 50	22,4,3	0	− 65	19,5,5	37	− 37
22,4,1	—	− 52	16,12,3	37	162	16,9,5	0	− 38
16,12,1	31	131	17,12,3	37	− 59	20,4,5	90	99
17,12,1	31	− 48	24,4,3	153	156	16,10,5	0	− 39
24,4,1	139	126	18,12,3	22	− 62	21,4,5	79	− 36
18,12,1	31	− 50	24,5,3	0	− 57	22,4,5	65	− 37
24,5,1	0	− 46	19,12,3	37	− 57	16,12,5	163	93
19,12,1	31	− 45	24,6,3	0	− 60	17,12,5	68	− 34
24,6,1	0	− 48	20,12,3	177	150	24,4,5	210	90
20,12,1	128	119	21,11,3	97	− 55	18,12,5	63	− 36
21,11,1	0	− 44	24,7,3	0	− 55	24,1,5	63	− 34
223	47	−100	22,10,3	103	− 59	19,12,5	52	− 34

Table 10. *Neighboring atoms and interatomic distances*

(The positions given refer to the pseudo-cell.)

- Each Ti at 0, 0, 0 has:
  - 2 Be (at 0, 0, 0·29; etc.) at 2·13 Å;
  - 6 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 2·55 Å;
  - 12 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·80 Å.
- Each Be at 0, 0, 0·29 has:
  - 1 Ti at 2·13 Å;
  - 6 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·13 Å;
  - 12 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 3·34 Å.
- Each Be near $\frac{1}{3}$, $\frac{2}{3}$, 0 has:
  - 1 or 2 Ti at 2·55 Å;
  - 4 or 2 Be (at 0, 0, 0·29; etc.) at 3·34 Å;
  - 2 or 4 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·2 Å;
  - 4 or 2 Be (at $\frac{1}{2}$, 0, $\frac{1}{4}$; etc.) at 2·3 Å.
- Each Be at $\frac{1}{2}$, 0, $\frac{1}{4}$ has:
  - 2 Be (at 0, 0, 0·29; etc.) at 2·13 Å;
  - 2 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 2·2 Å;
  - 2 Be (near $\frac{1}{3}$, $\frac{2}{3}$, 0; etc.) at 2·3 Å;
  - 4 Be (at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{4}$; etc.) at 2·12 Å;
  - 2 Ti at 2·8 Å.

If the beryllium atom which is displaced is considered more carefully, it will be seen that it may exist in at least four situations, namely: surrounded at its z level by none, one, two or three titanium atoms. If the beryllium atom is at the center of the triangle of surrounding titanium sites, it will be too close to any corner containing a titanium atom. It is unlikely, then, that three titanium atoms will surround a beryllium, and, therefore, also unlikely that no titanium atoms will surround it. Each of these beryllium atoms is probably surrounded by one or two titanium atoms at the corners of the titanium-site triangle and must move away from the titanium atoms. The Fourier synthesis (Fig. 2) shows the beryllium atoms to lie at 2·5 Å from some of the pseudo-cell corners, and atomic radii are consistent with this being a Be–Ti distance.

Though the structure is known only roughly, even this is encouraging for a structure which involves 624 atoms. The structure seems to involve a not quite fully ordered superlattice, and it seems possible that the nature of the disorder may yet become understandable.

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The Crystal Structure of Thiophene at −55° C.*

By S. C. Abrahams† and W. N. Lipscomb

School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.

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The crystal modification of thiophene in the range −38 to −98° C. is orthorhombic, space group either D_{2h}^{18}–*Bmab* or the non-centrosymmetric equivalent C_{2v}^{17}–*B2ab*, with no conclusive distinction possible from the data. The crystal structure has been determined on the basis of each of these possible space groups, with the use of three-dimensional Fourier sections based on visual intensity measurements from the entire reciprocal sphere. In *Bmab* each one of the four molecules occupies statistically any one of four equivalent positions related to one another by two mutually perpendicular mirror planes, both normal to the plane of the ring. In *B2ab*, these four positions reduce to two equivalent positions. These two possible structures show approximately equally good agreement with the observed data. The disorder has made it unwise to attempt determination of intramolecular bond distances, but the closest intermolecular approach of 3·7 Å indicates, as expected, that no very strong binding forces are present in the crystal. The unit-cell dimensions are $a = 9{\cdot}76$, $b = 7{\cdot}20$ and $c = 6{\cdot}67$ Å. The plane of the molecule is parallel to a, and makes an angle of 47·8° with b.

Introduction

Considerable advances have been achieved in the last decade in correlating the bond distances in polycyclic aromatic hydrocarbons, predicted from molecular-orbital and valance-bond treatments, with those experimentally measured. More recently, similar techniques have been applied to some heterocyclic molecules, and, in the case of thiophthen, the agreement between the calculated bond distances (Evans & de Heer, 1949) and the measured distances (Cox, Gillot & Jeffrey, 1949) has been most encouraging. The more simple sulfur analogue, thiophene, had been investigated by the electron-diffraction method by Schomaker & Pauling (1939), but when the molecular-orbital treatment was applied by Longuet-Higgins (1948) the agreement was not quite as good.

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† Present address: Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge 39, Mass., U.S.A.