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# A Structural study of the detallic compound $\mathrm{TiBe}_{12}$ 

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The structures of a numer of alloys of high beryllium content have reoently been determined. Wost of these proved to be $M B{ }_{13}$ compounds and were found by Baenaiger and Rundle (1948) to have the cubic. NaZn 13 struoture. The titanium compound, originally thought to be $\mathrm{mine}_{13}$, was found by Baensiger (2947) to be different from the others, and to be based on a hexagonal lattice.

Further examination of the compound by the author yielded X-ray diffraotion patterns whioh oxhibited a large number of unusual sxtinotions. Zaro and third layer Weissenberg diagrams, which are representative of the even and odd layers, taken with rotations around the six-fold axis, are shown in Figure 2 . The absences were suffioiently unusual to warrant an attempt at a complete struotural determination.

The struatural investigation presented number of unusual probleme and these problems $2 e d$ to the study of Fourier transforms and to the development of several new types of Fouricr syntheaes. The theory of these gyntheses is treated first in the theoretionl section. Then, using the results of this theory, the determination of the orystal structure of TiBe12 is considered.


Figure 1. 2. (hkO) and b. (hk3) Weissenberg photographs of TiBe ${ }_{12}$. (The prints have been onlarged.)

Any property of a orystal whioh is a function of position within the crystal, may be represented by means of a Fourier series (Brage, 1915). This fact has found considerable use in the determination of crystal atruotures. Several of the methods evolved are considered in the historical introduction.

The usual method of utilizing the Fourier aeries has ben to seek a Fourier expansion of some partioular physical property and to relate the Pourier coeffioi ents to quantities measured in X-ray diffraotion experiments. A somewhat different mothod is adopted hers. In the eections following the historical section the usual prodedure is reversed. There a physioal property is sought which has, as Fourier ooefficionte in its expansion, certain chosen parts of the observed $X-r a y$ data. The treatment has been oarried out for two speoial cases. The author belisved that such a treatment may be carried out for number of other cases. In fact, it may well be true, that a Fourier synthesis, made with any systamatically ohosen part of the X-ray data will have an easily interpretable maning, which may be found by methods similar to those used here.

## Hiatorioal Introduction

In 1915, Bragg first suggestod that any funotion of position in a orystalline lattice could be represented by means of a Fourier series. Duane (1925) extended Bragg's two dimensional series to three dimensions
and derived the aeries in the following form:

Hore, $\rho$ (xys) is the electron density funotion, $V$, the volume of the unit 0011, $\alpha$ (hk $l$ ), the phase angle, and $F(h k l)$, the structure faotor, defined by

$$
F(h k l)=\sum_{j=1}^{N} f_{j} \exp -2 \pi i\left(h x_{j}+k y_{j}+\ell_{q_{j}}\right)
$$

where $f_{j}$ is the atom form factor of the atom at $x_{j}, y_{j}, z_{j}$. (The parameters, as used in this thesis are fractional values and take on values between zero and one.)

It will been that, in this three dimensional form of the Fourier expansion of the electron density, all of the available structure factors are used.

In Bragg's original work one and two dimensional Fourier summations are derived. If

$$
\begin{aligned}
& \rho(x y)=\int_{0}^{1} \rho(x y z) d z \\
& \rho(x)=\int_{0}^{1} \int_{0}^{1} \rho(x y z) d y d z
\end{aligned}
$$

the Fourier expansions of $\rho(x y)$ and $\rho(x)$ take the form

$$
\begin{aligned}
& \rho(x y)=\frac{1}{V} \sum_{-\infty}^{+\infty} F(h k 0) \cos 2 \pi[h x+k y-\alpha(h k 0)] \\
& \rho(x)=\frac{1}{V} \sum_{-\infty}^{+\infty} F(h 00) \cos 2 \pi[h x-\alpha(h 00)] \quad .
\end{aligned}
$$

These forms oontain the unusual weight faotor $1 / V$. This is beoause $\rho$ ( $x y$ ) and $\rho(x)$ have been defined in parameter space rather than real space ae
is usually done. For more usual forms, see James (1948), and Booth (1948).
In these Fourier projections only a portion of the available structure factor data is used. Two dimensional projections may be made using the struoture factors represented by any plane of the reoiprocal lattice which passes through the origin. One dimensional projections may be made from any reoiprocal lattioc lina passing through the origin. But in neither of these are regions of the reoiprocal lattioe used which do not oontain the origin.

Other physioal properties, more remotely related to the electron density function, may be expanded in a Fourier series. One suoh quantity is the Patterson function defined by

$$
P(x y z)=\int_{0}^{1} \int_{0}^{1} \int_{0}^{1} \rho(x+u, y+v, z+w) \rho(u v w) d u d v d w .
$$

The Fourier development of this funotion was found by Patterson (1935) to have the form

$$
P(x y z)=\frac{1}{V} \sum \sum_{-\infty}^{+\infty} \Sigma|F(h k l)|^{2} \cos 2 \pi(h x+k y+\ell z) .
$$

The Patterson function has a maximum at $x, y$,, , whenever there are maxima in the eleotron density function at $u, v, w$, and at $x+u, y+v_{p}, z+w$. Thus the Patterson maxima oorrespond to the set of all possible vectors between the set of maxima in the elsotron density function. One and two dimensional projections of the Patterson function may be made in the same manner as the projeotions of the eleotron density function.

For the computation of the Patterson function, it is not necessary to know the phase angles $\alpha$ (hik $l$ ), which are not observed quantities. The portions of the reoiprooal lattice which must be used are, however, the same as in the electron density Fourier expansions.

A somawhet different kind of Pouriar synthesis has been suggested by Herker (1948a). He has shown that a hypothetieal disorder may be introduced into structure calalations by using only the reciprocal lattioe points one of whose indioss is a multiple of emall integer. For instance, if a Fourier synthesis is made using reciprocal lattioe points whose $l$ index is oven, the resulting density function at $x, y, z, g i v e s$ an average of the electron density function at $x, y, z$, and $x y, z+\frac{1}{3}$, Since this hypothetioal disorder concept has been used in the determination of the struoture of TiBe12, the derivation of the neoessery equations is reproduoed here.

The eleotron density at the points $x, y, z$, and $x, y, z+\frac{1}{2}$, is given by

$$
\begin{gathered}
\rho(x y z)=\frac{1}{V} \sum_{-\infty}^{+\infty} \sum F(h k l) \exp -2 \pi i(h x+k y+l z) \\
\rho\left(x, y, z+\frac{1}{n}\right)=\frac{1}{V} \Sigma \sum_{-\infty}^{+\infty} \Sigma F(h k l) \exp -2 \pi i\left(h x+k y+l z+\frac{1}{2} l\right) \\
=\frac{1}{V} \sum_{-\infty}^{+\infty} \sum_{\exp \left(-2 \pi i \frac{j}{2}\right) F(h k l) \exp -2 \pi i(h x+k y+l z)}^{\rho(x y z)+\rho\left(x, y, z+\frac{1}{2}\right)=\frac{1}{V} \sum_{-\infty}^{+\infty} \Sigma\left[1+\exp \left(-2 \pi i \frac{l}{2}\right)\right] F(h k l)} \\
\exp -2 \pi i(h x+k y+l z)
\end{gathered}
$$

$$
\begin{gathered}
\frac{1}{2}\left[\rho(x y z)+\rho\left(x, y, z+\frac{1}{2}\right)\right]=\frac{1}{V} \sum_{l e_{-} \sum_{-\infty}^{+\infty} \sum P(h k l) \exp -2 \pi i(h x+} \underset{k y+l z) .}{ } .
\end{gathered}
$$

A similar relation may be shown to exist for the average of the Patterson function.

The Fourier synthesis in a cell with hypothetical disorder is the only synthesis, which has thus far been considered, whioh uses a part of the
struoture factor data different from that used in the standard fourier and Patterson syntheses.
 that the Fourier aynthesis of the electrostatio potential field of the eleotrons be made instead of that of the oleotron density. Unfortunately, details of the method have not yot been publishod in a language familiar to the author. The method is mentioned here to call attention to the fact that Fourier synthesis need not be confined to the eleotron density or to the Patterson function.

A number of variations on the electron density and Patterson function syntheses have been devaloped and used in the interpretation of X-ray diffraction data. These are cummarized by Booth (1948). None of these methods offer any ingovations as to the portions of the reciprocal lattice used in making the expansion.

## The Fourier Transform

It is convenient, here, to introduce the concept of the Fourier transform as used by Wrinch (1946). The Fourier tranaform of a function, g(xys), dofined in real space, is given by

$$
\begin{aligned}
& w T(X Y Z)=\int_{-\infty}^{+\infty} \int_{-\infty}^{\infty} g(x y z) \exp 2 \pi i(x X+y Y+z Z) d x d y d z \\
& \text { where } w=\iint_{-\infty}^{+\infty} \int^{\infty} g(x y z) d x d y d x
\end{aligned}
$$

Reoiprocally, the traneform of $T(X Y Z)$ is given by

$$
E(x y z)=\int_{-\infty}^{+\infty} \int_{-\infty}^{\infty} T(X Y Z) \exp -2 \pi i(x X+y Y+z Z) d X d Y d Z
$$

The function $T(X Y Z)$ is called the transform of $g(x y z)$ and if $x, y, z$, are real space coordinates, $X, Y, Z$ may be identified with the reoiprocal space coordinates of orystallography.

If $g(x y z)$ represeats the electron density function, and is periodie, then $T(X Y Z)$ is differeat from zero only at a disorete set of pointse Those points are, in fact, the points of the reciprooal lattice coordinates, $h, k$, $\ell$ and $T(X Y Z)$ is the structure factor. In the periodio ase the last integral reduces to sumation over the disorete values of $X, X$, and $Z$.

It has been pointed out (Wrinoh, 1946) that the transform of a periodic distribution may be considered as made up of two parte: first, the transform of a nonmeriodic part of the distribution (the contents of a unit oell): and second, the transform of a lattioe, considered as point set. The first part is given preoisely by the equations above, while the seoond part is zero exoept at the points of the reoiprocal lattioe. In this sense, the transform of periodio function is the funation $T(X Y Z)$ at the pointa of the reciprooal lattioe and zero elsewhere.

Booause of this rolation we are able to evaluate the Fourier transfora in the integral form of the above equations, which is in many cases casier to evaluate than the corresponding summation. The transformation of the periodicity need not be considered at all sinoe it leads only to the disorete form of the realprocal lattice.

In the next aeotion the Fourier transform coneept desoribed here is used as a means of interpretation of several special types of data obtalned In the struotural work on $T \mathrm{SB}_{12}$.

The two transforms, whioh are derived below, proved to be of speoial

has besn used quite extonsively, particularly in the determination of the probabilitios in the postulated disordered structure. It is espeoially useful here, sinee the key to the short range order in the structure lies in the reflections with odd $l$ index. The transform of a partioular layer of reflections, with $\ell=1$, for example, yislds as much information ooncorning the order as three dimensional Fourier synthesis of the elsetron donsity and is considarably easier to obtain.

The seoond tranaform is of less practical value than the first, but is also of considerable theoretical interest. The abstraction of symmetry elements from the transform has been of use in one oase explained in a later section, but in general there is no advantage in carrying out the syathsis using this abstraction. The work involved in such a syathesis is also considerably greater.

## Transforms of Reoiprocal Lattios Planes

As we have seen in the historical section, Fourier syntheses heve been made using data based on planes or lines of the reolprocel lattioe passing through the origin. The restriction that the line or plane pass through the origin may, however, be rather simply romoved.

Any plane in reciprocal space is defined by the equation $2=Z_{2}$ (constant), if the rociprocel axes are chosen properly. Any line may be defined by the equations $Y=Y_{1}, Z=Z_{1}$. Considering first the Fourier transform of a plane in reciprooal space at oonstant 2 ,

$$
w I\left(x Y Z_{1}\right)=\iint_{-\infty}^{+\infty} \int g(x y z) \exp 2 \pi i\left(x X+y Y+z Z_{1}\right) d x d y d z
$$

and

$$
\int_{-\infty}^{+\infty} g(x y z) \exp 2 \pi i z Z_{1} d z=w \int_{-\infty}^{+\infty} T\left(X Y Z_{1}\right) \exp -2 \pi i(x X+y Y) d X d Y
$$

and if $g(x y z)$ is the periodic electron density function

$$
\int_{0}^{1} \rho(x y z) \exp 2 \pi i z 1_{1} d z=\frac{1}{V} \sum_{-\infty}^{+\infty} F\left(h k l_{1}\right) \exp -2 \pi i(h x+k y) .
$$

The replaciag of the integration by a sumation is a result of the. periodicity of $\rho(x y z)$ as explained earlier. $\quad \rho(x y z)$ is used in place of $g(x y z)$ and $h, k, l$, in place of $X, Y, Z$ to onphasize the shift from a general funotion defined in real space to the periodio eleotron density function. Real and imaginary parts of the above equation may beparated to give

$$
\int_{0}^{1} \rho(x y z) \cos 2 \pi z l_{1} d z=\frac{1}{V} \sum_{-\infty}^{+\infty} \sum_{\infty} F\left(h k l_{1}\right) \cos 2 \pi(h x+k y)
$$

and

$$
\int_{0}^{1} \rho(x y z) \sin 2 \pi z l_{1} d z=-\frac{1}{\nabla} \sum_{-\infty}^{+\infty} \sum^{\infty} F\left(h z l_{1}\right) \sin 2 \pi(h x+k y) e^{2}
$$

In a similar fashion, the Fourier synthesis along a line in reciprooal space oan be obtained. Thus,

$$
\begin{aligned}
& \int_{0}^{1} \int_{0}^{1} \rho(x y z) 00 \mathrm{z} 2 \pi\left(\mathrm{ky}+\ell_{1} z\right) d y d z=\frac{1}{V}-\sum_{-\infty}^{+\infty} F\left(h k_{1} l_{1}\right) 00 \sin h x \\
& \int_{0}^{1} \int_{0}^{1} \rho(x y z) \sin 2 \pi\left(k_{1} y+l_{1} z\right) d y d z=-\frac{1}{\nabla} \sum_{-\infty}^{+\infty} F\left(h k_{1} l_{1}\right) \sin 2 h x
\end{aligned}
$$

In using these equations in this structural stuad only the cosine sum mations were earried out, sinoe interest was cestered upon atoms lying at $z=0$ and $z=\frac{1}{R}$ and firat layer data was used. In other cases it might be useful to oarry out both the sine and cosine sume.

Isimilar formulae have been derived in a different form as an aid in the preoise location of peaks by clews and Cochran (1949).

It is possible, in many osses, to find the transform of that part of reciprocal spaoe, which oontains a set of reciprooal lattioe points from whioh all points of the reoiprocal lattice may be obtained by the operations of the symmetry elements which are present. In this seotion, the transform of reoiprooal lattioe points, which with the operations of an $n$-fold axis of rotation will generate the ontire reoiprocal lattioe, is derived.

The region in reciprocal space whioh when acted on by an n-fold symmetry axis will give all of reoiprocal spaoe, is best defined in cylindrical coordinates. If in the Fourier traneforn equations, the substitution
$x=\rho$ ool $\varphi$
$y=\rho \sin \varphi$
$X=$ Poos $\phi$
$Y=\operatorname{Psin} \phi$
is made, the equations become (Wrinoh, 1946)

$$
W T(P \phi z)=\int_{-\alpha}^{+\infty} \int_{0}^{2 \pi} \int_{0}^{\infty} \rho g(\rho \phi z) \exp 2 \pi i \rho P \cos (\varphi-\phi) \operatorname{xp} 2 \pi i \varepsilon z d \rho d \varphi d z
$$

$$
g(\rho \varphi \mathbb{Z})=\omega \int_{-\infty}^{+\infty} \int_{0}^{2 \pi} \int_{0}^{\infty} \operatorname{Pr}(P \phi z) \exp -2 \pi 1 \rho \operatorname{Poos}(\phi-\phi)
$$

exp - $2 \pi i z Z d P d \phi d Z$.
If the $n$-fold symotry axis lies in the $Z$ direction in reciprocal space, the equations

$$
T(P \phi Z)=T\left(P, \phi-\frac{2 \pi}{m}, Z\right) \cdots T\left(P, \phi-\frac{m-1}{m} 2 \pi, Z\right)
$$

are obtained.

The function $T^{\prime}(P \phi 2)$ is now defined by the equations

$$
\begin{gathered}
T^{\prime}(P \phi z)=T(P \phi z) \\
\frac{1}{2} T(P \phi z) \\
0
\end{gathered}
$$

$$
\begin{aligned}
& 0<\phi<\frac{2 \pi}{n} \\
& \phi=0 \text { or } \frac{2 \pi}{n} \\
& \text { elsewhere }
\end{aligned}
$$

T' ( $p$ ¢ 2 ) when repeated by the $n-f o l d$ symmetry axis, generates the function $T(P \phi z)$.

The meaning of the transform of the $\mathrm{T}^{\prime}$ function is now sought. In the transform of $T$, the integral over $\phi$ from 0 to $2 \pi$ may be reduced to a am of $\underline{n}$ integrals from 0 to $\frac{2 \pi}{\mu}$, to. Then,

$$
g(\rho \varphi z)=w \int_{-\infty}^{+\infty} \int_{0}^{\frac{2 \pi}{n}} \int_{0}^{\infty} \operatorname{PT}(P \phi z) \exp -2 \pi i \rho \operatorname{Poos}(\varphi-\phi)
$$

$$
\exp -2 \pi i z Z d P d \phi d Z
$$

$$
+\int_{-\infty}^{+\infty} \int_{\frac{2 \pi}{2}}^{2\left(\frac{2 \pi}{\pi}\right)} \int_{0}^{\infty} P T(P \phi z) \exp -2 \pi 1 \rho \operatorname{Poos}(\varphi-\phi)
$$

$$
\exp -2 \pi i z 2 d P d \phi d Z
$$

$$
+\int_{-\infty}^{+\infty} \int_{\frac{n-1}{m}}^{2 \pi} \int_{0}^{\infty} P T(P \phi z) \exp =2 \pi i \rho \operatorname{Poos}(\varphi-\phi)
$$

Now, if the transformations

$$
\begin{aligned}
& \phi^{\prime}=\phi \\
& \phi^{2}=\phi-\frac{2 \pi}{m} \\
& \cdot \cdot \\
& \phi^{2}=\phi-\frac{n-1}{m}(2 \pi)
\end{aligned}
$$

are made in the above equation, where the transformation $\phi^{i}$ is made in the
i'th term, the equation becomes

The superseripts have been omitted, sinee they are unnecessary and the relations

$$
T(P \phi z)=T\left(P, \phi-\frac{2 \pi}{n}, 2\right), \text { eto. }
$$

have been used.
Now, introducing the $T$ functions, defined above, $g(\rho \varphi s)$ beoomes

$$
\begin{aligned}
& g(\rho \varphi z)=\int_{-\infty}^{+\infty} \int_{0}^{2 \pi} \int_{0}^{\infty} \operatorname{PT}(P \phi z) \exp -2 \pi i \rho \operatorname{Pos}(\varphi-\phi) \\
&+\int_{-\infty}^{+\infty} \int_{0}^{2 \pi} \int_{0}^{\infty} \operatorname{PR}^{\prime}(P \phi Z) \exp -2 \pi i z Z d P d \phi d Z \\
& \exp -2 \pi i z 2 \operatorname{dPd} \phi d Z
\end{aligned}
$$

$$
\begin{gathered}
+w \int_{-\infty}^{+\infty} \int_{0}^{2 \pi} \int_{0}^{\infty} \operatorname{PI}^{1}(P \phi z) \exp -2 \pi i \rho \operatorname{Poos}\left(\varphi+\frac{m^{-1}}{m}(2 \pi)-\phi\right) \\
\exp -2 \pi i z Z \mathrm{dPd} \phi \mathrm{dz}
\end{gathered}
$$

$$
\begin{aligned}
& g(\rho \varphi z)=\int_{-\infty}^{+\infty} \int_{0}^{\frac{2 \pi}{m}} \int_{0}^{\infty} R T(P \phi z) \exp -2 \pi i \rho \operatorname{Pcos}(\phi-\phi) \\
& \exp -2 \pi i z z \mathrm{dPa} \phi \mathrm{dz} \\
& +\int_{-\infty}^{+\infty} \int_{0}^{\frac{2 \pi}{m}} \int_{0}^{\infty} P T(P \phi z) \exp -2 \pi i \rho \operatorname{Pcos}\left(\phi+\frac{2 \pi}{m}-\phi\right) \\
& \begin{array}{c}
+\pi \int_{-\infty}^{+\infty} \int_{0}^{\frac{2 \pi}{m}} \int_{0}^{\infty} \operatorname{PT}(p \phi z) \operatorname{sxp}-2 \pi i \rho \operatorname{Pcos}\left(\varphi+\frac{n-1}{m}(2 \pi)-\phi\right) \\
\exp -2 \pi i z z \operatorname{dPd} \phi d E .
\end{array}
\end{aligned}
$$

If now, the transform of $T{ }^{\prime}$ is denoted by $g^{\prime}$, so that

$$
\begin{array}{r}
g^{\prime}(\rho \varphi \phi)=\int_{-\infty}^{+\infty} \int_{0}^{2 \pi} \int_{0}^{\infty} P^{\prime}(P \phi Z) \exp -2 \pi i \rho \operatorname{Poos}(\phi-\phi) \\
\exp -2 \pi i z Z d P d \phi d Z
\end{array}
$$

and

$$
\begin{array}{r}
g^{*}\left(\rho, \varphi+\frac{2 \pi}{n}, z\right)=m \int_{-\infty}^{+\infty} \int_{0}^{2 \pi} \int_{0}^{\infty} P^{\prime}(P \phi Z) \exp -2 \pi i \rho \operatorname{Poos}\left(\varphi+\frac{2 \pi}{m}-\phi\right) \\
\exp -2 \pi i z Z d P d \phi d Z
\end{array}
$$

$g\left(\rho \rho_{2}\right)$ may be writton in terms of the $g^{\prime}(\rho \varphi \varepsilon)$ function as follows:
$g(\rho \varphi z)=g^{\prime}(\rho \varphi z)+E^{\prime}\left(\rho, \varphi+\frac{2 \pi}{m}, z\right)+\ldots+E^{\prime}\left(\rho, \varphi+\frac{m-1}{m}(2 \pi) z\right)$.

The last equation means that the transiorm of a function with n-fold axial symatry may be obtained by transforming only that part of the funotion whioh lies botween 0 and $\frac{2 \pi}{n}$, and subsequantly adding the valuea of the $E^{\prime}$ function at $(\rho \varphi, z),\left(\rho, \varphi+\frac{2 \pi}{m}, z\right), \ldots,\left(\rho, \varphi+\frac{n-1}{n}(2 \pi), z\right)$. From another point of view, the aymmetry axis is removed from the reciprocal space function and only the part independent of symetry is transformed. Then the symmetry axis is replaced in the transformed function.

These result are readily appliod to the oustomary Fouriar syntheses. Although the proof has been carrisd out in cylindrioal coordinates, the aotual sumation may be oarried out in the customary orystallographic coordinates. Sinoe the eleotron density function is real, only the real part of the $g^{\prime}$ function need be determined.

As an illustration, $g^{\prime}$ will be witten out for the case in which $g$ contains a six-fold symetry axis. In the hexagomal system, using hexagonal axes, the region in reciprocal spece bounded by the oylindrical coordinates

0 and $1 / 3 \pi$, is defined by $h$ and $k \geqslant 0$. To obtain $g$, therefore, only positive values of $h$ and $k$ ars included in the sum. Thus,

$$
E^{\prime}(x y z)=\frac{1}{V} \sum_{0}^{\infty} \sum_{0}^{\infty} \sum_{-\infty}^{+\infty} F^{\prime}(h k l) \exp -2 \pi i(h x+k y+l z),
$$

where $\mathrm{FI}^{\prime}$ is subject to the condition

$$
T(P \phi Z)=\frac{1}{3} T(P \phi Z) \text { at } \phi=0 \text { or } \frac{2 \pi}{n}
$$

## Therefore,

$F^{\prime}(h k l)=\frac{l}{8}(h k l)$ for $h$ or $k=0$.
To obtain the value of the electron density function, one sums the values of $g^{\prime}$ at the symmetry related points in real space. This is the oomon value of $\rho\left(\mathrm{xyz}_{\mathrm{z}}\right)$ at those points.

The $g$ ' Fouriar summation has been found useful in only one cese thus far. In the hexagonal system, it is sometimes useful in avoiding the higher indices entailed in the summation over all of the points of the reciprocal lattioc. This might be true, for instance, for summations carried out with the help of Beever-Lipscomb strips, or in other methode where an upper limit is set on the frequoncies which may be used.

In the preliminary work on the present structure, several Fourier syntheses wore made using this devioe. Reflections with indioes as high as (18.12.1) are present in the region in which $h$ and $k$ are positive. The symetry equivalent refleotions, generated by the three-fold axis are (12.30.1) and ( $30 \cdot 18 \cdot 1$ ). Sinoe the I.B.M. card sots used in the summation contained no frequencies above twenty, over one-third of the reflections would have to be omitted in the usual Fourier synthesis. In the synthesis
with symuetry abstracted, however, nearly all of the observed reflections could be used. The work referred to here led to no useable information concerning the strueture, and hence is not referred to in the structural determination.

The method has, however, soveral disadvantages. The sumation mast be carried out over a comisicerably larger portion of the cell than is usual and the mork involved is therefore increased. Only in the hexagonal or monoolinic systems does the method seem to offer any advantage whatever and even in these systems it would only rarely seem to offer any advantages over alternative methods of carrying out the sumation.

## THE STRUCTURE OF TIBe 12

As has been pointed out earlior, the interest in the TBe 12 truoture arose more from the somewhat umasual appearance of the x-ray diffraction patterns than from any other reason. In spite of this, the atructure is of interest as an additional metal strueture, whioh an adequate theory of metals should be able to explain. A few related points are diseusaed in the last section of this thesis.

The structure of TiBe 12 has not yot been fully determined. Indead, in a unit oell of this size, one might not have expeoted to be able to determine anything about the struoture had it not been for the remarkable pseudo aoll relation. The tructure which is finally suggested (for even this much is not complotely dafinite) is one in whioh each titanium atom lies in one or the other of two possible positions and there is a definite probability of occurrone of the titaniur at each site. The correlation that must exist between these probabilities has not been found. The berylliums are placed in idealized positions and although thors mast be displacomont from the ideal pesitions and although the oause of ach displacoment oan be postulated, the details have not been determined. These depend on the correlation of the probabilities of the titaniums, which is not know.

## Experimental Procedure

[^0]furnace, One sample obtained in this way had a small cavity in the center into which extended hexagonal noedies of $\mathrm{TIBe}_{12}$. There seemed to be only small amounts of aseond phase present, so it is ressonable that the compound contain only a littie less beryllium than TiBe $15^{\circ}$. An adequate chemical analysis of the compound itself has not been obtained, because of the diffioulty in obtaining samples known to be the oompound in sufficiently large quantities. These neodies ware easily separated from the matrix and several, about 1 mm in length and 0.05 to 0.1 mm in diameter, were ohosen for examination by X-ray diffraction. The face development on the needles proved to be ( 10 I 0 ) and orientation about the six-fold axis was an matter.

The following Heissenberg and Precession photographs were mades Cu $\mathbb{Z} \alpha$ radiation -- issenberg (hko) - (hk5)
mo $\mathbb{K} \alpha$ radiation -- Weissenberg (hk0) -- (hk•10)
Precossion (hko), (hOl), (hh l)
Ag $K \propto$ radistion -- Weissenberg ( h 0 l )
The CuIX piotures were taken by the multiple film teohnique. The Mo Ka Woissenberg with even $\&$ indioes and the $A g K a$ pictures were taken as aspies of timed exposures at doubled intervals of from $1 / 4$ to 16 hours. A Phillips diffraction unit was used for all piotures sxeept the Ag K $\alpha$ ones. Here homemade gas diffraotion unit was used.

Intensities were estimated by visual comparison of five multiple films (Robertion, 1943) or of six timed exposures. The intensities of all the CuK $K$ films, the $M O K$ Weissenberg films of even $l$ index, and the ( $00 l$ ) reflections from the $\mathrm{Ag} \mathrm{K} \propto$ film were estimated in this way.

Squares of the structure factors were oaloulated from the formula $I=\pi|r|^{2} G$
where $G$ is the Lorentz polarization factor obtained from tables given by lu (1943), $K$ is a constant which was used to put all atructure faotors on the same scale, and eventually determined to put them on an absolute basis. Adsorbtion and temperature fator oorrections were not used since both were small. That the temperature correction is small is shown by the consideration that reflections ocour well past the reoiprooal lattice points within the molybdenum sphere of refleotion. Relative intensities vary littlo on passing from Cu to ho radiation, which shows the adsorbtion corrootion also is negligible.

The absences which ocour are quite important and several very intonse diffraotion patterns were made, but no reflection whioh appeared to be part of the syotematic absences appeared on any film, no matter how intense.

Towards the end of the structural work, when a disordered structure was suspooted, number of Laue plotures were made with filtered and unfiltered Mo radiation. A stresking was obtained in the (hio) reaiprocal lattice plane in several directions but no streaking was found perpendicular to that plane. The Laus diagrams showed considerable ovidence of diffuse scattering but it could not be measured with the facilities available.

## The Unit Cell and Space Group

All of the diffraotion patterns obtained could be indexed on a hexagonal basis. The (hhl) Preoession piotures yield what are probably the most acourate values of the lattice constants. In terms of the repeat
distances along [001] and [110]. these ares to01 $-7.33 \pm .01$ A. $t_{110}=$ $29.44 \pm .01$ A. It will be seen that the $t_{001}$ distance is very nearly one quarter of the $t_{110}$ distance ( $7.36 \pm .01$ ). Since the two distances were mossured on the same film, it seems certain that the differenoe in the two Walues is real. The lattioe constants $a_{0}$ and $o$ are equal to $t_{110}$ and tool respectively. The $\begin{aligned} & \text { feis senberg diffraction patterns obtained with the orystal }\end{aligned}$ rotated around the 0 axia all show the diffraction aymmetry of $C_{68}$. This fixes the point symmetry as $D_{6 h}, C_{6 \%}$ or $D_{3 h}$. A great many extinotions cocur but the only one of possible significanoe in the determination of the space group, is ( $00 \ell$ ) when $l$ is odd. In the odd layer lines only those reflections oceur which lie along the edges of the series of hexagons, whioh are shown in Figure for the reciprocal lattice layer (hkl). The refleotion ( $00 \ell$ ) (odd) occurs at the center of one such hexagon, and is thus equivalent to (441), etc. whioh are also absent. It does not appear, therefore, that the absence of ( 00 l ) with $\&$ odd necessarily reveals the presence of a two-fold sor axis. The possible space groups are therefore the followingt $D_{6 h}^{1}(C 6 / m m m), D_{6}^{1}(C 62), D_{6}^{6}\left(C 63^{2}\right), C_{6 \mathrm{~V}}^{1}(C 6 m m), D_{3}^{1}(C 6 m 2)$, and $D_{3}^{8}$ (c豕2m).

## Division of the Problem

The even layer line Feissenberg and Precession diagrans, considered independently of the odd layers, may be indexed on the basis of a small pseudo oell. The oriantation of this pseudo cell with respeot to the true $0 e l 1$ is shown in Figure 3. The $C_{0}$ axis of the pseudo ocll is parallel to $0_{0}$ of the real cell and the angle between $a_{0}$ and $A_{0}$ is $90^{\circ}$. The lattice


Figure 2. The reoiprocal lattioe net (hkl). The indioated refleotions are present, the rest, absent.


Figure 3. The relative orientation of the real and pseudo colls. The o axis for both cells is perpendicular to the paper.
constants of the psoudo cell ares $A_{0}=4.23 A^{\circ} ; C_{0}=7.33 A^{\circ}$. The struoture of the pseudo cell can be determined from the intensities of the refleotion with even $\ell$ index, using standard methods. The real cell structure and the pseudo cell structure have been shown to be related as follows: (cf. p. 6) If the value of the electron density function in the real cellat and $z+\frac{3}{2}$ are averaged for all values of $x$ and $y$, and that value of the eleotron density pleced at both $z$ and $2+\frac{1}{2}$, the result is a unit oell made up of series of identioal units related by the peeudo oell primative translations. Each of these identical units is, in fact, a paoudo coll.

In other worda, the real cell consists of a series of psendo cell-like units differing from each other only in the division of a onstant electron density (for a given $x y$ ) between $z$ and $z+\frac{1}{3}$. If the $s$ truoture of the peoudo oell oan be determined from the intensities of reflections with even $l$ index, only the mature of the division between $z$ and $z+\frac{1}{2}$ need be determ mined to obtain the complete structure. In the carrying out of the latter step the intensities of reflections with odd $l$ index must be used. Thus the struotural determantion resolves itself into two distinot problems The structure of the pseudo cell and the removing of the ambiguity betwoen $z$ and $x+\frac{1}{2}$ at the various points in the real coll.

## The Struoture of the Psoudo Cell

From the observad donsity of 2.30 and a cell volume of $111.5 A^{3}$, the weight of the unit pseudo cell in molecular weight units is 154. This is compatible with the formulae $\mathrm{Ti}_{2} \mathrm{Be}_{5}$ or $\mathrm{TAB}{ }_{12}$. Altiough the experimental acouracy probably does not preclude $T i \mathrm{Ba}_{11}$ or TiBe13, the oalculated formula
is much oloser to TiBe 12 . The volume of the pseudo oell calculated from the atomic values of titanium and beryllium (from the structures of the
 quite unlikely in view of the method of preparation but was considered bsoause of the inadequato chemioal analysis.

The Patterson function projected on (001) has been obtained using the formula

$$
\begin{aligned}
P(x y) & =\sum_{0}^{\infty} \sum_{0}^{\infty}\left(F_{h \bar{k}}^{\prime 2}+F_{h k}^{\prime 2}\right) \cos h x \operatorname{cox} k y \\
& +\quad\left(F_{h \bar{k}}^{\prime}-F_{h k}^{\prime 2}\right) \sin h x \sin k y
\end{aligned}
$$

where $\quad F_{h k}^{\prime}=0$ if $h$ or $k=0$.

The profeotion was propared using the CuKa (hlo) Weissenberg data. The projection (Figure 4) shows three different peals with the poak heights Iisted in Table 1.

## Table 1

Paak heights from Patters on projection of psoudo coll on (001)

| $x$ | $y$ | Height |
| :---: | :---: | :---: |
| 0 | 0 | 690 |
| $1 / 3$ | $2 / 3$ | 200 |
| $1 / 2$ | 0 | 300 |

The possible interpretations of the Patterson projeotion in the various possible plane groups may now be considered. The projections of the pace groups $D_{6 h}^{I}, D_{6}^{1}, D_{6}^{6}, C_{67}^{1}$, yield the plane group $C_{6 \ell}^{I}$, while $D_{3 h}^{I}$ yields $C_{G \ell}^{I}$


Figure 4. Patterson projeation of pseudo cell on (001). The oontour lines have bean drawn at equal intervals and have not been smoothed. The irregularities indicate the approximate acouraoy of the data.
and $D_{3 h}^{3}$ yields $C_{3 \ell}^{I I}$. (Patterson, 1985).
The available positions in these point groups are -
In $C_{68}^{I}$ :
1: (a) 00.
2: (b) $1 / 3,2 / 3 ; 2 / 3,1 / 3$.
3: (o) $\frac{1}{2}, 0 ; 0, \frac{7}{2} ; \frac{1}{2}, \frac{1}{2} \cdot$
6: (d) $x 0 ; 0 x ; \overline{x x} ; \bar{x} 0 ; 0 \bar{x} ; x x$.
(ब) $x x ; x, \bar{x} ; x, 2 \bar{x} ; 2 \bar{x}, \bar{x} ; \bar{x}, x ; \bar{x}, 2 \bar{x} ; 2 x, x$.
$\operatorname{In} \mathrm{C}_{3 \ell}^{\mathrm{I}}:$
1: (a) 00 . (b) $1 / 3,2 / 3$. (c) $2 / 3,1 / 3$.
3: (d) $x, \bar{x} ; x, 2 x ; 2 \bar{x}, \bar{x}$.
6: (e) $x, y ; \bar{y}, x-y ; y-x, \bar{x} ; \bar{y}, \bar{x} ; y-x, y ; x, x-y$.
$\operatorname{Inc} \mathrm{Cl}_{8}^{\mathrm{II}}$
1: 00.
2: $1 / 3,2 / 3 ; 2 / 3,1 / 3$.
3: $x_{0} 0 x ; \overline{x x}$.
6: $x, y ; \bar{y}, x-y ; y-x, \bar{x} ; \bar{y}, \bar{x} ; y-x, y ; x, x-y$.
The possible placement of atoms for the improbable formula $\mathrm{Ti}_{2} \mathrm{Be}_{5}$ is oonsidered first. In the first place, if there are two titanium atoms in the unit cell, they must have the same $x y$ parameters, since if thoy do not, they must occur at 00 and $1 / 3,2 / 3$ (or $2 / 3,1 / 3$ ). In the latter case equivalent peake would appear on the Patterson at $x y$ and at $x-1 / 3, y-2 / 3$ and this does not ocour. With both titaniums at 00 or $1 / 3,2 / 3$ there is no arrangement of the berylliums which will give the observed peak heights, and further, the appearance of the odd layer lines cannot be explained. Thus the formula $\mathrm{TI}_{2} \mathrm{Be}_{5}$ may be eliminated. There remains $\mathrm{TIBe}_{12}$, which is muoh
more probable since the compound was preparsd in the presence of a large excese of beryllium.

The Patterson projection can be interpreted by means of the following positions in $\mathrm{C}_{6 \ell}^{\mathrm{I}}$ :

Ti in (a) 00.
2 Be in 2 (a) 00.
6 Be in $2(0) \frac{1}{3}, 0 ; 0, \frac{1}{2} ; \frac{1}{2}, \frac{1}{2}$.
4 Be in 2 (b) $1 / 3,2 / 3 ; 2 / 3,1 / 3$.
These positions are also possible in $c_{3}^{\frac{I}{3}}$ and $c_{\frac{I I}{I}}^{\frac{I}{l}}$, and the only possible variation is the displacement of the origin to $1 / 3,2 / 3$ in $C_{3}^{I}{ }_{l}$. This makes no difforence in the pseudo cell but must be considered in the transition to the real cell.

The Fourier projection on (001) Eives further evidence that these positions are approximately correct. This projection (Figure 5) was caloulated fron (hko) molybdenum $\mathbb{X} \alpha$ Weis senberg diffraotion data with aigns assignod from the structure factors calculated from the above positions. The integrated peak heighte on arbitrary soale are given in Table 2.

## Table 2

Integrated peak haights from Fourier projection of pseudo cell on (001)

| Hy | 87,141 |
| :---: | :---: |
| $\infty$ | 17,806 |
| $1 / 3,2 / 3$ | 15,793 |

These peak heighta agree very well with those expected for the postu-


Figure 5. Fourier projection of pseudo oell on (001).
lated $x$ and $y$ positione. It will be noticed that the peak at $1 / 3,2 / 3$ is partially resolved into three peaks. Sinoe there are only two beryllium atons at that position, this separation must represent a mall deviation from the peendo structure which ocours in expanding to the real structure. Such a deviation may be large onough to influence the intensities of the observed reflections of the hko planes, but not large onough in itself to onuse other reflections to appear. This is true because the intensity of a refleotion is proportional to the square of the structure factor, F. Since $(F+\delta)^{2}=F^{2}+2 F \delta+\delta^{2}$, a small ohange in parameters which changes $F$ to $P+\delta$ will change the intensity by $2 F \delta+\delta^{2}$. For a reflection where $F=0$ the intensity will now be only $\delta^{2}$.

Weisenberg and rotation piotures around of show that the (hko), (hks), and (hk8) intensities patteras are quite similar and that (hk2), (hk6), and (hklo) are also similar but different from the other set. Thus wo are led to postulate a layer structure for the pseudo cell, with atoms lying $1 / 4$ apart in s. Packing considerations then load to the following pseudo eell structure in $D_{6 h}^{1}$

1 II in (a) 000; or (b) 001/2.
2 Be in (e) 00z; 00E: 2 near $1 / 4$.

2 Be in (o) $1 / 3,2 / 3,0 ; 2 / 3,1 / 3,0$.
2 Be in (d) $1 / 3,2 / 3, \frac{1}{2} 12 / 3,1 / 3, \frac{1}{3}$.
Each of the aeta can be given an arbitrary parametar in some one of the other possible space groups, but the above parameter sets are the only ones whioh explain all the data. The one dimensional Fourier projection along 0 caloulated from Silver $X \alpha$ data shows that most of the atoms near
$1 / 4$ are in fact precisely at $1 / 2$, so $z_{2}=1 / 4$. (Pigure 6) There are small peaks near $1 / 4$ at 0.22 and 0.28 . Because hkJ reflections appear to be the strongest of the reflections with $l$ odd, and because of the size of the Ti atom, we take $z_{2}$ as 0.28 when $T i$ is at 000 and at 0.22 when $T i$ is at $00 \frac{1}{8}$, In Table 3, observed ( $00 \ell$ ) structure faotors are compared with those calculated for the above structure, and also with those caloulated with $\varepsilon_{1}$ at 0.27 and.29. It is seen that these intensities are not very sensitive to this 2 paramater, and that agreement is in every oase quite good if we except (004), whioh is the stroncest reflection appearing in the entire reoiprocal lattice. We presume that extinction causes the disorepanoy in $\mathrm{F}_{004}{ }^{*}$

In Table 4, observed and caloulated structure faotors are compared for all (hkl) refleotions with $l$ even which are observed with CuK a radiations. The (hk4) refleotions are somewhat sensitive to $x_{1}$, and 0.28 seoms to give the best fit.

## The Struoture of the Real Cell

The determination of the pseudo oell in the preceding section has left an ambiguity in the $z$ paramoter of the titanium and beryllium atoms at the $x=0, y=0$. The titanium atom may occur at $z=0$, or $z=\frac{1}{2}$, the two berylliums lyiag $0.28 \times 7.36 \mathrm{~A}$. away along the 2 axis. It is natural then to assume that in the true unit cell, this ambiguity will be completely removed and that enoh of the forty-eight titanium atoms in the unit cell will have a 2 parameter of oither 0 or $\frac{1}{2}$. Aa 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


Figure 6. One dimensional Fourier projection along o.

## Table 3

Comparison of oalculated and observed struature faotore for ( 00 l ) refleotions

| Index | ${ }^{\text {ob }}$ | $z_{2}=0.28$ | $\begin{aligned} & { }^{{ }_{001}}, 29^{*} \\ & z_{1}=0.2 \end{aligned}$ | $2_{1}=0.30$ |
| :---: | :---: | :---: | :---: | :---: |
| 002 | 11.6 | 9.1 | 9.4 | 9.7 |
| 004 | 25.0 | 33.1 | 32.4 | 31.7 |
| 006 | 9.8 | 6.3 | 7.5 | 8.7 |
| 008 | 15.2 | 15.5 | 14.8 | 13.3 |
| 0.0 .10 | 4.6 | 7.1 | 8.1 | 7.5 |
| $0 \cdot 0 \cdot 12$ | 10.0 | 9.9 | 9.2 | 9.5 |
| 0.0 .14 | 5.6 | 5.2 | 5.2 | 7.8 |

$$
\text { *Booth's correlation faotor, } R=\frac{\sum\left|F_{\mathrm{ag}}-F_{\mathrm{obs}}\right|}{\sum\left|F_{\mathrm{ob}}\right|}
$$

omfting $F_{004}$ for $\varepsilon=0.29$ is 0.14 .

Table 4
Calculated and observed strueture factors for the pseudo oell

| Prevado oell index | True index | $F_{\text {obs }}$ | $\mathrm{F}_{0.2}$ |
| :---: | :---: | :---: | :---: |
| 1.0.*.0 | 4.4.**0 | 15.0 | 12.6 |
| 1.1.**0 | 12.0*** | 20.9 | 21.6 |
| 2.0.*.0 | $8.8 . * * 0$ | 23.2 | 23.6 |
| 2.1.**0 | $16 \cdot 4 \cdot * \cdot 0$ | 10.8 | 8.2 |
| 3-0.**0 | 12.12.**0 | 15.3 | 17.1 |
| 2*2***0 | 24.0.*-0 | 25.9 | 26.5 |
| 3.1.**0 | 20.8.* 0 | 7.1 | 6.8 |
| $4 \cdot 0 \cdot * \cdot 0$ | 16.16*** | 17.9 | 16.6 |
| 3.2.**0 | $28 \cdot 4 \cdot * \cdot 0$ | 7.8 | 5.8 |
| 4.1.*.0 | 24.12.*.0 | 9.1 | 14.8 |
| 1-0.**2 | 4.4.*.2 | 15.2 | 13.1 |
| 1.1.**2 | 12.0.*.2 | 21.5 | 20.8 |
| 2.0.*.2 | $8 \cdot 8 \cdot * \cdot 2$ | 3.3 | -4.1 |
| 2.1.*.2 | 16.4.**2 | 12.7 | 8.4 |
| 3.0.*.2 | 12.12.**2 | 16.7 | 16.9 |
| 2-2*** | 24.0.*-2 | 6.2 | 4.6 |
| 3-1.**2 | 20.8.**2 | 11.3 | 12.4 |
| 4.0.*.2 | 16.16.**2 | 8.5 | -3.8 |
| 3.2.**2 | 28.4.**2 | 10.6 | 6.2 |
| 4.1.**2 | 24.12.*.2 | 9.7 | 12.5 |
| 1.0.** | $4.4 .{ }^{*} \cdot 4$ | 7.3 | 7.5 |
| 1.1.**4 | 12.0.*-4 | 15.8 | 16.3 |
| 2.0.**4 | 8.8.**4 | 17.5 | 19.0 |
| 2.1.**4 | 16.4.**4 | 7.6 | 6.2 |
| 3.0.**4 | 12.12.**4 | 21.3 | 13.6 |
| $2 \cdot 2 \cdot * * 4$ | 24-0.* 4 | 19.1 | 21.0 |
| 3.1.**4 | $20.8 . * \cdot 4$ | 5.7 | 5.4 |
| 4.0.** | $16.16 *^{*} \cdot 4$ | 14.4 | 13.1 |

*represents the third Bravais-lililer index which ocours in the hexagonal system.
sot, at say $\left(\frac{1}{2}, 0\right)$ is not always at $z=0$, or at $z=\frac{1}{2}$, but possesses definite probabilities for lying in one or the other of these positions.

As has been seen, the psoudo cell data give no indication of whether a Ti atom oncurs at $z=0$ or $z=\frac{1}{2}$. The peoudo cell structure, therefore gives no indication of the distribution of titanium atoms between 0 and $\frac{1}{3}$. It is neoessary to use reflections with $\ell$ odd to obtain information about this distribution.

The absence of ( $00 \ell$ ) reflections with $l$ odd is conclusive ovidence that there are equal numbers of titanium at $z=0$ and $z=\frac{1}{2}$. Indeed, as will be seen later, reflection whose strusture factor is $1 f_{1 i}$ should be olearly seen at low $\sin \theta$, and a separation of titanium between $z=0$ and $z=\frac{3}{2}$ in the ratio of 23,25 would give rise to e structure factor of $2 f_{\mathrm{Ti}}$ for all ( 00 l ) reflections with $l$ odd. There must, therefore, be twentyfour titanium at each levol.

The relative orientation of the real and pseudo cells are shown in Figure 3. The pseudo cell net picks out forty-sight points with the real cell whioh are equivalent excopt for the ambiguity in the $C_{0}$ direction. The two possible pseudo cell positions for the titanium atom oorrespond to two possible sete of positions in the real oell. The point positions $1 / 3$, $2 / 3$ occur in the psoudo cell in the spaoe group $D_{3 h}^{1}$, but when these positions are referred to the axes of the real oell, they are found to oocupy the positions of $0_{3}^{3}$. This happens because the two space groups differ only in the angle the vertical mirror plane makes with the $x$ and $y$ axes. In $\mathrm{D}_{3}^{\mathrm{s}} \mathrm{h}$ each of the symantry connected atomio sets hae a zero contribution to $\mathrm{F}_{401}$, and it is therefore impossible to explain the appearance of (401) with titanium in these pseudo-oell positions.

There remains, therofore, only the possibility that the titanium atoms ooour at 00 in the paeudo obll, and atome may be plaoed over the paeudo oell in origins in all of the possible apace groups.

All of the possible space groups possess in common a threswold axis. It will, therefore, be convenient to disouss the various arrangements of the atoms in terms of the three-fold sets and the atomic position in the $x$ plane are so listed in Table 6. The set $A(0,0,1 / 3,2 / 3 ; 2 / 3,1 / 3)$ is not a three-fold position because of the symmetry of the space groups. But since all of the other sets are true three-fold sets, this ons must be too, if the atoms are to be arranged with twonty-four atoms at $a=0$, and twentyfour at $z=\frac{1}{2}$. The relative positions of these three-fold sets are illustrated diagramatically in Figure 7.

A cystematic elimination will be carried out, and it will be shown that none of the ordered arrangements of the titanium atoms in the apace groups of the erystal class $\mathrm{D}_{\text {oh }}$ are oapable of explaining the data. Criterion of elimination

From the caloulated intensities of the pesudo cell refleotions, and the observed intensities of the reflections with evan and odd $l$ indices an estimate can be obtained as to the numbor of titanium atoms scattering in phase to the various refleotions of hol. Using the observed $F$ value of (002) and (401), and the oalculated Falue of (002) we find that the oaloulated value of $\frac{\mathrm{F}_{401}}{\mathrm{E}_{\mathrm{Ti}}-\mathrm{I}_{\mathrm{B}}}$ is about six or seven.

Sinoe refleotions were observed with intensities of less than a hundredth of that of (401), it would seem that for the absent refleotions


Figure 7. The relative position of the threefold titanium sets in the ry plane. The letters refer to the positions listed in Table 5.

## Table 5

The xy parameters of the three-fold titanium sets

| Set | Positions |
| :---: | :---: |
| A. | 0,0; $1 / 3,2 / 3 ; 2 / 3,1 / 3$ |
| B. | 1/4, $0,0,1 / 4,3 / 4,3 / 4$ |
| C. | $3 / 4,0 ; 0,3 / 4 ; 1 / 4,1 / 4$ |
| D. | 1/2,0; 0, 1/2, 1/2,1/2 |
| R. | 1/12,2/12; 1/12,11/12; 10/12,11/12 |
| $F$. | 2/12,1/12; 11/12,1/12; 11/12,10/12 |
| G. | 4/12,2/12; $10 / 12,8 / 12,10 / 12,2 / 12$ |
| H. | 2/12, $4 / 12 ; 8 / 12,10 / 12 ; 2 / 12,10 / 12$ |
| I. | 1/2, 1/4; $3 / 4,1 / 2 ; 3 / 4,1 / 4$ |
| J. | $1 / 4,1 / 2 ; 1 / 2,3 / 4 ; 1 / 4,3 / 4$ |
| \% | 5/12,1/12, 11/12,4/123 8/12,7/12 |
| L. | 1/12,5/12; $4 / 12,11 / 12 ; 7 / 12,8 / 12$ |
| \%. | 7/12,2/12: $10 / 12,5 / 12,7 / 12,5 / 12$ |
| H. | 2/12,7/12; 5/12, 10/12; 5/12,7/12 |
| 0. | 8/12,1/12; 11/12,7/12; 5/12,4/12 |
| P. | 1/12,8/12; $7 / 12,11 / 12 ; 4 / 12,5 / 12$ |

(101), (201), (301), and (211), 0.5fTi to $2.0 f_{\text {Ti }}$ would be conservative upper limit on F.

The proeess of elimination of the ordered structure was carried out roughly as follows. The contributions of each of the three-fold sets of titanium to the real part of the structure factors for several reflections were oaloulated. These are asembled in Table 6 whers the symbol Ink $l$ denotes the real part of what we have called the relative structure faotor.

Table 6
Contributions of the three-fold sets to the relative struoture factors

| Sots | $\mathrm{R}_{101}{ }^{*}$ | ${ }_{201}$ | $\mathbf{R}_{301}$ | $\mathbf{R}_{401}$ | ${ }^{8} 801$ | $\mathrm{R}_{111}$ | $\mathrm{R}_{221}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | 0 | 0 | 3 | 0 | 0 | 3 | 8 |
| B, C | 2 | -1 | 1 | 3 | 1 | -2 | -1 |
| D | -1 | 5 | -1 | 3 | -1 | -1 | 3 |
| S, F | $1 / 2+\sqrt{3}$ | 1/2 | -1 | -3/2 | 1/2- $\sqrt{5}$ | 1 | -1 |
| G, H | 1/2 | -3/2 | -1 | $-3 / 2$ | 1/2 | -1 | 3 |
| I, J | $-1$ | -1 | -1 | 3 | -1 | 1 | -1 |
| K, L | -1/2 | 1/2 | 1 | -3/2 | $-1 / 2$ | -1 | -1 |
| M, N | $1 / 2-\sqrt{8}$ | 1/2 | -1 | -3/2 | $1 / 2+\sqrt{3}$ | 1 | -1 |
| $0, P$ | $-1 / 2$ | 1/2 | 1 | -3/2 | $-1 / 2$ | -1 | -1 |

It is equal to the real part of the atructure factor divided by $f_{\text {mi }}$. This is similar to Harkar'a unitary struoture factor (Harker, 1948b), but it has not been normalised. For this reason it has been given a different name. The structure factors of the posible atomic arrangenents which place twentymfour atoms at $z=0$ and twenty $-f^{\prime}$ our at $z=\frac{1}{2}$ can be obtained by addIng struoture factor contributions obtained from Table for those atomic
sots lying at $z=0$ and multiplying by two. The atomio layer at $z \frac{2}{8}$ makes the same contribution to the struoture factors of the refleotion oonsidered since the etrueture faotors of the corresponding refleotions in the reoiprocal lattice layer with $l$ = 0 are identioally zoro.

To aid in the consideration of all the possible arrangements of the atome, arather simple aymbolism has bean used. This is desoribed in the next section.

The alimination symbolism

In Tables 5 and 6 the capital letters A, B, ote. have been used to represent the threemold atomio sets which oocur in the struoture. By BC will be mesnt the set ooncaining both set $B$ and set $C$.

In the calculation to follow the structure factors of all of the atomio arrangements compatible with the possible space groups are to be derived. As will be observed in Table 6 most of the three-fold sets oocur in pairs having the same oontribution to all of the Rhice 's. It is also found in the course of the oalculations, that various combinations of the sets have the ame contributions to all of the $g_{h k} l^{\prime} s^{*}$ When several atomio sets or combinations of atomio sets have the same oontribution, this frot will be reoognized by enclosing the set symbols, over each other, in parentheses. Thus ( 6 ) is used to reprgaent agts $B$ or $C$, whose gtruoture factor contributions are the same.

Fhen several sets have different struoture factors, for example the sets (A) and ( 8 ), and eithor of the sets may be chosen for the layer $2=$ ? for the spece group under consideration, the set symbols are written over each other in brackets. Thus sots ooourring over each other in parcathesis
have a common group of strueture factore, while those appearing above aach other in brackete have different walues for some of the structure factors considered.

In using the mybolism a series of braoketed terms arranged horizon= tally are derived by consideration of the possibilities within each space group. Then, all of the possible eets of atom having different structure factors are read from the array by ohoosing one set from each bracket, rejeoting any combinations so obtained, whieh have the same set appearing twice. There are aeveral set combinations which have the tame bructure factors, but only one of these combinations has been listed in the tables. Should it happen to have struoture factors which are compatible with the observed datasil other sets having the same structure factors are also oompatible and theae are readily found from the original array.

The use of this symbolism will be explained in detail in the consideration of $D_{6 h}$, and this should make ite masning clearer. Elimination of orderad struotures

The various possible spaee groups allow the following three, six, and twelve-fold sets:
$D_{6 h}^{1}, c_{6 v}^{1}, D_{6}^{1}-$
A, D, BC, EF, GH, MN, IJ, KLOP,
$D_{3}^{1}{ }_{h}-$
A, D, K, F, G, H, I, J, M, N, BC, LP, KO,
$D_{3}^{3}--$
A, B, C, D, EF, GH, IJ, KL, MN, OP.

The space group $D_{6}^{6}$ cannot be used, sinoe titanium atoms will be placed over aach other at 00.

Since (221) is present $R_{221}$ must be different irom zero, sinoe the imaginary part vanishes for each of the threemfold sets independently. An examination of Table 5 shows that, if (221) is not to vanish, we must have three or four of the asts $A, D, G, H$, at the same $s$ level. We therefore need to calculate the structure factors for atomic sets oontaining either ADGH, AGH, DGH, ADG, or ADF. The last two combinations oan ocour only in $D_{3 h}^{l}$. The various different weys in whioh the remaining atomic seta may be combined will now bo outlined.

In $D_{6 h}^{1}$ only the combination $A D G H$ need be considered, sinoe there are only two threesfold sete in $D_{6 h}^{l}$ and these must ocour at the same level if there are to be an even number of atoms at each leval. To oomplete the layer with ADGH, then, we must ohoose either KLOP, or any two of BC, EF,越, or IJ. We may therefore write the array


The interpretation of the array is fairly obvious in this oase, sinoe all of the strueture factors refer to only one combination of sets. The breckets plaoed over esch other represent a chol of of one or the other get of brackets.

The combinations chosen from this array arc listed in Table 7.
In $D_{3}^{1} h$ the layer at $z=0$ may contain any of the sets $A D O H, A G Z, D G H$, ADG, or ADH. With ADGH, must be chosen four thres-folds from the sets $E, F$,

I, J, M, N, BC, LP, KO. We may further divide the selection into that of two six-folds, one six-fold and two three-folds, or four three-folds. These choiaes may be represented by the array
$\left[\begin{array}{ll}(\mathrm{BC}) & \left(\mathrm{LP}_{\mathrm{KO}}\right)\end{array}\right]$
$[(A D G H)] \quad\left[\begin{array}{l}(\mathrm{BC}) \\ (\mathrm{CP}) \\ \mathrm{KO}\end{array}\right]$

| $\left[{ }_{\text {c }}^{\text {c }}\right.$ [ | $\left[{ }_{\text {P }}^{(2)}\right.$ |
| :---: | :---: |
| $\left(\mathrm{I}_{\mathrm{J}}\right.$ | ( $\left.\mathrm{I}_{3} \mathrm{~J}\right)$ |
| ( ${ }_{\text {M }}$ |  |



Table 7
Rolative structur factors for layer of
titaniun atoms at $2=0$ in D] titanium atoms at $z=0$, in Doh

| Sots | $\mathrm{R}_{102}$ | $\mathrm{R}_{201}$ | ${ }_{3}{ }_{3}$ | ${ }_{4}{ }_{401}$ | $\mathrm{R}_{501}$ | $\mathrm{R}_{111}$ | $\mathrm{R}_{221}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ADAHBCEF | $5+2 \sqrt{3}$ | -1 | 0 | 3 | $3-2 \sqrt{3}$ | 0 | 8 |
| BCIJ | 0 | -4 | 0 | 12 | 0 | 0 | 8 |
| BCMN | $3-2 \sqrt{3}$ | -1 | 0 | 3 | $3+2 \sqrt{3}$ | 0 | 8 |
| EFIJ | $-1+2 \sqrt{3}$ | -1 | -4 | 3 | -1-2 $\sqrt{3}$ | 4 | 8 |
| EFMN | 2 | 2 | -4 | -6 | 2 | 4 | 8 |
| I M | $-1-2 \sqrt{3}$ | -1 | -4 | 3 | $-1+2 \sqrt{3}$ | 4 | 8 |
| ELOP | -2 | 2 | 4 | -6 | -2 | -4 | 8 |

With DGH, AMH, $A D G$. and ATH we must ohoose five three-fold sets from E, F, I, J, M, N, B, C, LP, KO. The following arrays represent the ways in which this cat be done:

Two six folds

$$
\left[\begin{array}{ll}
(\mathrm{AGH}) & \\
(\mathrm{DGH}) & \\
(\mathrm{AD}) & \left(\begin{array}{ll}
G \\
\mathrm{H}
\end{array}\right]
\end{array}\right]\left[\begin{array}{ll}
(\mathrm{BC}) & \left(\frac{\mathrm{LP}}{\mathrm{LO}}\right)
\end{array}\right]\left[\begin{array}{c}
\mathrm{E} \\
\mathrm{E}_{\mathrm{J}} \\
\mathrm{I} \\
\left(\begin{array}{l}
J \\
\mathrm{H} \\
\mathrm{~N}
\end{array}\right]
\end{array}\right]
$$

One six-fold


No six-fole


| (AGH) | [ (EF) (IJ) |
| :---: | :---: |
| (DGH) | (IJ) (MN) |
| (AD) (G) | (EF) (MN) |
| $\left[\begin{array}{ll}\text { (HD) }\end{array}\right.$ |  |

These various possibilities are listed in Table 8.
In $D_{3 h}^{3}$ the layer at $2=0$ may contain ADGH, AGH, or DGH. ADG and ADH are not possible in this space group since $G$ and $H$ may not be separated. We are lead, therefore, to the following arrays:

With two six-folds

$\left[\begin{array}{ll}(\mathrm{ADOH})\end{array}\right]\left[\begin{array}{ll}(\mathrm{EF}) & (\mathrm{KL} \\ (\mathrm{OP} \\ (\mathrm{IJ}) & (\mathrm{KL} \\ & (\mathrm{OP}\end{array}\right]$
Where terms like (EF)(IJ) have beon omitted from the second expression, since these have already been considered in $D_{6}^{\frac{1}{h}}$.

Table 8
Relative structure factors for the layer of
titanium atoms at $a=0$ ，in $\mathrm{D}_{\mathrm{sh}}$

| Sets＊ | $\mathrm{R}_{101}$ | $\mathrm{R}_{201}$ | $\mathrm{R}_{301}$ | ${ }_{4}{ }_{401}$ | $\mathbf{R}_{501}$ | $\mathrm{R}_{111}$ | $\mathrm{H}_{221}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ADGUBCLP | 1 | －1 | 4 | 5 | 0 | －4 | 8 |
| BCEI | $3 / 2+\sqrt{3}$ | －5／2 | 0 | 15／2 | $3 / 2-\sqrt{3}$ | 0 | 8 |
| BCEM | 5 | －1 | 0 | 3 | 3 | 0 | 8 |
| BCIM | $3 / 2-\sqrt{3}$ | $-5 / 2$ | 0 | 15／2 | $3 / 2+\sqrt{8}$ | 0 | 8 |
| LPEI | $-3 / 2+\sqrt{3}$ | 竞 | 0 | $-3 / 2$ | $-3 / 2-\sqrt{3}$ | 0 | 8 |
| LPEM | 0 | 2 | 0 | －6 | 0 | 0 | 8 |
| LPIM | $-3 / 2-\sqrt{3}$ | 交 | 0 | －3／2 | $-3 / 2+\sqrt{3}$ | 0 | 8 |
| IJGE | －1 | －1 | －4 | 0 | －1 | 4 | 8 |
| EFIM | $\frac{1}{3}+\sqrt{8}$ | $\frac{1}{4}$ | －4 | －3／2 | $\frac{1}{8}=\sqrt{8}$ | 4 | 8 |
| MRES | $\frac{1}{2} \sqrt{3}$ | 者 | －4 | $-3 / 2$ | $\frac{1}{2}+\sqrt{3}$ | 4 | 8 |
| AGHBCLPR | $5 / 2+\sqrt{8}$ | $-7 / 2$ | 4 | －3／2 | $5 / 2-\sqrt{3}$ | －2 | 4 |
| $I$ |  | $-5$ | 4 | 3 | 1 | －2 | 4 |
| M | $5 / 2-\sqrt{5}$ | $-7 / 2$ | 4 | －3／2 | $5 / 2+\sqrt{3}$ | －2 | 4 |
| AGHBCEIM |  | －5 | 0 | 3 | 3 | 2 | 4 |
| EFI | $3+2 \sqrt{3}$ | －5 | 0 | 3 | 3－2 $\sqrt{3}$ | 2 | 4 |
| ETM | $9 / 2+\sqrt{8}$ | －7／2 | 0 | －3／2 | 9／2－$\sqrt{3}$ | 2 | 4 |
| IJ5 | $3 / 2+\sqrt{3}$ | －13／2 | 0 | 15／2 | $3 / 2-\sqrt{3}$ | 2 | 4 |
| I．M | $3 / 2-\sqrt{8}$ | －13／2 | 0 | 15／2 | $3 / 2+\sqrt{3}$ | 2 | 4 |
| MNE | 9／2－$\sqrt{3}$ | －7／2 | 0 | $-3 / 2$ | $9 / 2+\sqrt{3}$ | 2 | 4 |
| M INI | $3-2 \sqrt{3}$ | －5 | 0 | 3 | $3+2 \sqrt{3}$ | 2 | 4 |
| AGMLPEM | 0 | －2 | 0 | －6 | 0 | 2 | 4 |
| EFI | $2 \sqrt{3}$ | －2 | 0 | －6 | $-2 \sqrt{3}$ | 2 | 4 |
| EFM | $3 / 2+\sqrt{3}$ | $-1 / 2$ | 0 | －21／2 | $3 / 2-\sqrt{3}$ | 2 | 4 |
| IJ ${ }^{\text {d }}$ | $-3 / 2+\sqrt{3}$ | －7／2 | 0 | －3／2 | $-3 / 2-\sqrt{3}$ | 2 | 4 |
| IM | $-3 / 2-\sqrt{8}$ | $-7 / 2$ | 0 | －3／2 | $-3 / 2+\sqrt{3}$ | 2 | 4 |
| 铞安 | 3／2－$\sqrt{8}$ | $-1 / 2$ | 0 | －21／2 | $3 / 2+\sqrt{8}$ | 2 | 4 |
| MNI | $-23$ | －2 | 0 | －6 | 23 | 2 | 4 |
| AGHEFInIM | $1 / 2+\sqrt{8}$ | －7／2 | －4 | －3／2 | 1／2－$\sqrt{3}$ | －2 | 4 |
| IJTELS | $1 / 2-\sqrt{3}$ | －7／2 | －4 | $-3 / 2$ | $1 / 2+\sqrt{3}$ | －2 | 4 |
| ETVNI | 2 | －2 | －4 | －6 | 2 | －2 | 4 |

[^1]Table 8 (continued)

| Sets | $\mathrm{R}_{101}$ | $\mathrm{R}_{201}$ | $\mathrm{R}_{301}$ | $\mathrm{R}_{401}$ | $\mathrm{R}_{501}$ | $\mathrm{R}_{111}$ | $\mathrm{R}_{221}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| DGHBCLPE | $3 / 2+\sqrt{3}$ | -1/2 | 0 | $3 / 2$ | $3 / 2-\sqrt{3}$ | -6 | 4 |
| I |  | -2 | 0 | 6 |  | -6 | 4 |
| M | $3 / 2-\sqrt{3}$ | -1/2 | 0 | 3/2 | $3 / 2+\sqrt{3}$ | -6 | 4 |
| DGEBCEIM | 2 | -2 | -4 | 6 | 2 | -2 | 4 |
| EFI | $2+2 \sqrt{8}$ | -2 | -4 | 6 | $2-2 \sqrt{3}$ | -2 | 4 |
| BFM | $7 / 2+\sqrt{3}$ | -1/2 | -4 | 3/2 | 7/2- $\sqrt{3}$ | -2 | 4 |
| IJE | $1 / 2+\sqrt{8}$ | -7/2 | -4 | 21/2 | $1 / 2-\sqrt{3}$ | -2 | 4 |
| IM | $1 / 2-\sqrt{3}$ | -7/2 | -4 | 21/2 | $1 / 2+\sqrt{3}$ | -2 | 4 |
| Me | $7 / 2-\sqrt{3}$ | -1/2 | -4 | 3/2 | $7 / 2+\sqrt{3}$ | -2 | 4 |
| ManI | $2-2 \sqrt{3}$ | -2 | -4 | 6 | $2+2 \sqrt{8}$ | -2 | 4 |
| DGHLPETM | -1 | 1 | -4 | -8 | -1 | -2 | 4 |
| EFI | $-1+2 \sqrt{3}$ | 1 | -4 | -3 | -1-2 $\sqrt{3}$ | -2 | 4 |
| EFM | $1 / 2+\sqrt{3}$ | 5/2 | -4 | -15/2 | $1 / 2-\sqrt{3}$ | -2 | 4 |
| 15 | $-5 / 2+\sqrt{3}$ | -1/2 | -4 | $3 / 2$ | $-5 / 2-\sqrt{3}$ | -2 | 4 |
| In | -5/2- $\sqrt{3}$ | $-1 / 2$ | -4 | 3/2 | $-5 / 2+\sqrt{3}$ | -2 | 4 |
| ME | 1/2- $\sqrt{3}$ | $5 / 2$ | -4 | -15/2 | $1 / 2+\sqrt{3}$ | -2 | 4 |
| mis | -1-2 $\sqrt{3}$ | 1 | -4 | -3 | $-1+2 \sqrt{3}$ | -2 | 4 |
| DGHEPIN | $-1 / 2+\sqrt{3}$ | -1/2 | -8 | $3 / 2$ | $-1 / 2-\sqrt{8}$ | -6 | 4 |
| IJMane | $-1 / 2-\sqrt{3}$ | $-1 / 2$ | -8 | 3/2 | $-1 / 2+\sqrt{3}$ | -6 | 4 |
| EFMNI | 1 | 1 | -8 | -3 | 1 | -6 | 4 |
| ADOBCLPE | $1+\sqrt{3}$ | 1 | 4 | 2 | $1-\sqrt{3}$ | -2 | 4 |
| I |  | $\frac{3}{2}$ | 4 | 15/2 |  | -2 | 4 |
| $\underline{M}$ | 1- $\sqrt{3}$ | 1 | 4 | 2 | $\underline{1+\sqrt{3}}$ | -2 | 4 |
| ADGBCEIM | $3 / 2$ | $-\frac{1}{2}$ | 0 | 15/2 | $3 / 2$ | 2 | 4 |
| EFI | $3 / 2+2 \sqrt{3}$ | - $\frac{1}{2}$ | 0 | 15/2 | $3 / 2-2 \sqrt{3}$ | 2 | 4 |
| EFM | $3+\sqrt{3}$ | 1 | 0 | 3 | $3-\sqrt{3}$ | 2 | 4 |
| IJE | $\sqrt{3}$ | -2 | 0 | 12 | $-\sqrt{3}$ | 2 | 4 |
| In | - $\sqrt{3}$ | -2 | 0 | 12 | $\sqrt{3}$ | 2 | 4 |
| NITE | 3- $\sqrt{3}$ | 1 | 0 | 3 | $3+\sqrt{3}$ | 2 | 4 |
| 1015 | $3 / 2-2 \sqrt{3}$ | - $\frac{1}{2}$ | 0 | 15/2 | $3 / 2+2 \sqrt{3}$ | 2 | 4 |
| ADGLPEIM | -3/2 | $5 / 2$ | 0 | $-3 / 2$ |  | 2 | 4 |
| EFI | $-3 / 2+2 \sqrt{3}$ | $5 / 2$ | 0 | $-3 / 2$ | $-3 / 2-2 \sqrt{3}$ | 2 | 4 |
| EFM |  | 4 | 0 | -6 | $-\sqrt{3}$ | 2 | 4 |
| IJE | $-8+\sqrt{3}$ | 1 | 0 | 3 | $-3-\sqrt{3}$ | 2 | 4 |
| IM | -3- $\sqrt{3}$ | 1 | 0 | 3 | $-3+\sqrt{3}$ | 2 | 4 |
| KNE | - $\sqrt{3}$ |  | 0 |  | $\sqrt{3}$ | 2 | 4 |
| ADCEPIJM | -3/2-2 ${ }^{\text {a }}$ | $5 / 2$ | - | $-3 / 2$ 3 | -10 ${ }^{3}$ | -2 | 4 |
| IJmas | $-1-\sqrt{3}$ | 1 | -4 | 3 | $-1+\sqrt{3}$ | -2 | 4 |
| Eftani | $\frac{1}{8}$ | 5/2 | -4 | -3/2 | 2 | -2 | 4 |

$\left[\begin{array}{c}(\mathrm{AGH}) \\ (\mathrm{DGII})\end{array}\right] \quad\left[\begin{array}{c}(\mathrm{EF}) \\ (\mathrm{IJ}) \\ (\mathrm{KL}) \\ (\mathrm{MN}) \\ (\mathrm{KL} \\ \mathrm{OP}\end{array}\right] \quad\left[\begin{array}{c}\mathrm{B} \\ \mathrm{C}\end{array}\right]$

With one aix-fold
$\left[\begin{array}{l}\text { (ADGH })(B C)]\end{array} \quad\left[\begin{array}{c}\text { (ER }) \\ (\mathrm{IJ}) \\ (\mathrm{MN}) \\ \mathrm{KL} \\ \mathrm{OP})\end{array}\right]\right.$

These possibilities are listed in Table 9.
It has been shown earlier that If $_{\text {TI }}$ is a conservative uppor limit for the reflections which are systematioally absent. This means that $\mathrm{R}_{\text {hke }}<0.5$ for these reflections and an examination of Tables 7,8 , and 9 shows that in every case at least one of $R_{101}, R_{201}, R_{301}$, or $R_{111}$ is greater than this. Thus, none of the possible ordered structures will explain the observed absences.

A disordered struoture.

Since no ordered structure can be found, the struoture must be partially disordered.

There is independent evidence whioh lends support to the idea of a disordared etructure. The original Weissenberg patterns themselves led to an early suspioion that the structure was not wholly ordered, since, as can be seen from Figure 1, certain of the spots on the odd layer pictures appear to be diffuse.

The Lave diffraction patterns, taken with molybdenum radiation also give svidenoe of disorder. (of. Experimental Methods seation). The

Table 9
Relative struoture factors for layer of titanium atoms at $=0$, in $D_{h}^{3}$

| Sets | $\mathrm{R}_{101}$ | $\mathrm{R}_{202}$ | $\mathrm{R}_{301}$ | $\mathrm{H}_{401}$ | $\mathrm{R}_{601}$ | $\mathrm{R}_{111}$ | $\mathrm{R}_{221}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ADGHEFKL | $2 \sqrt{3}$ | 2 | 0 | -6 | $-2 \sqrt{3}$ | 0 | 12 |
| IJKL | -3 | -1 | 0 | 3 | -3 | 0 | 12 |
| MNKL | $-2 \sqrt{3}$ | 2 | 0 | -6 | $2 \sqrt{3}$ | 0 | 12 |
| bCKL | 1 | -1 | 4 | 3 | 1 | -4 | 12 |
| AGHEFIJB | $2+2 \sqrt{3}$ | -4 | -2 | 3 | 1-2 $\sqrt{3}$ | 4 | 4 |
| EfxLb | $2+2 \sqrt{3}$ | -2 | 2 | -6 | $2-2 \sqrt{3}$ | 0 | 4 |
| miman | 4 | -2 | -2 | -6 | 4 | 4 | 4 |
| IKLA | -1 | -5 | 2 | 3 | -1 | 0 | 4 |
| I JMMB | $1-2 \sqrt{3}$ | -4 | -2 | 3 | $1+2 \sqrt{3}$ | 4 | 4 |
| KLINNB | 2-2 $\sqrt{3}$ | -2 | 2 | -6 | $2+2 \sqrt{3}$ | 0 | 4 |
| deherisb | $2 \sqrt{3}$ | -1 | -6 | 6 | $-2 \sqrt{3}$ | 0 | 4 |
| EFKLB | $1+2 \sqrt{3}$ | 1 | -2 | -3 | $1-2 \sqrt{8}$ | 0 | 4 |
| Eminb | 3 | 1 | -6 | -3 | -3 | 0 | 4 |
| IJKLB | -2 | -2 | -2 | 6 | -2 | -4 | 4 |
| IJNas | $-2 \sqrt{3}$ | -1 | -6 | 6 | $2 \sqrt{3}$ | 0 | 4 |
| KLMAB | $1-2 \sqrt{5}$ | 1 | -2 | -3 | $1+2 \sqrt{3}$ | -4 | 4 |

streaking observed in these photographs indioate a streaking in the reciprocal lattice in planes perpendioular to $\underline{o}^{*}$. This streaking is oharacteristio of a two-dimensional disorder. (Zachariasen, 1945). The details of the non-Brage scattering in these photographs could not be determined with the facilitios that were available, so that little olse could be detarmined oonoerning the details of the disorder.

Nature of the disorder. It has been found possible to explain the over all intensity patterns quite satisfractorily on the basis of a partially disordered structure in $D_{6 h}^{1}$. Mo reasonable method oould be found by which the remaining possible spaoe groups could be investigated with respeot to disordering and little attempt was made to find a disordered atruoture in other groups. It can hardly be expeoted that any suah 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 are not known, each of the atomic sets of titanium in $D_{6 h}^{1}$ must be treated as independent. It is assumed that for each eet (one of whose atoms ocours at xy) there is a definite probability, $p_{x y}$, that the set ocour at $z=0$, and a probability of $1-p_{x y}$ that it ocour at $z=\frac{1}{a}$. Since the disorder is probably a twodimensional one, the $\mathrm{Ti}-\mathrm{Be}-\mathrm{Be}-\mathrm{Ti}$ ohains oocurring in the o direction are probably completely ordered along their length, but eaoh chain may start at - ither $s=0$ or $z=\frac{1}{6}$ with a probability that depende on its position in the (001) plane.

Equations for absence. Since the titanium $x, y$ parameters are all multiples of one-twelfth, the contributions of the titanium to $F(h k l)$ is
poriodic in $h$ and $k$ for all possible titanium combinations, and this, together with the symatry of $D_{6 h}^{1}$ allows only eight of the structure fiactors in each of the odd layers to be independent. Thus the titanium contribution to the structure factors of the first layer will have only the values $f_{T j} R(h k R)$, where $R$ takes on only eight distinct values.

The reflaotion (101), (201), (301), (111) and (441) are all absent and R(hk l ) for these reflections take a different form for each of these reflections. All other absent reflections have the same form for $R$ as one of these, so these reflections may be taken as representative of all the abeent reflections. If it is demanded that the absent reflections have ero structure factors, a set of five simultaneous equations in the eight probabilities that the oight atomic sets be at $z=0$ can be obtained. One of thes equations has irrational coeffioients, and the equating of its rational and irrational parts yialds an additional equation.

The atructure factor for the reflactions with odd $l$ indices may be written in the form

$$
\begin{aligned}
F(h k l) & =\sum_{j} f p_{x_{j} y_{j}} \cos 2 \pi\left(h x_{j}+k y_{j}\right) \\
& +f\left(1-p_{x_{j} y_{j}}\right) \cos 2 \pi\left(h x_{j}+k y_{j}\right) \\
F(h k l) & =\sum_{j} f\left(2 p_{x_{j} y_{j}}-1\right) \cos 2 \pi\left(h x_{j}+k y_{j}\right)
\end{aligned}
$$

where $f=f_{\text {rif }}+2 f_{B_{0}}$ oos $\varepsilon_{1}$, and $p_{x_{j}} y_{j}$, the probability that the atom at $x_{j} y_{y}$ lie at $z=0$.

The beryllium atoms at $z=1 / 4$ and $z=3 / 4$ do not occur in this expression because their structure factors oancel out preaisely. The berylliums at $z=0$ and $z=\frac{1}{2}$ are omitted beoause although they may not oocur over each other at procisely the same xy position, they very nearly do. In any
oase the vanishing of the approximate structure factor as written is a nooessary condition for the ranishing of the total struoture factor, since the periodic absences cannot be explained by a cancelling of the periodio titanium atructure factor contributions by the non-periodic beryllium oontributions. The beryllium structure factors are not periodic unless they 1ie in the ideal pseudo cell positions, in which case their structure factor contributions would cancel as do those of the berylliums at $z=1 / 4$ and 3/4. The titanium structure factor contributions alone must be zero or very nearly so and they are assumed to be zero. Here a particular $x_{j} y_{j}$ is used to represent the entire atomic set in $p_{x_{j}} y_{j}$.

From $F(101)=0$
$p(1 / 12,2 / 12)=p(7 / 12,2 / 12)$
and $-p\left(\frac{1}{8}, 0\right)+2 p(1 / 4,0)+2 p(1 / 12,2 / 12)+p(4 / 12,2 / 12)-2 p\left(\frac{1}{2}, 1 / 4\right)$
$-2 p(5 / 12,1 / 12)=4$
from $F(201)=0$
$3 \mathrm{p}\left(\frac{2}{2}, 0\right)-\mathrm{p}(1 / 4,0)+2 \mathrm{p}(1 / 12,2 / 12)-3 \mathrm{p}(4 / 12,2 / 12)-2 \mathrm{p}\left(\frac{1}{2}, 1 / 4\right)$
$+2 \mathrm{p}(5 / 12,1 / 12)=0$
from $F(301)=0$
$6 p(0,0)-2 p\left(\frac{1}{2}, 0\right)+4 p(1 / 4,0)-8 p(1 / 12,2 / 12)-4 p(4 / 12,2 / 12)$
$-4 \mathrm{p}\left(\frac{1}{3}, 1 / 4\right)+8 \mathrm{p}(5 / 12,1 / 12)=1$
from $F(112)=0$
$6 p(0,0)-2 p\left(\frac{1}{2}, 0\right)-4 p(1 / 4,0)+4 p(1 / 12,2 / 12)-4 p(4 / 12,2 / 12)$
$+4 p(4 / 12,2 / 12)+4 p\left(\frac{1}{2}, 1 / 4\right)-8 p(5 / 12,1 / 12)=0$
and from $F(441)=0$,
$p(0,0)+p\left(\frac{1}{2}, 0\right)+2 p(1 / 4,0)+2 p(1 / 12,2 / 12)+2 p(4 / 12,2 / 12)$
$+2 p(7 / 12,2 / 12)+2 p\left(\frac{3}{2}, 1 / 4\right)+4 p(5 / 12,1 / 12)=8$

The equations are consistent, sinee the cosfficiont and augmented matrices are both of rank five. Only the equation $F(101)=0$ leads to two equations sinoe it is the only one to contain both rational and irrational ooeffioients.

The equations may be solved in teras of two of the probabilities which have been taken to be $p(0,0)$ and $p\left(\frac{3}{\mathrm{~B}}, 0\right)$. The solutions are:

$$
p(5 / 12,1 / 12)=17 / 80+3 / 10 p(0,0)-3 / 5 p\left(\frac{1}{2}, 0\right)
$$

$p\left(\frac{1}{2}, 1 / 4\right)=2 / 10-11 / 10 p(0,0)+7 / 10 p\left(\frac{3}{3}, 0\right)$
$p(4 / 12,2 / 12)=1 / 8+3 / 2 p(0,0)-\frac{1}{2} p\left(\frac{1}{2}, 0\right)$
$p(7 / 12,2 / 12)=p(1 / 12,2 / 12)=9 / 10+1 / 20 p(0,0)-7 / 20 p\left(\frac{3}{2}, 0\right)$
$p(1 / 4,0)=29 / 20-16 / 10 p(0,0)+12 / 10 p\left(\frac{1}{6}, 0\right)$
It will be seen that the equations are not sufficient to determine a unique set of probabilities. The intensities of the present reflections must, therefore, be used. Sinoe there ars three independent structure faotors among the present refleotions, there will not neqessarily be a set of probabilities which satisfy the above set of equations and also give the oorreat intensities for the present refleotions. It was in fact found as is shown in the next section thet no set of probabilitios which put the present reflections in the right order of intensities, would satisfy the above set of equations.

Fourier transforms. As representatives of the thres independent struoture factors of the refleotions whioh are actually present on the odd layers, (401), (501), and (221) will be used.

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 faotors because the number of permutations is far too great. In the present oase,
however, this is possible since only three independent sign assigments 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 $s 1 \mathrm{gns}$.

It is difficult to see how the small possible displacements of the pseudo cell berylliums could cause a sign reversal from that required by the titaniums and yet fail to oause an absent refleotion to appear, so there will be only four possiblo variations in the signs of the structure factors of the appearing first layer reflectione. Changing all the eigns of the first layer structure factors will have the affect of adding to all of the $z$ parameters in the struoture and will yield the aeme strueture with the origin displaced by $\frac{1}{2}$ in the 2 direction. Therefore, the sign of (401) may arbitrarily be taken as positive, and the various combinations of posim tive and negative signs be taken for (501) and (221). These sign combinations may be represented schematically by

$$
\begin{equation*}
(401) \quad(501) \tag{221}
\end{equation*}
$$

| $I$ | + | - | - |
| :--- | :--- | :--- | :--- |
| $I I$ | + | + | - |
| $I I I$ | + | - | + |
| $I V$ | + | + | + |

The various possible struoture 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 reierred to by the same Roman numeral. Thus, structures I will have the structure factor of (401) and related structure factors positive, and the struoture faotors of (501) and (601), and the struoture factors related to them, negative.

Firat layar Fourier syntheses were made with each of the possible sign combinations. The sums were carried out first with the three-fold axis abstracted as outlined in the theoretioal section and later, by inoreasing the frequencies of the International Business Leohine card set to thirty, in order to inalude a majority of the reflections obtained with Cu $K \propto$ X-rays. In the latter case the following formula was used:

$$
\begin{aligned}
R(x y)= & \sum_{0}^{\infty} \sum_{0}^{\infty}\left(F^{\prime} h k \ell+F^{\prime} h k \ell\right) \cos 2 \pi h x \cos 2 \pi k y \\
& \left(F^{\prime} h \bar{k} \ell-F^{\prime} h k \ell\right) \sin 2 \pi h x \sin 2 \pi k y \\
& \text { with } F^{\prime} h_{k \ell}=0 \text { if } \quad \text { or } k=0
\end{aligned}
$$

The values of the peak heights for the four sumations are given in Table 10. The sums of all of the peak heights for each of the struotures is also included, for reasons diacussed below.

The interpretation of the first layer transforms is partioularly simple in this oase. In the theoretical seotion, the formula

$$
\mathbb{R}(x y)=\int_{0}^{1} \rho(x y z) \cos 2 \pi l_{1} z d z
$$

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

$$
\begin{aligned}
R^{2}(x y) & =\int_{0}^{1} \rho\left(x, y, x+\frac{l}{z}\right) \cos 2 \pi l_{1} z d z \\
& =\int_{\frac{1}{2}}^{\frac{3}{2}} \rho(x y z) \cos 2 \pi\left(l_{1} z+\frac{l_{1}}{2}\right) d z \\
& =R(x y) \text { if } l_{1} \text { is odd. }
\end{aligned}
$$

Table 10
Peak heights from the $F(h k$ 1) Fouriar syntheses and the probabilities deduced thereform

| Sots | Atomio position |  |  |
| :--- | :---: | :---: | :---: |

* To probabilities have been determined for these structures.

If the structure were perfeotly 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 10 that this is not the oase.

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 $\mathrm{R}(\mathrm{xy})$ over all the titanium sites must be zero. This oonsideration 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 heighte. The probebilities have been assigned by maing use of the fact that the pak heights are proportional to ${ }^{2 p_{x}} y_{j}-1$. These probabilities are also listed in Table 10 . In both oases the maximum peak has boen assigned a probability of one, and the probabilities have been rounded off to give a set of small rational fraotions.

It will be seen that neither of the two trial probability combinations satisfy the conditions for the vanishing of the structure factors of the absent reflections. In partioular $p(7 / 12,2 / 12) \neq p(1 / 12,2 / 12)$, for either of the structures.

In Table 11 the pertinent structure factors are evaluated for the two cases. It is obvious that the first set, obtained from the $p^{\prime} s$ derived from the sign oombination $F(401)$ positive, $F(501)$ negative, and $F(221)$ negative gives the better oorrelation with the observed data. Not only do most of the struoture factors of the absent reflections vanish but the structure faotors of the present reflections ere put in the observed order.

Since the Fourier synthesis of the first layer data is a new method, a three-dimensional Fourier sumation $\rho(x y 0)$ was made as a ohook using all of the Cu $K \alpha$ data with the sign assignment $I$, which gave the beat fit above. The peak heights from this sumation are given in Table l2. The

Table 11

Comparison of the relative struoture faotors for the two disordered struotures. I, and II

|  | Structure I | Struature II | Observed presonoe |
| :---: | :---: | :---: | :---: |
| $\mathrm{B}_{101}$ | -0.2 | 1.80 | absont |
| $\mathrm{R}_{201}$ | 0 | -0.75 | absent |
| $\mathrm{H}_{301}$ | 0 | -0.5 | absent |
| $\mathrm{R}_{401}$ | 7 | 7.25 | present |
| $\mathrm{R}_{501}$ | -1.72 | -0.26 | present |
| $\mathrm{R}_{121}$ | -0.5 | 0.16 | absent |
| $\mathrm{R}_{221}$ | -1.75 | 3.5 | present |
| $\mathrm{R}_{441}$ | 0 | 0 | absent |

probabilities obtained from the $F(h k l)$ synthesis are also inoluded and they Will be seen to parallal the peak hoights. Thay are not proportional to them, as might have been expeoted. This is due partly to an incorreot background in the three-dimensional synthesis and partly to a laok of correlation between the verious layers which went into the three-dimensional synthesis. This lack of correlation arises beoause the streaking of the odd leyer refleotions appears differently in the (hol), used for correlation, than it does in the (hk $\ell$ ) films. The agreement between the prob-
abilities and the peak heights seems to be good onough, however, to confirm the postulated probabilities.

Structure $I$, then, seems to satisfy all of the requirements of the obsorved data. That the agreement is fairly good, in apite of the lack of

Table 12
Three-dimensional Fourier Section (xyo)
for the sign assignment I

| Sets | Atomic position | Peak hoights | Probability that set is at $z=0$ |
| :---: | :---: | :---: | :---: |
| A | 00 | 6500 | 1/4 |
|  | 1/3,2/3 | 4500 | 1/4 |
| $\mathrm{B}, \mathrm{C}$ | 1/4,0 | 9000 | $3 / 4$ |
| D | 1/2,0 | 8960 | $3 / 4$ |
| I, J | 1/2,1/4 | 10000 | 1 |
| M, N | 7/12,2/12 | 4600 | 1/8 |
| K,L, $\mathrm{O}, \mathrm{P}$ | 5/12,1/12 | 7100 | 1/2 |
| E,F | 1/12,2/12 | 6600 | $1 / 2$ |
| G, H | 4/12,2/12 | 4200 | 1/8 |

refinements is shown by the oomparison in Table 13 where oalculated and observed structure factors are recorded for three of the odd layers.

Adjacent raflections are, in most cases, placed in the observed order with approximately the oorrect intensity ratios. It could not be expeoted that reflections farther apart would axhibit 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 $\&$ more strongly than might be expected, some minor adjustment of the $z$ parameters of the berylliums at $z=0$ and $\frac{2}{2}$ or $1 / 4$ and $3 / 4$ might be indicated.

Table 13

Caleulated and observed struoture
factors for Struoture I

| Index | $\mathrm{F}_{\text {obs }}$ | $\mathrm{F}_{\mathrm{oal}}$ |
| :---: | :---: | :---: |
| 2.2**1 | 40 | $-100$ |
| 3.1.**1 | 40 | -93 |
| 4.0.*.1 | 123 | 249 |
| 5.0.* 21 | 58 | -90 |
| 6.0.**1 | 57 | -94 |
| 7.0.* 1 | 65 | -85 |
| 8.0.**1 | 167 | 222 |
| 8.1.*.1 | 42 | -81 |
| $8 \cdot 2 \cdot * \cdot 1$ | 43 | -85 |
| 8.3.**1 | 46 | -78 |
| 6.6.**1 | 42 | -82 |
| 7.5.*.1 | 42 | -76 |
| 8*4** 2 | 152 | 201 |
| 9.4.**1 | 47 | -73 |
| 10.4.*.1 | 48 | -76 |
| 11.4***1 | 52 | -68 |
| 12*4** | 52 | 176 |
| 13.3.**1 | 0 | -63 |
| 14*2**.1 | 0 | -67 |
| 12*5** 1 | 54 | -62 |
| 15.1**.1 | 0 | -62 |
| 12.6.**1 | 56 | -65 |
| 16.0.*.1 | 47 | 163 |
| 12.7**.1 | 60 | -60 |
| 17*0** 1 | 47 | -60 |
| 10.10*** | 53 | -63 |
| 11.9** 1 | 53 | -69 |
| 12*8** 1 | 134 | 158 |
| 18.0** 1 | 50 | -62 |
| 13*8** 1 | 50 | -57 |
| 19.0.*.1 | 53 | -56 |
| 14.8.**1 | 53 | -60 |
| 20.0.* 1 | 138 | 147 |
| $15 \cdot 8 \cdot * 1$ | 54 | -54 |
| 20.1***1 | 49 | -54 |

[^2]Table 13 (oontinued)

| Index | $\mathrm{F}_{\mathrm{obz}}$ | $\mathrm{F}_{\text {cal }}$ |
| :---: | :---: | :---: |
| 20.2.*-1 | 49 | -56 |
| 16.8**-1 | 100 | 141 |
| 17.7.*.2 | 49 | -53 |
| 18.6.**1 | 49 | -66 |
| 20.3**.1 | 49 | -62 |
| 19.5.*.1 | 49 | -52 |
| 16.9.**1 | 0 | -52 |
| 20.4.*.1 | 142 | 137 |
| 16.10.**1 | 0 | -54 |
| 21.4**.1 | 52 | -50 |
| $22.4 * * * 1$ | 0 | -52 |
| 16.12.**1 | 20 | 131 |
| 17.12.*.2 | 20 | -48 |
| 24*4***1 | 89 | 126 |
| 18.12***1 | 20 | -50 |
| 24.5.**1 | 0 | -46 |
| 19.12*** | 20 | -4 |
| 24.6** 1 | 0 | -48 |
| 20.12***1 | 82 | 119 |
| 21*11**1 | not observed | -44 |
| 24*7***1 | not obeerved | -44 |
| 22.10**.1 | not observed | -47 |
| $23 \cdot 9 \cdot * \cdot 1$ | not observed | -44 |
| 24*8**1 | not observed | 116 |
| 20.13** 1 | 20 | -43 |
| $2 \cdot 2 \cdot * \cdot 5$ | 47 | -100 |
| 3.1.**3 | 47 | -93 |
| $4 \cdot 0 \cdot * \cdot 8$ | 232 | 249 |
| 5*0.**3 | 108 | -92 |
| 6.0.**8 | 126 | -98 |
| 7.0.*.8 | 137 | -89 |
| 8.0.** 8 | 372 | 234 |
| $8 \cdot 1$ **3 | 86 | -86 |
| 8.2.**3 | 92 | -93 |
| 8-3.**3 | 93 | -85 |
| $6 \cdot 6 \cdot * \cdot 3$ | 58 | -88 |
| 7-5.**8 | 58 | -82 |
| $8 \cdot 4 * * \cdot 3$ | 239 | 218 |
| 9*4.**3 | 60 | -80 |
| 10.4.**3 | 51 | -84 |

Table 13 (oontinued)

| Index | $F_{\text {obs }}$ | $\mathrm{F}_{\text {eal }}$ |
| :---: | :---: | :---: |
| $11.4 . * \cdot 3$ | 38 | -77 |
| 12*4*** | 179 | 204 |
| 13.8.*-3 | 36 | -76 |
| 14.2.**3 | 36 | -81 |
| 12.5.**3 | 36 | -76 |
| 15.1**3 | 36 | -75 |
| 12.6.**3 | 47 | -80 |
| 16.0.**3 | 179 | 198 |
| 12.7.*.3 | 43 | -73 |
| 17-0.**3 | 37 | -78 |
| 10.10.**3 | 43 | -77 |
| 11.9.**3 | 45 | -72 |
| 12.8.**3 | 209 | 190 |
| 18.0.**8 | 37 | -75 |
| 13.8.*.5 | 43 | -69 |
| 19.0.*.3 | 37 | -69 |
| 14.8.**3 | 43 | -74 |
| 20.0.**3 | 202 | 182 |
| 15*8*** | 43 | -67 |
| 20.1*** | 43 | -67 |
| 20.2.*.3 | 43 | -71 |
| 16.8.*.3 | 204 | 177 |
| 17.7.*.3 | 43 | -66 |
| $18 \cdot 6 \cdot * \cdot 3$ | 48 | -70 |
| 20.3.** 5 | 48 | -86 |
| 19.5.*.8 | 43 | -65 |
| 16.9.*.8 | 43 | -65 |
| 20.4.**3 | 204 | 173 |
| 16.10*** | 30 | -70 |
| $21.4 \cdot * \cdot 8$ | 0 | -62 |
| 22.4***3 | 0 | -65 |
| 16.12*** | 37 | 162 |
| 17.12.**3 | 37 | -59 |
| $24 \cdot 4 \cdot * \cdot 3$ | 153 | 156 |
| 18.12.**3 | 22 | -62 |
| $24 \cdot 5 \cdot * \cdot 3$ | 0 | -57 |
| 19.12.**3 | 37 | -57 |
| 24.6.*.3 | 0 | -60 |
| 20.12.**3 | 177 | 150 |
| 21.11*** | 97 | -55 |

Table 13 (continued)

| Index | $\mathrm{F}_{\text {obs }}$ | $F_{\text {orl }}$ |
| :---: | :---: | :---: |
| 24.7*** | 0 | -56 |
| 22.10***3 | 103 | -69 |
| 23.9*** | 105 | -55 |
| 24.8.*-3 | 174 | 144 |
| 20.15*** | 30 | -54 |
| 28.0.*.8 | 21 | 150 |
| 2.2.**5 | 54 | -54 |
| 3*1***6 | 57 | -50 |
| 4.0.**5 | 192 | 135 |
| $5 \cdot 0 * * \cdot 5$ | 83 | -50 |
| 6.0.**5 | 83 | -53 |
| 7-0.**5 | 81 | -50 |
| 8.0.*.5 | 171 | 132 |
| 8.1.**5 | 52 | -49 |
| 8.2.**5 | 57 | -52 |
| $8.3 .{ }^{*} \cdot 5$ | 57 | -48 |
| $6 \cdot 6 \cdot * \cdot 5$ | 58 | -50 |
| 7.5.*.5 | 58 | -47 |
| 8.4.*.5 | 267 | 126 |
| 9.4.*.5 | 74 | -46 |
| 20.4***5 | 69 | -48 |
| 11.4.**5 | 61 | -44 |
| 12.4.*.5 | 201 | 117 |
| 13.3.**5 | 0 | -44 |
| 14.2.**5 | 0 | -47 |
| 12.5.**5 | 65 | -43 |
| 15.1.**5 | 0 | -43 |
| $12 \cdot 6 \cdot * \cdot 5$ | 71 | -45 |
| $16 \cdot 0 \cdot * \cdot 5$ | 37 | 112 |
| 12.7** 5 | 77 | -41 |
| 17-0.**5 | 29 | -41 |
| 10.10.*.5 | 87 | -43 |
| 11.9.*.5 | 87 | -40 |
| 12.8.**5 | 275 | 108 |
| 18.0.**5 | 32 | -43 |
| 13.8.**.5 | 08 | -40 |
| 19.0.*.5 | 37 | -40 |
| 14.8.*.5 | 48 | -42 |
| 20.0.*.5 | 300 | 103 |
| 15.8.*.5 | 0 | -39 |

Table 13 (continued)

| Index | Fobs | $\mathrm{F}_{\mathrm{Cal}}$ |
| :---: | :---: | :---: |
| 20.1**.5 | 77 | -38 |
| 20.2*** | 71 | -41 |
| 16.8.*.5 | 183 | 103 |
| 17.7** 5 | 24 | -38 |
| 18.6.**5 | 32 | -40 |
| 20.3*** | 65 | -38 |
| 19.5*** | 37 | -37 |
| 16*9**.6 | 0 | -38 |
| 20.4**.5 | 90 | 99 |
| 16*10**.5 | 0 | -39 |
| 21.4**.5 | 79 | -\$6 |
| 22.4.*.5 | 65 | -37 |
| 16.12*** | 163 | 93 |
| 17-12*** | 68 | -34 |
| 24*4*** | 210 | 90 |
| 18*12*** | 65 | -36 |
| 24*5***5 | 0 | -84 |
| 19-12***5 | 62 | -34 |

The real test is, however, that this structure explains the absenoes and no other structure has been found whioh will do this. It must be admitted that other disordered structures may exist whioh will explain the data equally well. There might be, for instance, disordered structures in any of the other possible spaoe groups whioh would do this. Without further knowledge of the diffuse soattering without which no idea of the relations between the various probabilities oan be obtained, there seems to be little use in trying to proceed further. The absenoes are explained by the present structure and no other structure oould do that much better.

Further refinoments. The structure, as it now stands, is admittedly only a rough approximation. If the disordered struoture, which has beon postulated is correot, there is little immediate hope of refining the beryllium positions. It was seen from the pseudo oell Fourier projection (Figure 5) that oertain of the beryllium atoms mat show small displaoments from their ideal paeudo oell positions. These displacements oertainly depend on the relative positions of adjacent titanium atoms. If the titaniums were perfectly ordered, size considerations alone might make it possible to find acourately the beryllium displacement. As maters stand now, the magnitude of this displacement oan be found from the Fourier projeotion but the direction of an individual displacement cannot be found and could not be unless the oorrelation among the titanium probabilities were known.

If the beryllium whioh is displaced is considered more carefully, it will be seen that it may oxist in at last four aituations, namely: surrounded at its 2 level by none, one, two, or three, titaniums. If the beryllium is at the center of the triangle of surrounding titanium sites, it will be too close to any corner containing a titanium. It is unlikely,
then, that three titaniums will surround a beryllium and therefore also unlikely that no titaniums will surround it. Each of these beryllium is probably surrounded, therefors, by one or two titanium atoms at the cornars of the titanium aite triangle and must move away from the titaniums. The Fourier (Figure 6) shows the beryllyuns to lie at 2.5 A from some of the pseudo cell corners and atomio radii cre consistent with this being a beryllium titantum distance.

If the oorrelation among the titanium probabilities could be found, the positions of the beryllium atoms at each of these sites could be found. This could be done, also, by a trial and error prooedure using the observed intensities of the odd layer lies, but suoh a prooedure mould involve hundreds of parameters and is innractioal unless those parameters could be guessed in advanee. But such g guess involves the correlation of the titanium probabilities meationed before. The ideal beryllium positions must, therefore, be regarded as the best approximation that aan be made.

## DISCUSSION

The final struoture is represented schenatioally in Figures 8 and 9. The iractions in Figure $B$ are the probabilities, deduced earlier, that the titanium atom ooourring over that xy position ocour at $z=0$. Figure 9 shows one-half of a psoudo cell portion of the roal cell with the titanium atoms in ordered positions. The portion shown has a height of ${ }^{2}{ }_{0}$ and the complete peeudo oell portion is obtained by the operation of horizontal mirror planes at $2=0$ and $2=\frac{1}{2}$. In the true cell, similarly ordered pseudo oell portions will occur throughout the structure, with various orientations and with the pseudo oell origineither at $z=0$ or $z=1$. The 1madiate aurroundings of the various kinds of atoms are, however, similar throughout the structure. Figure 9 also shows the se surrounding atoms around one of the titanium atoms and around one each of the three crystallographically different beryllium atoms.

Without further knowledge of the relative positions of the titanium atoms, little can be said conoerning the reasons for the unusual disorder appearing in the struoture. There, at least, is some rationality in the titaniun positions, since if they are to ocour with the given xy paramere and in two layers eparated by $z=\frac{2}{2}$, there is no ordered structure whioh will preserve the correct titanium-beryllium distanoes in the xy plane. As was pointed out earlier, the three titanium atoms surrounding the beryllium atom at the pseudo cell position $1 / 3,2 / 3$ cannot all have the same $z$ parameter if a reasonable titanium-beryllium distanoe is to be maintained. A number of the ordered structures whioh wore examined in some detail in the


Figure 8. A schematic representation of the titanium positions in the final structure. The titaniums oocur over tha indioated positions at $z=0$ or $z=\frac{1}{2}$, and the fractions are the probabilities that the atom at that ry position oocur at $z=0$.


Figure 9. One half of an ordered pseudo cell portion of the real cell. The coordination polyhedra of the various atoms are also shown. The larger circles are titanium atoms, the smaller, beryllium.
course of the eliminstion of the ordersd struatures containing this forbidden grouping of titanium atoms in the same laysr. All of the possible ordered struotures could not be examined in such detail but if this grouping ocours in all of them the structure is disordered because no ordered struoture will preserve the correct interatomic distances.

We may conjecture that the various probabilities in the partially disordered coll arise through a partial ordering of some completely disordered structure. Indeed, the sharp reflections alone the even layers and (401), (801), ete. 7 can be explained by a disordered structure in which the titanfum at 00 and at positions, all of whose parameters are multiples of $1 / 4$, are at $z=0$, and the other titaniums have a probability of $1 / 4$ for occurring at $z=0$. This structure makes the structure faotors of all absent reflections zero and, in addition, yielda zero structure factor for (501), (221), and the refleotions related to these. The final structure might, then, represent the greatest amount of ordering the system could achieve while maintaining the proper interatomic distanoes.

In Table 14 are given the numbers and distanaes of atoms within the true cell. Some of the distances found may be explained very nicely if the bond orders are ohosen properly. Each titanium is bonded to eight berylliume, two at 2.18 A and six at 2.55 A . The sum of the titanium and berylliun coordination number twelve matallic radif is 2.59 , while the sum of their single bond radil is 2.21 A. (Pauling, 1947). These considerations lead to a titanium valency of four $(6 / 12+2=4)$. The beryllium at $0,0,0.29$ has six beryllium atoms at 2.13 A , which is near the coordination number twelve distanee. There is also the one titanium at the single bond distance, 2.13 A , so this beryllium has a valenoy of two.

Table 14
Noighboring atoms and interatomio distances*

Each Ti at 000 has:
2 Be (at $0,0,0.29$; etc.) at 2.13 A
6 Be (near $1 / 3,2 / 3,0 ;$ eto.) at 2.55 As
12 Be (at $\frac{1}{\mathrm{c}}, 0,1 / 4$; etc.) at 2.80 A .
Each Be at 0,0,0,29 has:
1 Ti at 2.13 A ;
6 Be (at $\frac{1}{2}, 0,1 / 4 ;$ eto.) at 2.13 A
12 Be (near $1 / 3,2 / 3,0$; etc.) at 3.34 A .
Eroh Be near $1 / 3,2 / 3,0$ has:
1 or 2 Ti at 2.55 A ;
4 or 2 Be (at $0,0,0.29$; to.) at 3.34 A
2 or 4 Be (at $\frac{1}{2}, 0,1 / 4 ;$ eto.) at 2.2 A ;
4 or 2 Be (at $\frac{1}{2}, 0,1 / 4 ;$ etc.) at 2.3 A .
Eech Be at $\frac{1}{2}, 0,1 / 4$ has:
2 Be (at $0,0,0.29$; ete.) at 2.13 A ;
2 Be (near $1 / 3,2 / 3,0_{3}$ eto.) at 2.2 As
2 Be (near $1 / 3,2 / 3,0 ;$ eto.) at $2.3 \mathrm{~A}_{3}$
4 Be (at 点妾, 1/4; etc.) at 2.12 AB
2 II
at 2.8 A .
*The positions givon refer to the pseudo oell.

The berylliume at $\frac{1}{k} 01 / 4$, etc., lie in a haxagonal net perpendioular to $0_{0}$, and are nearly closest packed within this net. In addition, each one is bonded to four other beryllium atoms, two above and two below at a slightly greater distance. Thus, these berylliums have a coordination number of about ten and the distanoes are oompatible with this.

Finally, the berylliums near $1 / 3,2 / 3,0$ seom to be less strongly bound. It is possible, sinoe the direction of the shift of these berylliums with respeot to the titanium atons is not determined by the data but is merely assumed, that some of these beryllium are bound more strongly to one of the adjacent titanium atoms. This again is pure oonjeoture.

The structure of the metallic compound TiBe 12 has been investigated. The compound was found to cryatallize in the hexagonal systom with lattioe constanta, $a_{0}=29.44 \pm .01 \mathrm{~A}, c_{0}=7.33 \pm .01 \mathrm{~A}$. The Laue diffraction olass is $D_{6 h}$ and the space group of the postulated disordered atructure is $D_{6 h}^{1}$ (06/mma).

The intensities of reflections with even $l$ index have been used to - tablish a pseudo cell structure from whioh the various interatomio distances have been determined. The pseudo cell contained an ambiguity, since it did not diatinguiah between the points $x, y, z$, and $x, y, z+\frac{1}{c}$. This ambiguity is only partially resolved in the final struoture, for it was found that only partially disordered structure would explain the absence of the large number of extinot reflections. All possible ordered struetures in any of the possible space groups were aystematically eliminated and only one disordered structure was found whioh would explain the absences in $D_{6}^{\frac{1}{6}}$.

The short range order of the struoture has been explained satisfactorily but, while the long range partial disordering may be made to appear not too unreasonable, no truly satisfactory explanstion of the details of the disordering has been found.

A study of Fourier transforme was of holp in the structural determination. The most important result of this study was the development of a mew method of fourier synthesis, using data obtained from aingle layer line,

[^3]
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[^0]:    A sample of $\mathrm{THE}_{12}$ was obtained by the heating of titanium-beryllium mixtures in the atomio ratio of about $1: 15$ to about $1400^{\circ} \mathrm{C}$, in an induotion

[^1]:    Each group has eight letters representing the eight three－fold sets． Letters which have been omitted are the same as those dirsetly above．

[^2]:    *represente the third Bravais-Miller index,

[^3]:    other than the zeroth. The interpretation of such syntheses was found to be quite simple in the present struotural determination and is used to find the postulated structure.

