NOTE TO USERS

This reproduction is the best copy available.



A STRUCTURAL STUDY OF THE METALLIC COMPOUND TiBe12

by

Richard Frank Rasuchle

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved :

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Noad of Major Department

Signature was redacted for privacy.

Dean of Graduate College



Iowa State College

UMI Number: DP12918

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.



UMI Microform DP12918

Copyright 2005 by ProQuest Information and Learning Company. All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

> ProQuest Information and Learning Company 300 North Zeeb Road P.O. Box 1346 Ann Arbor, MI 48106-1346

TABLE OF CONTENTS

INTRODUCTION	1
THE THEORY OF FOURIER TRANSFORMS	3
Historical Introduction	3 7 9 11
THE STRUCTURE OF TiBe 12	17
Experimental Procedure	17 19 20 23 30
Criterion of elimination	35 39 40 46
Nature of the disorder	48 48 51 63
DISCUSSION	65
SUMMARY	71
LITERATURE CITED	73
ACKNOWLEDGMENTS	74

QD951 R121s

T9606

INTRODUCTION

The structures of a number of alloys of high beryllium content have recently been determined. Most of these proved to be MBe_{13} compounds and were found by Baenziger and Rundle (1948) to have the cubic, $NaZn_{13}$ structure. The titanium compound, originally thought to be TiBe₁₃, was found by Baenziger (1947) 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 diffraction patterns which exhibited a large number of unusual extinctions. Zero 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 1. The absences were sufficiently unusual to warrant an attempt at a complete structural determination.

The structural investigation presented a number of unusual problems and these problems led to the study of Fourier transforms and to the development of several new types of Fourier syntheses. The theory of these syntheses is treated first in the theoretical section. Then, using the results of this theory, the determination of the crystal structure of TiBe₁₂ is considered.



Ъ.



Figure 1. a. (hk0) and b. (hk3) Weissenberg photographs of TiBe₁₂. (The prints have been enlarged.)

THE THEORY OF FOURIER TRANSFORMS

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

The usual method of utilizing the Fourier series has been to seek a Fourier expansion of some particular physical property and to relate the Fourier coefficients to quantities measured in X-ray diffraction experiments. A somewhat different method is adopted here. In the sections following the historical section the usual procedure is reversed. There a physical property is sought which has, as Fourier coefficients in its expansion, certain chosen parts of the observed X-ray data. The treatment has been carried out for two special cases. The author believed that such a treatment may be carried out for a number of other cases. In fact, it may well be true, that a Fourier synthesis, made with any systematically chosen part of the X-ray data will have an easily interpretable meaning, which may be found by methods similar to those used here.

Historical Introduction

In 1915, Bragg first suggested that any function of position in a crystalline lattice could be represented by means of a Fourier series. Duane (1925) extended Bragg's two dimensional series to three dimensions

and derived the series in the following form:

$$p(x,y,z) = \frac{1}{V} \sum_{-\infty}^{+\infty} F(hk \ell) \cos 2 \pi [(hx + ky + \ell Z) - \alpha (hk \ell)]$$
.
Here, $p(xyz)$ is the electron density function, V, the volume of the unit cell, $\alpha (hk \ell)$, the phase angle, and $F(hk \ell)$, the structure factor, defined by

$$F(hk l) = \sum_{j=1}^{N} f_{j} exp - 2 \pi i(hx_{j} + ky_{j} + lz_{j})$$

where $f_{\frac{1}{2}}$ is the atom form factor of the atom at $x_{\frac{1}{2}}$, $y_{\frac{1}{2}}$, $z_{\frac{1}{2}}$. (The parameters, as used in this thesis are fractional values and take on values between zero and one.)

It will be seen 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

$$\rho(xy) = \int_{0}^{1} \rho(xyz) dz$$
$$\rho(x) = \int_{0}^{1} \int_{0}^{1} \rho(xyz) dy dz$$

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

$$\rho(\mathbf{x}\mathbf{y}) = \frac{1}{\mathbf{y}} \stackrel{+\infty}{\leq} F(\mathbf{h}\mathbf{k}\mathbf{0}) \cos 2\pi \left[\mathbf{h}\mathbf{x} + \mathbf{k}\mathbf{y} - \mathbf{a}(\mathbf{h}\mathbf{k}\mathbf{0})\right]$$
$$\rho(\mathbf{x}) = \frac{1}{\mathbf{y}} \stackrel{+\infty}{\leq} F(\mathbf{h}\mathbf{0}\mathbf{0}) \cos 2\pi \left[\mathbf{h}\mathbf{x} - \mathbf{a}(\mathbf{h}\mathbf{0}\mathbf{0})\right] .$$

These forms contain the unusual weight factor 1/V. This is because $\rho(xy)$ and $\rho(x)$ have been defined in parameter space rather than real space as 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 structure factors represented by any plane of the reciprocal lattice which passes through the origin. One dimensional projections may be made from any reciprocal lattice line passing through the origin. But in neither of these are regions of the reciprocal lattice used which do not contain the origin.

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

$$P(xyz) = \int_{0}^{1} \int_{0}^{1} \int_{0}^{1} p(x + u, y + v, z + w) p(uvw) dudvdw.$$

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

$$P(xyz) = \frac{1}{\nabla} \mathcal{E} \underbrace{\mathcal{E}}_{-\infty}^{+\infty} \mathcal{E} \left| F(hk \varrho) \right|^2 \cos^2 \pi (hx + ky + \varrho z).$$

The Patterson function has a maximum at x, y, z, whenever there are maxima in the electron density function at u,v,w, and at x + u, y + v, z + w. Thus the Patterson maxima correspond to the set of all possible vectors between the set of maxima in the electron density function. One and two dimensional projections of the Patterson function may be made in the same manner as the projections of the electron density function.

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

A somewhat different kind of Fourier synthesis has been suggested by Harker (1948a). He has shown that a hypothetical disorder may be introduced into structure calculations by using only the reciprocal lattice points one of whose indices is a multiple of a small integer. For instance, if a Fourier synthesis is made using reciprocal lattice points whose \mathcal{A} index is even, the resulting density function at x,y,z, gives an average of the electron density function at x, y, z, and x y, $z + \frac{1}{2}$. Since this hypothetical disorder concept has been used in the determination of the structure of TiBe₁₂, the derivation of the necessary equations is reproduced here.

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

$$\begin{split} \rho(\mathbf{x}\mathbf{y}\mathbf{z}) &= \frac{1}{\nabla} \quad \boldsymbol{\Sigma} \stackrel{+ \infty}{\boldsymbol{\Sigma}} \boldsymbol{\Sigma} \quad \mathbf{F}(\mathbf{hk} \; \boldsymbol{\ell}) \exp - 2 \; \pi \; \mathbf{i} \left(\mathbf{h}\mathbf{x} + \mathbf{k}\mathbf{y} + \boldsymbol{\ell} \; \mathbf{z}\right) \\ \rho(\mathbf{x}, \mathbf{y}, \mathbf{z} + \frac{1}{2}) &= \frac{1}{\nabla} \quad \boldsymbol{\Sigma} \quad \boldsymbol{\Sigma} \quad \mathbf{F}(\mathbf{hk} \; \boldsymbol{\ell}) \; \exp - 2 \; \pi \; \mathbf{i} \left(\mathbf{h}\mathbf{x} + \mathbf{k}\mathbf{y} + \boldsymbol{\ell} \; \mathbf{z} + \frac{1}{2} \boldsymbol{\ell}\right) \\ &= \frac{1}{\nabla} \quad \boldsymbol{\Sigma} \quad \boldsymbol{\Sigma} \quad \boldsymbol{\Sigma} \quad \mathbf{E} \quad \exp(-2 \; \pi \; \frac{1}{2}) \quad \mathbf{F}(\mathbf{hk} \; \boldsymbol{\ell}) \; \exp - 2 \; \pi \; \mathbf{i} \left(\mathbf{h}\mathbf{x} + \mathbf{k}\mathbf{y} + \boldsymbol{\ell} \; \mathbf{z}\right) \\ \rho(\mathbf{x}\mathbf{y}\mathbf{z}) + \rho(\mathbf{x}, \mathbf{y}, \mathbf{z} + \frac{1}{2}) = \frac{1}{\nabla} \quad \boldsymbol{\Sigma} \quad \boldsymbol{\Sigma} \quad \mathbf{\Sigma} \quad \left[1 + \exp(-2 \; \pi \; \frac{1}{2})\right] \mathbf{F}(\mathbf{hk} \; \boldsymbol{\ell}) \\ &= \mathbf{x}\mathbf{p} - 2 \; \pi \; \mathbf{i} \left(\mathbf{h}\mathbf{x} + \mathbf{k}\mathbf{y} + \boldsymbol{\ell} \; \mathbf{z}\right) \\ \mathbf{z} \quad \left[\rho(\mathbf{x}\mathbf{y}\mathbf{z}) + \rho(\mathbf{x}, \mathbf{y}, \mathbf{z} + \frac{1}{2})\right] = \frac{1}{\nabla} \quad \boldsymbol{\Sigma} \quad \boldsymbol{\Sigma} \quad \mathbf{\Sigma} \quad \mathbf{E} \quad \mathbf{F}(\mathbf{hk} \; \boldsymbol{\ell}) \; \exp - 2 \; \pi \; \mathbf{i} \left(\mathbf{h}\mathbf{x} + \mathbf{k}\mathbf{y} + \boldsymbol{\ell} \; \mathbf{z}\right) \\ \frac{1}{2} \left[\rho(\mathbf{x}\mathbf{y}\mathbf{z}) + \rho(\mathbf{x}, \mathbf{y}, \mathbf{z} + \frac{1}{2})\right] = \frac{1}{\nabla} \quad \boldsymbol{\Sigma} \quad \boldsymbol{\Sigma} \quad \mathbf{\Sigma} \quad \mathbf{E} \quad \mathbf{F}(\mathbf{hk} \; \boldsymbol{\ell}) \; \exp - 2 \; \pi \; \mathbf{i} \left(\mathbf{h}\mathbf{x} + \mathbf{k}\mathbf{y} + \boldsymbol{\ell} \; \mathbf{z}\right) \\ \mathbf{k}\mathbf{y} + \boldsymbol{\ell} \; \mathbf{z} \right), \end{split}$$

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, which uses a part of the

structure factor data different from that used in the standard Fourier and Patterson syntheses.

Another recent development has been a suggestion by Konobeevskii (1948) that the Fourier synthesis of the electrostatic potential field of the electrons be made instead of that of the electron density. Unfortunately, details of the method have not yet been published 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 electron density or to the Patterson function.

A number of variations on the electron density and Patterson function syntheses have been developed and used in the interpretation of X-ray diffraction data. These are summarized by Booth (1948). None of these methods offer any innovations 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 transform of a function, g(xyz), defined in real space, is given by

wT(XYZ) =
$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} g(xyz) \exp 2\pi i(xX + yY + zZ) dxdydz$$

where w =
$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} g(xyz) dxdydz.$$

Reciprocally, the transform of T(XYZ) is given by

$$g(xyz) = w \int \int_{-\infty}^{+\infty} \int T(XYZ) \exp - 2\pi i(xX + yY + zZ) dXdYdZ.$$

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

If g(xyz) represents the electron density function, and is periodic, then T(XYZ) is different from zero only at a discrete set of points. Those points are, in fact, the points of the reciprocal lattice coordinates, h, k, g; and T(XYZ) is the structure factor. In the periodic case the last integral reduces to a summation over the discrete values of X, Y, and Z.

It has been pointed out (Wrinch, 1946) that the transform of a periodic distribution may be considered as made up of two parts: first, the transform of a non-periodic part of the distribution (the contents of a unit cell); and second, the transform of a lattice, considered as a point set. The first part is given precisely by the equations above, while the second part is zero except at the points of the reciprocal lattice. In this sense, the transform of a periodic function is the function T(XYZ) at the points of the reciprocal lattice and zero elsewhere.

Because of this relation we are able to evaluate the Fourier transform in the integral form of the above equations, which is in many cases easier to evaluate than the corresponding summation. The transformation of the periodicity need not be considered at all since it leads only to the discrete form of the reciprocal lattice.

In the next section the Fourier transform concept described here is used as a means of interpretation of several special types of data obtained in the structural work on TiBe₁₂.

The two transforms, which are derived below, proved to be of special interest in the determination of the TiBe₁₂ structure. The first transform

has been used quite extensively, particularly in the determination of the probabilities in the postulated disordered structure. It is especially useful here, since the key to the short range order in the structure lies in the reflections with odd \mathcal{A} index. The transform of a particular layer of reflections, with $\mathcal{A} = 1$, for example, yields as much information concerning the order as a three dimensional Fourier synthesis of the electron density and is considerably easier to obtain.

The second transform 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 case explained in a later section, but in general there is no advantage in carrying out the synthesis using this abstraction. The work involved in such a synthesis is also considerably greater.

Transforms of Reciprocal Lattice Planes

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

Any plane in reciprocal space is defined by the equation $Z = Z_1$ (constant), if the reciprocal 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 reciprocal space at constant Z,

$$wT(XYZ_1) = \int_{-\infty}^{+\infty} \int g(xyz) \exp^{2\pi i (xX + yY + zZ_1)} dxdydz$$

and

$$\int_{-\infty}^{+\infty} g(xyz) \exp 2\pi i z Z_1 dz = w \int_{-\infty}^{+\infty} T(XYZ_1) \exp - 2\pi i (xX + yY) dXdY_1$$

and if g(xyz) is the periodic electron density function

The replacing of the integration by a summation is a result of the . periodicity of $\rho(xyz)$ as explained earlier. $\rho(xyz)$ is used in place of g(xyz) and h,k, l, in place of X,Y,Z to emphasize the shift from a general function defined in real space to the periodic electron density function.

Real and imaginary parts of the above equation may be separated to give

$$\int_{0}^{1} \rho(xyz) \cos 2\pi z \ell_{1} dz = \frac{1}{\nabla} \sum_{-\infty}^{+\infty} F(hk \ell_{1}) \cos 2\pi (h x + ky)$$

and

$$\int_{0}^{1} \rho(xyz) \sin 2\pi z \ell_{1} dz = -\frac{1}{\nabla} \stackrel{\rightarrow}{\underset{-\infty}{\Sigma}} F(hk\ell_{1}) \sin 2\pi (hx + ky).^{1}$$

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

$$\int_{0}^{1} \int_{0}^{1} \rho(\mathbf{x}\mathbf{y}\mathbf{z}) \cos 2\pi (\mathbf{k}\mathbf{y} + \mathcal{R}_{i}\mathbf{z}) d\mathbf{y} d\mathbf{z} = \frac{1}{\nabla} - \sum_{\infty}^{+\infty} F(\mathbf{h}\mathbf{k}_{1}\mathcal{R}_{i}) \cos 2\pi \mathbf{h}\mathbf{x}$$
$$\int_{0}^{1} \int_{0}^{1} \rho(\mathbf{x}\mathbf{y}\mathbf{z}) \sin 2\pi (\mathbf{k}_{1}\mathbf{y} + \mathcal{R}_{i}\mathbf{z}) d\mathbf{y} d\mathbf{z} = -\frac{1}{\nabla} \sum_{-\infty}^{+\infty} F(\mathbf{h}\mathbf{k}_{1}\mathcal{R}_{i}) \sin 2\mathbf{h}\mathbf{x}.$$

In using these equations in this structural study only the cosine summations were carried out, since interest was centered upon atoms lying at z = 0 and $z = \frac{1}{2}$ and first layer data was used. In other cases it might be useful to carry out both the sine and cosine sums.

¹Similar formulae have been derived in a different form as an aid in the precise location of peaks by Clews and Cochran (1949).

Transforms of Points Not Equivalent by Symmetry

It is possible, in many cases, to find the transform of that part of reciprocal space, which contains a set of reciprocal lattice points from which all points of the reciprocal lattice may be obtained by the operations of the symmetry elements which are present. In this section, the transform of reciprocal lattice points, which with the operations of an n-fold axis of rotation will generate the entire reciprocal lattice, is derived.

The region in reciprocal space which when acted on by an n-fold symmetry axis will give all of reciprocal space, is best defined in cylindrical coordinates. If in the Fourier transform equations, the substitution

x	*	9 00#	φ	У		ያ	sin	Р
X	-	Pcos Ø		Y	-	Psi	.nΦ	

is made, the equations become (Wrinch, 1946)

$$wT(P\varphi Z) = \int_{-\infty}^{+\infty} \int_{0}^{2\pi} \int_{0}^{\infty} g(g\varphi Z) exp2\pi i \rho Pcos(\varphi - \varphi) exp2\pi i z Z d\rho d\varphi dz$$
$$g(\varphi \varphi Z) = w \int_{-\infty}^{\infty} \int_{0}^{2\pi} \int_{0}^{\infty} PT(P\varphi Z) exp - 2\pi i \rho Pcos(\varphi - \varphi)$$

 $exp - 2\pi izZ dPd\phi dZ$.

If the n-fold symmetry axis lies in the Z direction in reciprocal space, the equations

 $T(P \varphi Z) = T(P, \varphi - \frac{2\pi}{2}, Z) \cdot \cdot \cdot T(P, \varphi - \frac{\pi}{2}/2\pi, Z)$

are obtained.

The function $T^{*}(P \varphi Z)$ is now defined by the equations

$$T'(P\varphi Z) = T(P\varphi Z) \qquad 0 < \varphi < \frac{2\pi}{2}$$

$$\frac{1}{2}T(P\varphi Z) \qquad \varphi = 0 \quad \alpha \quad \frac{2\pi}{2}$$

$$0 \qquad \text{elsewhere}$$

 $T^*(P \varphi Z)$ when repeated by the n-fold symmetry axis, generates the function $T(P \varphi Z)$.

The meaning of the transform of the T' function is now sought. In the transform of T, the integral over ϕ from 0 to 2π may be reduced to a sum of <u>n</u> integrals from 0 to 2π , etc. Then,

$$g(\varphi \varphi z) = w \int_{-\infty}^{+\infty} \int_{0}^{\frac{2\pi}{m}} \int_{0}^{\infty} PT(P\varphi Z) \exp - 2\pi i \rho P\cos(\varphi - \varphi)$$

$$exp - 2\pi i z Z dPd\varphi dZ$$

$$+ w \int_{-\infty}^{+\infty} \int_{\frac{2\pi}{m}}^{2(\frac{2\pi}{m})} \int_{0}^{\infty} PT(P\varphi Z) \exp - 2\pi i \rho P\cos(\varphi - \varphi)$$

$$exp - 2\pi i z Z dPd\varphi dZ$$

Now, if the transformations

$$\phi' = \phi$$

$$\phi^2 = \phi - \frac{2\tau}{\pi}$$

$$\phi^* = \phi - \frac{m-1}{\pi} (2\pi)$$

are made in the above equation, where the transformation ϕ^{\star} is made in the

i'th term, the equation becomes

$$g(\varphi \varphi_{Z}) = w \int_{0}^{+\infty} \int_{0}^{\frac{2\pi}{m}} \int_{0}^{\infty} PT(P\varphi_{Z})exp - 2\pi i\rho Pcos(\varphi - \varphi)$$

$$exp - 2\pi izZ dPd\varphi dZ$$

$$+ w \int_{0}^{+\infty} \int_{0}^{\frac{2\pi}{m}} \int_{0}^{\infty} PT(P\varphi_{Z})exp - 2\pi i\rho Pcos(\varphi + \frac{2\pi}{m} - \varphi)$$

$$exp - 2\pi izZ dPd\varphi dZ$$

$$+ \cdots$$

$$+ w \int_{-\infty}^{+\infty} \int_{0}^{\frac{2\pi}{m}} \int_{0}^{\infty} PT(P\varphi_{Z})exp - 2\pi i\rho Pcos(\varphi + \frac{m-1}{m}(zn) - \varphi)$$

$$exp - 2\pi izZ dPd\varphi dZ.$$

The superscripts have been omitted, since they are unnecessary and the relations

$$T(P\varphi Z) = T(P, \varphi - \frac{2\pi}{2}, Z)$$
, etc.

have been used,

Now, introducing the T' functions, defined above, $g(g \varphi s)$ becomes

$$g(\rho \varphi z) = w \int_{-\infty}^{+\infty} \int_{0}^{2\pi} \int_{0}^{\infty} PT^{*}(P\varphi Z) exp - 2\pi i \rho Pcos(\varphi - \varphi)$$

$$exp - 2\pi i z Z dPd\varphi dZ$$

$$+ w \int_{-\infty}^{+\infty} \int_{0}^{2\pi} \int_{0}^{\infty} PT^{*}(P\varphi Z) exp - 2\pi i \rho Pcos(\varphi + \frac{2\pi}{2} - \varphi)$$

$$exp - 2\pi i z Z dPd\varphi dZ$$

If now, the transform of T' is denoted by g', so that

$$g'(\varphi \varphi z) = w \int_{-\infty}^{+\infty} \int_{0}^{1\pi} \int_{0}^{\infty} PT'(P \varphi Z) exp - 2\pi i \rho Poos(\varphi - \varphi)$$

exp - 2\pi i z dPd \u03c6 dZ

and

$$g'(\rho, \varphi + \frac{2\pi}{m}, \mathbf{z}) = \mathbf{w} \int_{0}^{+\infty} \int_{0}^{2\pi} \int_{0}^{\infty} P\mathbf{T}'(P\varphi Z) \exp - 2\pi i \rho \operatorname{Pcos}(\varphi + \frac{2\pi}{m} - \varphi) \exp - 2\pi i z Z dPd\varphi dZ,$$

 $g(g \not \varphi z)$ may be written in terms of the $g'(g \not \varphi z)$ function as follows:

$$g(\boldsymbol{\rho} \boldsymbol{\varphi} \boldsymbol{z}) = g^{\dagger}(\boldsymbol{\rho} \boldsymbol{\varphi} \boldsymbol{z}) + g^{\dagger}(\boldsymbol{\beta}, \boldsymbol{\varphi} + \frac{2\pi}{n}, \boldsymbol{z}) + \dots + g^{\dagger}(\boldsymbol{\rho}, \boldsymbol{\varphi} + \frac{m-1}{n}(2\pi), \boldsymbol{z}).$$

The last equation means that the transform of a function with n-fold axial symmetry may be obtained by transforming only that part of the function which lies between 0 and $\frac{2\pi}{\Omega}$, and subsequently adding the values of the g' function at $(g \neq z)$, $(f, g + \frac{2\pi}{\Omega}, z)$, . . . , $(f, g + \frac{m-i}{\Omega}(2\pi), z)$. From another point of view, the symmetry axis is removed from the reciprocal space function and only the part independent of symmetry is transformed. Then the symmetry axis is replaced in the transformed function.

These results are readily applied to the customary Fourier syntheses. Although the proof has been carried out in cylindrical coordinates, the actual summation may be carried out in the customary crystallographic coordinates. Since the electron density function is real, only the real part of the g' function need be determined.

As an illustration, g' will be written out for the case in which g contains a six-fold symmetry axis. In the hexagonal system, using hexagonal axes, the region in reciprocal space bounded by the cylindrical coordinates 0 and $1/3 \pi$, is defined by h and k > 0. To obtain g', therefore, only positive values of h and k are included in the sum. Thus,

$$g'(xyz) = \frac{1}{\sqrt{2}} \sum_{o}^{\infty} \sum_{e=\infty}^{+\infty} F'(hk \ell) \exp - 2\pi i(hx + ky + \ell z),$$

where F' is subject to the condition

$$T'(P \Phi Z) = \frac{1}{2}T(P \Phi Z)$$
 at $\Phi = 0$ or $\frac{2\pi}{n}$

Therefore,

 $F'(hkl) = \frac{1}{2}F(hkl)$ for h or k = 0.

To obtain the value of the electron density function, one sums the values of g' at the symmetry related points in real space. This is the common value of $\rho(xyz)$ at those points.

The g' Fourier summation has been found useful in only one case 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 lattice. This might be true, for instance, for summations carried out with the help of Beever-Lipscomb strips, or in other methods where an upper limit is set on the frequencies which may be used.

In the preliminary work on the present structure, several Fourier syntheses were made using this device. Reflections with indices as high as (18.12.1) are present in the region in which h and k are positive. The symmetry equivalent reflections, generated by the three-fold axis are $(12.\overline{30.1})$ and $(\overline{30.18.1})$. Since the I.B.M. card sets 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 symmetry abstracted, however, nearly all of the observed reflections could be used. The work referred to here led to no useable information concerning the structure, and hence is not referred to in the structural determination.

The method has, however, several disadvantages. The summation must be carried out over a considerably larger portion of the cell than is usual and the work involved is therefore increased. Only in the hexagonal or monoclinic 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 summation.

THE STRUCTURE OF TiBe12

As has been pointed out earlier, the interest in the TiBe₁₂ structure arose more from the somewhat unusual appearance of the x-ray diffraction patterns than from any other reason. In spite of this, the structure is of interest as an additional metal structure, which an adequate theory of metals should be able to explain. A few related points are discussed in the last section of this thesis.

The structure of TiBe₁₂ has not yet been fully determined. Indeed, in a unit cell of this size, one might not have expected to be able to determine anything about the structure had it not been for the remarkable pseudo cell relation. The structure which is finally suggested (for even this much is not completely definite) is one in which each titanium atom lies in one or the other of two possible positions and there is a definite probability of occurrence of the titanium at each site. The correlation that must exist between these probabilities has not been found. The berylliums are placed in idealised positions and although there must be a displacement from the ideal positions and although the cause of such a displacement can be postulated, the details have not been determined. These depend on the correlation of the probabilities of the titaniums, which is not known.

Experimental Procedure

A sample of TiBe₁₂ was obtained by the heating of titanium-beryllium mixtures in the atomic ratio of about 1:15 to about 1400°C, in an induction

furnace. One sample obtained in this way had a small cavity in the center into which extended hexagonal needles of TiBe_{12} . There seemed to be only small amounts of a second phase present, so it is reasonable that the compound contain only a little less beryllium than TiBe_{15} . An adequate chemical analysis of the compound itself has not been obtained, because of the difficulty in obtaining samples known to be the compound in sufficiently large quantities. These needles were easily separated from the matrix and several, about 1 mm in length and 0.05 to 0.1 mm in diameter, were chosen for examination by X-ray diffraction. The face development on the needles proved to be (1010) and orientation about the six-fold axis was an easy matter.

The following Weissenberg and Precession photographs were made: Cu K & radiation -- Weissenberg (hkO)--(hk5) (hOl)

Mo Ka radiation -- Weissenberg (hk0) -- (hk·10) Precession (hk0),(h0l),(hhl)

Ag K a radiation -- Weissenberg (hOl)

The Cu Ka pictures were taken by the multiple film technique. The Mo Ka Weissenberg with even \mathcal{L} indices and the Ag Ka pictures were taken as a series of timed exposures at doubled intervals of from 1/4 to 16 hours. A Phillips diffraction unit was used for all pictures except the Ag Ka ones. Here a homemade gas diffraction unit was used.

Intensities were estimated by visual comparison of five multiple films (Robertson, 1943) or of six timed exposures. The intensities of all the Cu Ka films, the Mo Ka Weissenberg films of even \mathcal{L} index, and the (00 \mathcal{L}) reflections from the Ag Ka film were estimated in this way. Squares of the structure factors were calculated from the formula $I = K |F|^2 G$

where G is the Lorentz polarization factor obtained from tables given by Lu (1943), K is a constant which was used to put all structure factors on the same scale, and eventually determined to put them on an absolute basis. Adsorbtion and temperature factor corrections were not used since both were small. That the temperature correction is small is shown by the consideration that reflections occur well past the reciprocal lattice points within the molybdenum sphere of reflection. Relative intensities vary little on passing from Cu to Mo radiation, which shows the adsorbtion correction also is negligible.

The absences which occur are quite important and several very intense diffraction patterns were made, but no reflection which appeared to be part of the systematic absences appeared on any film, no matter how intense.

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

The Unit Cell and Space Group

All of the diffraction patterns obtained could be indexed on a hexagonal basis. The (hh l) Precession pictures yield what are probably the most accurate values of the lattice constants. In terms of the repeat

distances along [001] and [110], these are: $t_{001} = 7.33 \div .01$ A. $t_{110} =$ 29.44 \pm .01 A. It will be seen that the t distance is very nearly one quarter of the t_{110} distance (7.36 \pm .01). Since the two distances were measured on the same film, it seems certain that the difference in the two values is real. The lattice constants a, and o, are equal to t_{110} and t_{001} respectively. The Weissenberg diffraction patterns obtained with the crystal rotated around the c axis all show the diffraction symmetry of C_{60} . This fixes the point symmetry as D_{6h} , C_{6v} , or D_{3h} . A great many extinctions occur but the only one of possible significance in the determination of the space group, is (00 l) when l is odd. In the odd layer lines only those reflections occur which lie along the edges of the series of hexagons, which are shown in Figure ? for the reciprocal lattice layer (hkl). The reflection (00 Q) (odd) occurs at the center of one such hexagon, and is thus equivalent to (441), etc. which are also absent. It does not appear, therefore, that the absence of $(00 \ l)$ with $\ l$ odd necessarily reveals the presence of a two-fold sorew axis. The possible space groups are therefore the following: D_{Sh}^1 (C6/mmm), D_6^1 (C62), D_6^6 (C6₃2), C_{6v}^1 (C6mm), D_{3h}^1 (C6m2), and D_{3h}^3 (C62m).

Division of the Problem

The even layer line Weissenberg and Precession diagrams, considered independently of the odd layers, may be indexed on the basis of a small pseudo cell. The orientation of this pseudo cell with respect to the true cell is shown in Figure 3. The C_0 axis of the pseudo cell is parallel to c_0 of the real cell and the angle between a_0 and A_0 is 90°. The lattice



Figure 2. The reciprocal lattice net (hkl). The indicated reflections are present, the rest, absent.



Figure 3. The relative orientation of the real and pseudo cells. The <u>c</u> axis for both cells is perpendicular to the paper.

constants of the pseudo cell are: $A_0 = 4.23A^\circ$; $C_0 = 7.33A^\circ$. The structure of the pseudo cell can be determined from the intensities of the reflection with even \mathcal{A} 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 cell at z and $z + \frac{1}{2}$ are averaged for all values of x and y, and that value of the electron density placed at both z and $z + \frac{1}{2}$, the result is a unit cell made up of a series of identical units related by the pseudo cell primative translations. Each of these identical units is, in fact, a pseudo cell.

In other words, the real cell consists of a series of pseudo cell-like units differing from each other only in the division of a constant electron density (for a given xy) between z and $z + \frac{1}{2}$. If the structure of the pseudo cell can be determined from the intensities of reflections with even g index, only the mature of the division between z and $z + \frac{1}{2}$ need be determined to obtain the complete structure. In the carrying out of the latter step the intensities of reflections with odd g index must be used. Thus the structural determination resolves itself into two distinct problems: The structure of the pseudo cell and the removing of the ambiguity between z and $z + \frac{1}{2}$ at the various points in the real cell.

The Structure of the Pseudo Cell

From the observed density 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 Ti₂Be₅ or TiBe₁₂. Although the experimental accuracy probably does not preclude TiBe₁₁ or TiBe₁₃, the calculated formula

is much closer to TiBe_{12} . The volume of the pseudo cell calculated from the atomic values of titanium and beryllium (from the structures of the pure metals) is 110 A⁵ for TiBe_{12} , and 112 A⁵ for Ti_2Be_5 . Ti_2Be_5 seems quite unlikely in view of the method of preparation but was considered because of the inadequate chemical analysis.

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

$$P(xy) = \sum_{o}^{\infty} \sum_{o}^{\infty} (F_{hk}^{\prime 2} + F_{hk}^{\prime 2}) \cos hx \cos ky + (F_{hk}^{\prime 2} - F_{hk}^{\prime 2}) \sin hx \sin ky,$$

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

The projection was prepared using the $CuK \propto (hkO)$ Weissenberg data. The projection (Figure 4) shows three different peaks with the peak heights listed in Table 1.

Ta	b	10]
	-		

Peak heights from Patterson projection of pseudo cell on (001)

teriere displayed in sector (in the line		neignt
0	0	690
1/3	2/3	200
1/2	0	300

The possible interpretations of the Patterson projection in the various possible plane groups may now be considered. The projections of the space groups D_{6h}^1 , D_6^1 , D_6^6 , C_{6v}^{-1} , yield the plane group C_{6g}^1 , while D_{3h}^1 yields C_{3g}^1



Figure 4. Patterson projection of pseudo cell on (001). The contour lines have been drawn at equal intervals and have not been smoothed. The irregularities indicate the approximate acouracy of the data. and D_{3h}^3 yields C_{3g}^{II} . (Patterson, 1935). The available positions in these point groups are -In CI : 1: (a) 00. 2: (b) 1/3,2/3;2/3,1/3. 3: (c) 글,0;0,글;글,글. 6: (d) x0;0x;xx;x0:0x;xx. (e) xx;x,x;x,2x;2x,x;x,x;x,2x;2x,x; In CI : 1: (a) 00. (b)1/3.2/3. (c)2/3.1/3. 3: (d) $x_1 \overline{x_1} x_2 2 x_1 2 \overline{x_1} \overline{x_2}$ 6: (e) $x_{,y}, \overline{y}, \overline{x} - y_{,y} - x_{,x}, \overline{y}, \overline{x}, \overline{y} - x_{,y}, x_{,x} - y_{,x}$ In CII 1: 00. 2: 1/3,2/3; 2/3,1/3. 3: x0; 0x;xx. 6: x,y; y,x-y; y-x,x; y,x; y-x,y; x,x-y.

The possible placement of atoms for the improbable formula Ti_2Be_5 is considered 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 they do not, they must occur at 00 and 1/3, 2/3 (or 2/3, 1/3). In the latter case equivalent peaks would appear on the Patterson at xy and at x - 1/3, y - 2/3 and this does not occur. 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 Ti_2Be_5 may be eliminated. There remains $TiBe_{12}$, which is much more probable since the compound was prepared in the presence of a large excess of beryllium.

The Patterson projection can be interpreted by means of the following positions in C_{60}^{I} :

Ti in (a) 00.

2 Be in 2(a) 00.

6 Be in 2(c) \$,0;0,1;2,2.

4 Be in 2(b) 1/3,2/3; 2/3,1/3.

These positions are also possible in $C_{3\ell}^{I}$ and $C_{3\ell}^{II}$, and the only possible variation is the displacement of the origin to 1/3,2/3 in $C_{3\ell}^{I}$. This makes no difference in the pseudo cell but must be considered in the transition to the real cell.

The Fourier projection on (001) gives further evidence that these positions are approximately correct. This projection (Figure 5) was calculated from (hkO) molybdenum K \propto Weissenberg diffraction data with signs assigned from the structure factors calculated from the above positions. The integrated peak heights on an arbitrary scale are given in Table 2.

Table 2

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

XV	Height
00	87,141
1/3,2/3	17,806
1/2,0	15,793

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



Figure 5. Fourier projection of pseudo cell on (001).

lated x and y positions. It will be noticed that the peak at 1/3, 2/3 is partially resolved into three peaks. Since there are only two beryllium atoms at that position, this separation must represent a small deviation from the pseudo structure which occurs in expanding to the real structure. Such a deviation may be large enough to influence the intensities of the observed reflections of the hkO planes, but not large enough in itself to cause other reflections to appear. This is true because the intensity of a reflection is proportional to the square of the structure factor, F. Since $(F + \delta)^2 = F^2 + 2F\delta + \delta^2$, a small change in parameters which changes F to $F + \delta$ will change the intensity by $2F\delta + \delta^2$. For a reflection where F = 0 the intensity will now be only δ^2 .

Weissenberg and rotation pictures around <u>e</u> show that the (hkO), (hk4), and (hk8) intensities patterns are quite similar and that (hk2), (hk6), and (hk10) are also similar but different from the other set. Thus we are led to postulate a layer structure for the pseudo cell, with atoms lying 1/4apart in s. Packing considerations then lead to the following pseudo cell structure in $D_{\rm 5h}^1$:

1 Ti in (a) 000; or (b) 001/2. 2 Be in (e) 002; 00z: z near 1/4. 6 Be in (i) 1/20z2; 01/2z2; 1/2/2z2; 1/2/2z2; 1/2/2z2; 1/2/2z2; with s2 near 1/4. 2 Be in (e) 1/3,2/3,0; 2/3,1/3,0. 2 Be in (d) 1/3,2/3,1/3,1/3,1/3,1/3.

Each of the sets can be given an arbitrary parameter in some one of the other possible space groups, but the above parameter sets are the only ones which explain all the data. The one dimensional Fourier projection along c calculated from Silver K a data shows that most of the atoms near 1/4 are in fact precisely at 1/2, so $z_2 = 1/4$. (Figure 6) There are small peaks near 1/4 at 0.22 and 0.28. Because hk3 reflections appear to be the strongest of the reflections with \pounds odd, and because of the size of the Ti atom, we take z_1 as 0.28 when Ti is at 000 and at 0.22 when Ti is at $00\frac{1}{3}$. In Table 3, observed (00 \pounds) structure factors are compared with those calculated for the above structure, and also with those calculated with z_1 at 0.27 and,29. It is seen that these intensities are not very sensitive to this s parameter, and that agreement is in every case quite good if we except (004), which is the strongest reflection appearing in the entire reciprocal lattice. We presume that extinction causes the discrepancy in F_{004} .

In Table 4, observed and calculated structure factors are compared for all (hk ℓ) reflections with ℓ even which are observed with CuK a radiations. The (hk4) reflections are somewhat sensitive to \mathbf{z}_1 , and 0.28 seems to give the best fit.

The Structure of the Real Cell

The determination of the pseudo cell in the preceding section has left an ambiguity in the z parameter 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 lying 0.28 x 7.36 A. away along the z axis. It is natural then to assume that in the true unit cell, this ambiguity will be completely removed and that each of the forty-eight titanium atoms in the unit cell will have a z parameter of either 0 or $\frac{1}{2}$. As will be shown later it is impossible to explain the structure on this basis. While it is certainly true that each titanium has a z parameter of 0 or $\frac{1}{2}$, an individual titanium



Figure 6. One dimensional Fourier projection along <u>c</u>.
Index	Fobs	z ₁ = 0.28	Foal z1 = 0.29*	z 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
800	15.2	16.5	14.8	13.3
0+0+10	4.6	7.1	8.1	7.5
0+0+12	10 .0	9.9	9.2	9.5
0+0+14	5.6	5.2	5.2	7.8

Comparison of calculated and observed structure factors for (OO 2) reflections

Table 3

*Booth's correlation factor, $R = \sum |F_{eal} - F_{obs}|$ $\sum |F_{obs}|$

omitting F_{004} for z = 0.29 is 0.14.

.

Pseudo cell index	True index	Fobs	Foa
1•0•*•0	4 • 4 • * • 0	15.0	12.0
1.1.*.0	12.0.**.0	20.9	21.0
2.0.*.0	8.8.*.0	23.2	23.
2 • 1 • * • 0	16+4+*+0	10.8	8.
3+0+*+0	12.12.*.0	15.3	17.
2 + 2 + * + 0	24.0.**.0	25.9	26.
3+1+*+0	20+8+*+0	7.1	6.
4+0+*+0	16.16.*.0	17.9	16.
3.2.*.0	28 . 4 . * . 0	7.8	5.
4•1•*•0	24 • 12 • * • 0	9.1	14.
1.0.*.2	4 • 4 • * • 2	15.2	13.
1.1.*.2	12.0.*.2	21.5	20.
2.0.*.2	8+8+*+2	3.3	- 4.
2.1.*.2	16+4+*+2	12.7	8.
3 • 0 • * • 2	12 • 12 • * • 2	16.7	16.
2 • 2 • * • 2	24.0.*.2	6.2	4.
3-1-*-2	20+8+*+2	11.5	12.
4+0+*+2	16•16•*•2	3.5	-3.
3+2+*+2	28.4.*.2	10.6	6.
4 + 1 + * + 2	24 • 12 • * • 2	9.7	12.
1•0•*•4	4.4.*.4	7.3	7.
1.1.*.4	12.0.*.4	15.8	16.
2.0.*.4	8+8+*+4	17.5	19.
2.1.*.4	16+4 + *+4	7.6	6.
3.0.*.4	12.12.*.4	11.3	13.
2 • 2 • * • 4	24 • 0 • * • 4	19.1	21.(
3 • 1 • * • 4	20+8+*+4	5.7	5.
4 + 0 + * + 4	16.16.*.4	14.4	13.

Calculated	and	observed	structure	factors
	for	the pseud	do cell	

Table 4

*represents the third Bravais-Miller index which occurs in the hexagonal system.

set, at say $(\frac{1}{2}, 0)$ 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 pseudo cell data give no indication of whether a Ti atom occurs at z = 0 or $z = \frac{1}{2}$. The pseudo cell structure, therefore, gives no indication of the distribution of titanium atoms between 0 and $\frac{1}{2}$. It is necessary to use reflections with \mathcal{A} odd to obtain information about this distribution.

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

The relative orientation of the real and pseudo cells are shown in Figure 3. The pseudo cell net picks out forty-eight points with the real cell which are equivalent except for the ambiguity in the C_0 direction. The two possible pseudo cell positions for the titanium atom correspond to two possible sets of positions in the real cell. The point positions 1/3, 2/3 occur in the pseudo cell in the space group D_{3h}^1 , but when these positions are referred to the axes of the real cell, they are found to occupy the positions of D_{3h}^2 . This happens because the two space groups differ only in the angle the vertical mirror plane makes with the x and y axes. In D_{3h}^2 each of the symmetry connected atomic sets has a zero contribution to F_{401} , and it is therefore impossible to explain the appearance of (401) with titanium in these pseudo-cell positions.

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

All of the possible space groups possess in common a three-fold axis. It will, therefore, be convenient to discuss the various arrangements of the atoms in terms of the three-fold sets and the atomic position in the x y plane are so listed in Table 5. 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 one must be too, if the atoms are to be arranged with twenty-four atoms at z = 0, and twentyfour at $z = \frac{1}{2}$. The relative positions of these three-fold sets are illustrated diagrammatically in Figure 7.

A systematic elimination will be carried out, and it will be shown that none of the ordered arrangements of the titanium atoms in the space groups of the crystal class D_{6h} are capable of explaining the data.

Criterion of elimination

From the calculated intensities of the pseudo cell reflections, and the observed intensities of the reflections with even and odd \mathcal{L} indices an estimate can be obtained as to the number of titanium atoms scattering in phase to the various reflections of hO \mathcal{L} . Using the observed F value of (002) and (401), and the calculated F value of (002) we find that the calculated value of $\frac{F_{401}}{f_{Ti} - f_{Be}}$ is about six or seven.

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



Figure 7. The relative position of the three-fold titanium sets in the xy plane. The letters refer to the positions listed in Table 5.

Table	5
-------	---

. . .

Set	Positions						
A.	0,0; 1/3,2/3; 2/3,1/3						
Β.	1/4,0; 0,1/4; 3/4,3/4						
С.	3/4,0; 0,3/4; 1/4,1/4						
D.	1/2,0; 0,1/2; 1/2,1/2						
В.	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						
K.	5/12,1/12; 11/12,4/12; 8/12,7/12						
L.	1/12,5/12; 4/12,11/12; 7/12,8/12						
м.	7/12,2/12, 10/12, 5/12, 7/12,5/12						
N.	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						

The xy parameters of the three-fold titanium sets

(101), (201), (301), and (111), 0.5f_{Ti} to 1.0f_{Ti} would be a conservative upper limit on F.

The process 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 calculated. These are asembled in Table 6 where the symbol $R_{hk,l}$ denotes the real part of what we have called the relative structure factor.

T	ab	10	6
	. v		•

Sets	R_101	^R 201	R ₃₀₁	R401	R ₅₀₁	R ₁₁₁	R ₂₂₁
4	0	0	3	0	0	3	8
B.C	ĩ	-1	ĩ	5	ĩ	-1	-1
D	-1	5	-1	3	-1	-1	3
E.F	$1/2 + \sqrt{3}$	1/2	-1	-3/2	$1/2 - \sqrt{5}$	ī	-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	$1/2 - \sqrt{3}$	1/2	-1	-3/2	$1/2 + \sqrt{3}$	1	-1
0,P	-1/2	1/2	1	-3/2	-1/2	-1	-1
*	Real part:	P					

Contributions of the three-fold sets to the relative structure factors

 $*_{R_{101}} = \frac{\text{Real part } F_{101}}{f_{Ti}}$

It is equal to the real part of the structure factor divided by f_{Ti} . This is similar to Harker's unitary structure factor (Harker, 1948b), but it has not been normalized. For this reason it has been given a different name.

The structure factors of the possible atomic arrangements which place twenty-four atoms at z = 0 and twenty-four at $z = \frac{1}{2}$ can be obtained by adding structure factor contributions obtained from Table 6 for those atomic sets lying at z = 0 and multiplying by two. The atomic layer at $z = \frac{1}{2}$ makes the same contribution to the structure factors of the reflection considered since the structure factors of the corresponding reflections in the reciprocal lattice layer with $\mathcal{L} = 0$ are identically zero.

To aid in the consideration of all the possible arrangements of the atoms, a rather simple symbolism has been used. This is described in the next section.

The elimination symbolism

In Tables 5 and 6 the capital letters A, B, etc. have been used to represent the three-fold atomic sets which occur in the structure. By BC will be meant the set containing both set B and set C.

In the calculation to follow the structure factors of all of the atomic arrangements compatible with the possible space groups are to be derived. As will be observed in Table 6 most of the three-fold sets occur in pairs having the same contribution to all of the $R_{hk\ell}$'s. It is also found in the course of the calculations, that various combinations of the sets have the same contributions to all of the $R_{hk\ell}$'s. When several atomic sets or combinations of atomic sets have the same contribution, this fact will be recognized by enclosing the set symbols, over each other, in parentheses. Thus $\binom{B}{C}$ is used to represent sets B or C, whose structure factor contributions are the same.

When several sets have different structure factors, for example the sets (A) and $\binom{B}{C}$, and either of the sets may be chosen for the layer z = 0 for the space group under consideration, the set symbols are written over each other in brackets. Thus sets occurring over each other in parenthesis

have a common group of structure factors, while those appearing above each other in brackets have different values for some of the structure factors considered.

In using the symbolism a series of bracksted terms arranged horizontally are derived by consideration of the possibilities within each space group. Then, all of the possible sets of atoms having different structure factors are read from the array by choosing one set from each bracket, rejecting any combinations so obtained, which have the same set appearing twice. There are several set combinations which have the same structure factors, but only one of these combinations has been listed in the tables. Should it happen to have structure factors which are compatible with the observed dataall other sets having the same structure factors are also compatible and these are readily found from the original array.

The use of this symbolism will be explained in detail in the consideration of D_{gh}^{1} , and this should make its meaning clearer.

Elimination of ordered structures

The various possible space groups allow the following three, six, and twelve-fold sets:

D¹_{6h} , C¹_{6v} , D¹₆ --A, D, BC, EF, GH, MN, IJ, KLOP, D¹_{3h} --A, D, E, F, G, H, I, J, M, N, BC, LP, KO, D⁵_{3h} --A, B, C, D, EF, GH, IJ, KL, MN, OP. The space group D_6^6 cannot be used, since titanium atoms will be placed over each other at 00.

Since (221) is present R_{221} must be different from zero, since the imaginary part vanishes for each of the three-fold sets independently. An examination of Table 5 shows that, if (221) is not to vanish, we must have three or four of the sets A, D, G, H, at the same z level. We therefore need to calculate the structure factors for atomic sets containing either ADGH, AGH, DGH, ADG, or ADH. The last two combinations can occur only in D_{Sh}^1 . The various different ways in which the remaining atomic sets may be combined will now be outlined.

In D_{6h}^1 , only the combination ADGH need be considered, since there are only two three-fold sets in D_{6h}^1 and these must occur at the same level if there are to be an even number of atoms at each level. To complete the layer with ADGH, then, we must choose either KLOP, or any two of BC, EF, MN, or IJ. We may therefore write the array

$$\begin{bmatrix}
 (BC) \\
 (EF) \\
 (MN) \\
 (IJ)
 \end{bmatrix}
 \begin{bmatrix}
 (BC) \\
 (EF) \\
 (MN) \\
 (IJ)
 \end{bmatrix}
 \begin{bmatrix}
 (BC) \\
 (EF) \\
 (MN) \\
 (IJ)
 \end{bmatrix}$$

The interpretation of the array is fairly obvious in this case, since all of the structure factors refer to only one combination of sets. The brackets placed over each other represent a choice of one or the other set of brackets.

The combinations chosen from this array are listed in Table 7.

In D_{3h}^{1} the layer at z = 0 may contain any of the sets ADGH, AGH, DGH, ADG, or ADH. With ADGH, must be chosen four three-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 choices may be represented by the array



Table 7

Relative structure factors for layer of titanium atoms at z = 0, in Dgh

		· · · · · · · · · · · · · · · · · · ·			021		
Sets	R ₁₀₁	R201	^R 301	R401	R 501	R ₁₁₁	R ₂₂₁
ADGHBCEF	3+2 √3	-1	0	3	3-2 /3	0	8
BCIJ	0	-4	0	12	0	0	8
BCMN	3-2 / 3	-1	0	3	3+2 / 3	0	8
EFIJ	-1+2 /3	-1	-4	3	-1-2 / 3	4	8
EFMN	2	2	-4	-6	2	4	8
I JMN	-1-2 /3	-1	-4	3	-1+2/3	4	8
ELOP	-2	2	4	-6	-2	-4	8

With DGH, AGH, ADG, and ADH we must choose five three-fold sets from E, F, I, J, M, N, B, C, LP, KO. The following arrays represent the ways in which this can be done; Two six folds



 $\begin{bmatrix} (AOH) \\ (DGH) \\ (AD) \\ (H) \end{bmatrix} \begin{bmatrix} (BC) \\ (LP) \\ (KO) \end{bmatrix} \begin{bmatrix} (E) \\ (I) \\ (M) \\ (M) \end{bmatrix}$

No six-fold

	(AGH) (EF)(IJ)	$\binom{M}{N}$
(DGH)	(DGH) (IJ)(MN)	
$ \begin{array}{c} \textbf{(AD)} & \textbf{(G)} \\ \textbf{(H)} & \textbf{(H)} \\ \textbf{(H)} \end{array} $	$(AD) \begin{pmatrix} G \\ H \end{pmatrix} = \begin{pmatrix} (EF) \end{pmatrix} \begin{pmatrix} MN \end{pmatrix}$	(I) (J)

These various possibilities are listed in Table 8.

In D_{3h}^{3} the layer at z = 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



Where terms like (EF)(IJ) have been omitted from the second expression, since these have already been considered in D_{6h}^1 .

Table 8	
---------	--

Relative structure factors for the layer of titanium atoms at $\mathbf{z} = 0$, in $D\mathbf{z}_{u}$

Sets	^R 101	^H 201	^R 301	R401	^R 501	[*] 111	^R 221
ADGHBCLP	1	-1	4	3	0	-4	8
BCEI	3/2+ √3	-5/2	0	15/2	3/2- 53	0	8
BCEM	3	-1	0	5	3	0	8
BCIM	3/2- 5	-5/2	0	15/2	3/2 +5	0	8
LPEI	-3/2+√ 3	1	0	-3/2	-3/2- 5	0	8
LPEN	0	2	0	-6	0	0	8
LPIM	-3/2- /3	_글	0	-3/2	-3/2+ 5	0	8
IJME	-1	-ĩ	-4	o	-1	4	8
EFIM	<u>}</u> +√8	붋	-4	-3/2	1-5	4	8
MNE I	<u>1</u> - /3	T	-4	-3/2	±+ /3	4	8
AGHBCLPE	5/2+ 5	-7/2	4	-3/2	5/2- 5	-2	4
I	1	-5	4	3	1	-2	4
M	5/2- 5	-7/2	4	-3/2	5/2+ 5	-2	4
AGHBCEIM	3	-5	0	3	3	2	4
EFI	\$+2 √3	-5	0	3	3-2 /3	2	4
EFN	9/2+ 5	-7/2	0	-3/2	9/2- /3	2	4
IJE	$3/2 + \sqrt{3}$	-13/2	0	15/2	3/2- 13	2	4
IM	3/2- \3	-13/2	0	15/2	3/2+ 53	2	4
MNE	9/2- √3	-7/2	0	-3/2	9/2+ 53	2	4
MNI	3-2 /3	-5	0	3	3+2 / 3	2	4
AGHLPEIN	0	-2	0	-6	0	2	4
EFI	2 /3	-2	0	-6	-2 / 3	2	4
EFM	3/2+ 5	-1/2	0	-21/ 2	$3/2 - \sqrt{3}$	2	4
I JE	-3/2+ /3	-7/2	0	-3/2	-3/2- /3	2	4
IJN	-3/2- 5	-7/2	0	-3/2	-3/2+ /3	2	4
MNE	3/2- 5	-1/2	0	-21/2	3/2+ 5	2	4
MNI	-2 3	-2	0	-6	2 3	2	4
AGHEFIJM	$1/2 + \sqrt{3}$	-7/2	4	-3/2	$1/2 - \sqrt{3}$	-2	4
I JMNE	$1/2 - \sqrt{3}$	-7/2	-4	-3/2	$1/2 + \sqrt{3}$	-2	4
EFMNI	2	-2	-4	-6	2	-2	4

,

*Each group has eight letters representing the eight three-fold sets. Letters which have been omitted are the same as those directly above.

Sets	R ₁₀₁	^R 201	R ₃₀₁	R401	^R 501	R ₁₁₁	R ₂₂₁
DGHBCLPE I M DGHBCEIM EFI	$3/2 + \sqrt{3}$ 0 $3/2 - \sqrt{3}$ 2 $2 + 2 \sqrt{3}$	-1/2 -2 -1/2 -2 -2	0 0 -4 -4	3/2 6 3/2 6 6	$3/2 - \sqrt{3}$ 0 $3/2 + \sqrt{3}$ 2 $2 - 2 \sqrt{3}$	-6 -6 -2 -2	4 4 4 4 4
EFM IJE IJM MNE MNI	$7/2 + \sqrt{3} \\ 1/2 + \sqrt{3} \\ 1/2 - \sqrt{3} \\ 7/2 - \sqrt{3} \\ 2 - 2\sqrt{3} \\ 3$	-1/2 -7/2 -7/2 -1/2 -2	-4 -4 -4 -4	3/2 21/2 21/2 3/2 6	$7/2 - \sqrt{3} \\ 1/2 - \sqrt{3} \\ 1/2 + \sqrt{3} \\ 7/2 + \sqrt{3} \\ 2 + 2\sqrt{3} \\ 3$	-2 -2 -2 -2	444
DGHLPEIM EFI EFM IJE IJM	$ \begin{array}{c} -1 \\ -1+2\sqrt{3} \\ 1/2+\sqrt{3} \\ -5/2+\sqrt{3} \\ -5/2-\sqrt{3} \end{array} $	1 5/2 -1/2 -1/2	-4 -4 -4 -4	-3 -3 -15/2 3/2 3/2	$ \begin{array}{c} -1 \\ -1-2 \sqrt{3} \\ 1/2 - \sqrt{3} \\ -5/2 - \sqrt{3} \\ -5/2 + \sqrt{3} \end{array} $	-2 -2 -2 -2 -2	4 4 4 4 4 4
MNE MNI DGHEF IJM IJMNE EFMNI	$ \frac{1/2 - \sqrt{3}}{-1 - 2\sqrt{3}} \\ -1/2 + \sqrt{3} \\ -1/2 - \sqrt{3} \\ 1 $	5/2 1 -1/2 -1/2 1	4 8 8 8	-15/2 -3 3/2 3/2 -3	$\frac{1/2 + \sqrt{3}}{-1+2\sqrt{3}}$ -1/2 - $\sqrt{3}$ -1/2 + $\sqrt{3}$ 1	-2 -2 -6 -6	4 4 4 4
ADGBCLPE I M ADGBCEIM EFI	$ \begin{array}{c} 1+\sqrt{3} \\ \frac{1}{2} \\ 1-\sqrt{3} \\ 3/2 \\ 3/2+2\sqrt{3} \end{array} $		4 4 0 0	2 15/2 2 15/2 15/2	$1 - \sqrt{3}$ $\frac{1}{2}$ $1 + \sqrt{3}$ $3/2$ $3/2 - 2\sqrt{3}$	-2 -2 -2 2 2	4 4 4 4 4
EFM IJE I JM MNE MNI	$ \begin{array}{r} 3 + \sqrt{3} \\ \sqrt{3} \\ - \sqrt{3} \\ 3 - \sqrt{3} \\ 3/2 - 2 \sqrt{3} \end{array} $	1 -2 -2 1 -1	0 0 0 0	3 12 12 3 15/2	3- /3 - /3 /3 3+ /3 3/2+2 /3	2 2 2 2 2	4 4 4 4
ADGLPEIM EFI EFM IJE IJM	-3/2 -3/2+2 \3 \3 -3+ \3 -3- \3	5/2 5/2 4 1 1	0 0 0 0	-3/2 -3/2 -6 3 3	-3/2 -3/2-2 \3 - \3 -3- \3 -3+ \3	2 2 2 2 2 2	4 4 4 4
MNE MNI ADGEFIJM IJMNE EFMNI	$ \begin{array}{r} -\sqrt{3} \\ -3/2 - 2\sqrt{3} \\ -1 + \sqrt{3} \\ -1 - \sqrt{3} \\ \frac{1}{2} \\ \end{array} $	4 5/2 1 1 5/2	0 0 -4 -4 -4	-6 -3/2 3 3 -3/2		2 2 -2 -2 -2	4 4 4 4

Table 8 (continued)



With one six-fold

(ADGH)(BC)	(EF) (1J) (MN) (KL)

These possibilities are listed in Table 9.

It has been shown earlier that lf_{Ti} is a conservative upper limit for the reflections which are systematically absent. This means that $R_{hk,\ell} < 0.5$ 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 structure.

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

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

The Laue diffraction patterns, taken with molybdenum radiation also give evidence of disorder. (cf. Experimental Methods section). The

Relative structure factors for layer of titanium atoms at z = 0, in D_{3h}

Sets	R ₁₀₁	R ₂₀₁	R301	R401	R ₅₀₁	R ₁₁₁	R ₂₂₁
ADGHEFKL	2/3	2	0	-6	-2 /3	0	12
IJKL	-3	-1	0	3	-3	0	12
MNK L	-2 5	2	0	-6	2 / 3	0	12
BCKL	1	-1	4	3	1	-4	12
AGHEFIJB	1+2 / 3	-4	-2	3	1-2 / 3	4	4
EFKLB	2+2/3	-2	2	-6	$2 - 2\sqrt{3}$	0	4
EFMNB	4	-2	-2	-6	4	4	4
IJKLB	-1	-5	2	3	-1	0	4
IJMNB	1-2 /3	-4	-2	3	1+2 /3	4	4
K LMNB	2-2 /3	-2	2	- 6	2+2 /3	0	4
DGHEF I JB	2 / 3	-1	-6	6	-2 5	0	4
EFKLB	1+2 /3	1	-2	-3	1-2 /3	0	4
EFMNB	3	1	-6	-3	-3	0	4
IJKLB	-2	-2	-2	6	-2	-4	4
IJMNB	-2 /3	-1	-6	6	2 / 3	0	4
KLMNB	1-2 / 3	1	-2	-3	1+2 / 3	-4	4

.

streaking observed in these photographs indicate a streaking in the reciprocal lattice in planes perpendicular to \underline{c}^* . This streaking is characteristic of a two-dimensional disorder. (Zachariasen, 1945). The details of the non-Bragg scattering in these photographs could not be determined with the facilities that were available, so that little else could be determined concerning the details of the disorder.

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

Since the diffuse, non-Bragg scattering has not been studied and, consequently, the correlation among the disorder sites are not known, each of the atomic sets of titanium in D_{6h}^1 must be treated as independent. It is assumed that for each set (one of whose atoms occurs at xy) there is a definite probability, p_{xy} , that the set occur at z = 0, and a probability of $1 - p_{xy}$ that it occur at $z = \frac{1}{2}$. Since the disorder is probably a twodimensional one, the Ti-Be--Be-Ti chains occurring in the <u>e</u> direction are probably completely ordered along their length, but each chain may start at either z = 0 or $z = \frac{1}{2}$ with a probability that depends on its position in the (OO1) plane.

Equations for absence. Since the titanium x,y parameters are all multiples of one-twelfth, the contributions of the titanium to F(hk g) is

periodic in h and k for all possible titanium combinations, and this, together with the symmetry of D_{6h}^1 allows only eight of the structure factors 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 $f_{Ti} R(hk P)$, where R takes on only eight distinct values.

The reflections (101), (201), (301), (111) and (441) are all absent and R(hk 2) 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 absent reflections. If it is demanded that the absent reflections have zero structure factors, a set of five simultaneous equations in the eight probabilities that the eight atomic sets be at z = 0 can be obtained. One of these equations has irrational coefficients, and the equating of its rational and irrational parts yields an additional equation.

The structure factor for the reflections with odd $\mathcal L$ indices may be written in the form

 $F(hk l) = \underset{i}{\leq} f_{p_{\mathbf{x}_{ij}\mathbf{y}_{ij}}} \cos 2 \pi (h\mathbf{x}_{ij} + k\mathbf{y}_{ij}) + \frac{f(1 - p_{\mathbf{x}_{ij}\mathbf{y}_{ij}}) \cos 2 \pi (h\mathbf{x}_{ij} + k\mathbf{y}_{ij})}{F(hk l) = \underset{i}{\leq} f(2p_{\mathbf{x}_{ij}\mathbf{y}_{ij}} - 1) \cos 2 \pi (h\mathbf{x}_{ij} + k\mathbf{y}_{ij})}$ where $f = f_{\mathrm{Ti}} + 2f_{\mathrm{Be}} \cos z_{1}$, and $p_{\mathbf{x}_{ij}\mathbf{y}_{ij}}$, the probability that the atom at $\mathbf{x}_{ij}\mathbf{y}_{ij}$ 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 cancel out precisely. The berylliums at z = 0 and $z = \frac{1}{2}$ are omitted because although they may not occur over each other at precisely the same xy position, they very nearly do. In any

50

case the vanishing of the approximate structure factor as written is a necessary condition for the vanishing of the total structure factor, since the periodic absences cannot be explained by a cancelling of the periodic titanium structure factor contributions by the non-periodic beryllium contributions. The beryllium structure factors are not periodic unless they lie 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 $x_{ij}y_{j}$ is used to represent the entire atomic set in $p_{x_{ij}y_{ij}}$.

From F(101) = 0

p(1/12, 2/12) = p(7/12, 2/12)

- and $-p(\frac{1}{3}, 0) + 2p(1/4, 0) + 2p(1/12, 2/12) + p(4/12, 2/12) 2p(\frac{1}{2}, 1/4)$ -2p(5/12, 1/12) = 4from F(201) = 0 $3p(\frac{1}{2}, 0) - p(1/4, 0) + 2p(1/12, 2/12) - 3p(4/12, 2/12) - 2p(\frac{1}{2}, 1/4)$
- + 2p(5/12, 1/12) = 0from F(301) = 0
- $6p(0, 0) 2p(\frac{1}{3}, 0) + 4p(1/4, 0) 8p(1/12, 2/12) 4p(4/12, 2/12)$ $- 4p(\frac{1}{3}, 1/4) + 8p(5/12, 1/12) = 1$ from F(111) = 0

$$\begin{aligned} & 6p(0, 0) - 2p(\frac{1}{2}, 0) - 4p(1/4, 0) + 4p(1/12, 2/12) - 4p(4/12, 2/12) \\ & + 4p(4/12, 2/12) + 4p(\frac{1}{2}, 1/4) - 8p(5/12, 1/12) = 0 \\ & \text{and from F (441)} = 0, \end{aligned}$$

 $p(0, 0) + p(\frac{1}{2}, 0) + 2p(1/4, 0) + 2p(1/12, 2/12) + 2p(4/12, 2/12)$ + $2p(7/12, 2/12) + 2p(\frac{1}{2}, 1/4) + 4p(5/12, 1/12) = 8$ The equations are consistent, since the coefficient and augmented matrices are both of rank five. Only the equation F(101) = 0 leads to two equations since it is the only one to contain both rational and irrational coefficients.

The equations may be solved in terms of two of the probabilities which have been taken to be p(0, 0) and $p(\frac{1}{2}, 0)$. The solutions are:

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

$$p(\frac{1}{3}, 1/4) = 2/10 - 11/10 p(0, 0) + 7/10 p(\frac{1}{3}, 0)$$

$$p(4/12, 2/12) = 1/8 + 3/2 p(0, 0) - \frac{1}{2}p(\frac{1}{2}, 0)$$

$$p(7/12, 2/12) = p(1/12, 2/12) = 9/10 + 1/20 p(0, 0) - 7/20p(\frac{1}{3}, 0)$$

$$p(1/4, 0) = 29/20 - 16/10 p(0, 0) + 12/10 p(\frac{1}{3}, 0)$$

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. Since there are three independent structure factors among the present reflections, there will not necessarily be a set of probabilities which satisfy the above set of equations and also give the correct intensities for the present reflections. It was in fact found as is shown in the next section that no set of probabilities which put the present reflections in the right order of intensities, would satisfy the above set of equations.

Fourier transforms. As representatives of the three independent structure factors of the reflections which 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 factors because the number of permutations is far too great. In the present case, however, this is possible since only three independent sign assignments need be applied to the first layer data. This procedure necessitates the assumption that any deviations of beryllium atoms from their idealized positions will not affect the assignment of signs.

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

	(401)	(501)	(221)
I	+		-
II	+	+	-
III	+	-	+
IV	+	+	+.

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

First layer Fourier syntheses were made with each of the possible sign combinations. The sums were carried out first with the three-fold axis abstracted as outlined in the theoretical section and later, by increasing the frequencies of the International Business Machine card set to thirty, in order to include a majority of the reflections obtained with Cu K \triangleleft X-rays. In the latter case the following formula was used:

$$R(xy) = \bigotimes_{0}^{\infty} \bigotimes_{0}^{\infty} (F'_{hk\ell} + F'_{hk\ell}) \cos 2\pi hx \cos 2\pi ky$$
$$- (F'_{hk\ell} - F'_{hk\ell}) \sin 2\pi hx \sin 2\pi ky$$
with $F'_{hk\ell} = 0$ if h or $k = 0$

The values of the peak heights for the four summations are given in Table 10. The sums of all of the peak heights for each of the structures is also included, for reasons discussed below.

The interpretation of the first layer transforms is particularly simple in this case. In the theoretical section, the formula

 $R(xy) = \int_{0}^{1} p(xyz) \cos 2\pi l_{1} z dz$

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

$$R^{*}(xy) = \int_{0}^{1} \rho(x,y,x + \frac{1}{2}) \cos 2\pi l_{1} z dz$$
$$= \int_{1}^{\frac{3}{2}} \rho(xyz) \cos 2\pi (l_{1}z + \frac{l_{1}}{2}) dz$$
$$= -R(xy) \text{ if } l_{1} \text{ is odd.}$$

Table	10
-------	----

Sets	Atomic position	<u>Structure I</u> Peak heights	Probability that set is at z = 0
A	00	-531	1/4
B,C	1/4,0	919	3/4
D	<u></u> 120	9 3 7	3/4
I,J	±,1/4	1650	1
M, N	7/12,2/12	-1180	1/8
K,L,O,P	5/12,1/12	-175	
E,F	1/12,2/12	72	ż.
G,H	4/12,2/12	-1284	1/8
Weighted	sum	180	
		Structure II	Probability that set
Sets		Peak heights	is at z = 0
A		531	8/12
B,C		581	8/12
D		2011	1
I,J		1312	10/12
M, N		-1618	1/12
K,L,O,P		-695	3/12
E,F		-366	5/12
G,H		332	7/12
Weighted	sum	732	
		· • •	
	St	ructure III	Structure IV
Sets	Ŧ	'eak heights	Peak heights
A		1687	2761
B,C		1637	1299
D		207	1281
I,J		906	568
M,N		666	228
K,L,O,P		-257	-695
E,F		~586	-1024
G,H		-1284	-210
Weighted	sum	10596	8952

Peak heights from the F(hk 1) Fourier syntheses and the probabilities deduced thereform

*No probabilities have been determined for these structures.

If the structure were perfectly ordered, one would expect peaks of only two kinds at titanium sites, equal to each other in absolute magnitude but the one the negative of the other. It is readily apparent from Table 10 that this is not the case.

Although the structure is not entirely ordered, it still must be true that there are as many titanium atoms at z = 0 as at $z = \frac{1}{2}$. For this reason the sum of R(xy) over all the titanium sites must be zero. This consideration eliminates the sign assignments III and IV. In the two remaining syntheses, probabilities may be assigned to each titanium set which will explain the observed peak heights. The probabilities have been assigned by making use of the fact that the peak heights are proportional to $2p_{x_{ij}y_{j}} = 1$. These probabilities are also listed in Table 10. In both cases the maximum peak has been assigned a probability of one, and the probabilities have been rounded off to give a set of small rational fractions.

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 particular $p(7/12, 2/12) \pm p(1/12, 2/12)$, 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's derived from the sign combination F(401) positive, F(501) negative, and F(221)negative gives the better correlation with the observed data. Not only do most of the structure factors of the absent reflections vanish but the structure factors of the present reflections are put in the observed order.

Since the Fourier synthesis of the first layer data is a new method, a three-dimensional Fourier summation $\rho(xy^0)$ was made as a check using all of the Cu Ka data with the sign assignment I, which gave the best fit above. The peak heights from this summation are given in Table 12. The

Table 11

	Structure I	Structure II	Observed presence
R ₁₀₁	-0,2	1.30	absent
R ₂₀₁	0	-0.75	absent
R301	0	-0 .5	absent
R401	7	7.25	present
R ₅₀₁	-1.72	-0,26	present
R ₁₁₁	-0,5	0.16	absent
^R 221	-1.75	3.5	present
R441	0	0	absent

Comparison of the relative structure factors for the two disordered structures, I, and II

probabilities obtained from the F(hkl) synthesis are also included and they will be seen to parallel the peak heights. They are not proportional to them, as might have been expected. This is due partly to an incorrect background in the three-dimensional synthesis and partly to a lack of correlation between the various layers which went into the three-dimensional synthesis. This lack of correlation arises because the streaking of the odd layer reflections appears differently in the $(hO \ell)$, used for correlation, than it does in the $(hk \ell)$ films. The agreement between the probabilities and the peak heights seems to be good enough, however, to confirm the postulated probabilities.

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

Sets			Probability that
*****	Atomic position	Peak heights	set is at z = 0
A	00	6500	1/4
	1/3,2/3	4500	1/4
B,C	1/4.0	9000	3/4
<u>ת</u>	1/2,0	89 60	3/4
I,J	1/2,1/4	10000	l
M, N	7/12.2/12	4500	1/8
K,L,O,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

Three-dimensional Fourier Section (xy0) for the sign assignment I

Table 12

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

Adjacent reflections are, in most cases, placed in the observed order with approximately the correct intensity ratios. It could not be expected that reflections farther apart would exhibit agreement between the observed and calculated structure factors and they do not. Because the extent of the variation of the observed structure factor from the calculated value within each layer seems to depend on \pounds more strongly than might be expected, some minor adjustment of the z parameters of the berylliums at z = 0 and $\frac{1}{2}$ or 1/4 and 3/4 might be indicated.

Table 13

Index	Fobs	Foal
2.2.*.1	40	-100
3.1.*.1	40	-93
4.0.*.1	123	249
5.0.**.1	58	-90
6+0+*+1	57	-94
7+0+*+1	65	-85
8+0+*+1	167	222
8•1•*•1	42	-81
8.2.*.1	43	-85
8•3•*•1	45	-78
6+6+*+1	42	-82
7+5+*+1	42	-76
8-4-*-1	152	201
9•4•*•1	47	-73
10+4+*+1	48	-76
11.4.*.1	52	-68
12 • 4 • * • 1	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	6 0	-60
17•0•*•1	47	-60
10•10•**•1	53	-63
11.9.**+1	53	-59
12+8+*+1	134	158
18•0•*•1	50	-62
13+8+*+1	50	-57
19.0.*.1	53	-56
14.8.1.1	53	-60
20+0+*+1	133	147
15.8.*.1	54	-54
20+1+ ⁺ +1	49	-54

Calculated and observed structure factors for Structure I

*represents the third Bravais-Miller index.

Index	Fobs	Fcal
20+2+*+1	49	-56
16.8.*.1	100	141
17.7.*.1	49	-53
18.6.*.1	49	-56
20+3+*+1	49	-52
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.*.1	20	-48
24•4•*•1	89	126
18.12.*.1	20	-50
24 • 5 • * • 1	0	-46
19•12•*•1	20	-45
24+6+*+1	0	-48
20+12+*+1	82	119
21•11•*•1	not observed	-44
24+7+*+1	not ob served	-44
22+10+*+1	not observed	-47
23 •9•*•1	not ob served	-44
24 • 8 • * • 1	not observed	116
20•13•*•1	20	-43
2 • 2 • * • 3	47	-100
3•1• [*] •8	47	-93
4+0+_+3	232	249
5+0+ ~+3	108	-92
6•0• *•3	126	-98
7+0+ *+8	137	-89
8•0• * • 5	372	234
8•1• ~ •3	86	-86
8+2+**3	92	-93
8 • 3 • * • 3	93	-85
6 • 6 • * • 3	58	-88
7 • 5 • 7 • 8	58	-82
8+4+***3	239	218
9+4 • 7 • 3	60	-80
10+4+*+3	51	-84

Table 13 (continued)

Index	Fobs	Fcal
11•4•*•3	38	-77
12 • 4 • * • 3	179	204
13.8.*.8	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	-73
10+10+*+3	43	-77
11•9•1•3	45	-72
12+8+ - + 3	209	190
18+0+*+5	37	-75
13 • 8 • * • 3	43	-69
19•0•*•3	37	-69
14.8.7.3	43	-74
20.0 3	202	182
15+8+**3	43	-67
20+1+*+3	43	-67
20 • 2 • * • 3	43	-71
16-8-1-3	204	177
17+7	43	-66
18.6.7.3	43	-70
20 • 3 • * • 3	43	-66
19.5.*.3	43	-65
16•9• *•\$	43	-65
20-4	204	173
16.10.1.8	30	-70
21•4•*•3	0	-62
22 • 4 • * • 3	0	-65
16•12• *• 5	37	162
17-12	37	-59
24 • 4 • 7 • 3	153	156
18 • 12 • 7 • 3	22	-62
24 • 5 • * • 3	0	-57
19+12+-+5	37	-57
24. 6 3	0	-60
20-12	177	150
21 • 11 • * • 3	97	-55

Table 13 (continued)

Index	Fobs	Fcal
24 • 7 • * • 3	0	-55
22 . 10 . * . 3	103	-59
23 . 9 . * . 3	105	-55
24 . 8 . * . 3	174	144
20+13 +*+3	30	-54
28+0+ [*] •3	21	150
2 • 2 • * • 5	54	-54
3+1+*+5	57	-50
4.0.*.5	192	135
5+0+*+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 • [*] • 5	57	-48
6+6+*+5	58	-50
7•5•**•5	58	-47
8+4+*•5	267	126
9 • 4 • * •5	74	-46
10+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 • 1 • 5	0	-43
12.6.7.5	71	-45
16.0	37	112
12 • 7 • ⁻ • 5	77	-41
17•0•*•5	2 9	-41
10.10.7.5	87	-43
11.9.7.5	87	-40
12.8.7.5	275	108
18•0•*•5	32	-43
13 .8 . * .5	68	-40
19+0+-5	37	-40
14.8.7.5	48	-42
20.0 5	300	103
15+8+ +5	0	-39

•

Table 13 (continued)

Index	Fobs	Fcal
20+1+*+5	77	-38
20+2+*+5	71	-41
16 • 8 • * • 5	153	103
17+7+*+5	24	-38
18+6+*+5	32	-40
20 • 3 • * • 5	65	-38
19.5.*.5	37	-37
16+9+*+5	0	-38
20.4.*.5	90	99
16+10+*+5	0	-39
21+4+*+5	79	-36
22 • 4 • * • 5	65	-37
16.12.*.5	163	93
17-12-*-5	. 68	-54
24 • 4 • * • 5	210	90
18+12+*+5	63	-36
24 • 5 • * • 5	0	
19-12-*-5	52	-34

Table 13 (continued)

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

Further refinements. The structure, as it now stands, is admittedly only a rough approximation. If the disordered structure, which has been postulated is correct, there is little immediate hope of refining the beryllium positions. It was seen from the pseudo cell Fourier projection (Figure 5) that certain of the beryllium atoms must show small displacements from their ideal pseudo cell positions. These displacements certainly depend on the relative positions of adjacent titanium atoms. If the titaniums were perfectly ordered, size considerations alone might make it possible to find accurately the beryllium displacement. As matters stand now, the magnitude of this displacement cannot be found and could not be unless the correlation among the titanium probabilities were known.

If the beryllium which is displaced is considered more carefully, it will be seen that it may exist in at least four situations, namely: surrounded at its z level by none, one, two, or three, 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 berylliums is probably surrounded, therefore, by one or two titanium atoms at the corners of the titanium site triangle and must move away from the titaniums. The Fourier (Figure 5) shows the berylliums to lie at 2.5 A from some of the pseudo cell corners and atomic radii are consistent with this being a beryllium titanium distance.

If the correlation 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 procedure using the observed intensities of the odd layer lies, but such a procedure would involve hundreds of parameters and is impractical unless those parameters could be guessed in advance. But such a guess involves the correlation of the titanium probabilities mentioned before. The ideal beryllium positions must, therefore, be regarded as the best approximation that can be made.

DISCUSSION

The final structure is represented schematically in Figures 8 and 9. The fractions in Figure 8 are the probabilities, deduced earlier, that the titanium atom occurring over that xy position occur at z = 0. Figure 9 shows one-half of a pseudo cell portion of the real cell with the titanium atoms in ordered positions. The portion shown has a height of $\frac{1}{2}e_0$ and the complete pseudo cell portion is obtained by the operation of horizontal mirror planes at z = 0 and $z = \frac{1}{2}$. In the true cell, similarly ordered pseudo cell portions will occur throughout the structure, with various orientations and with the pseudo cell origin either at z = 0 or $z = \frac{1}{2}$. The immediate surroundings of the various kinds of atoms are, however, similar throughout the structure. Figure 9 also shows these 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 concerning the reasons for the unusual disorder appearing in the structure. There, at least, is some rationality in the titanium positions, since if they are to occur with the given xy parameters and in two layers separated by $z = \frac{1}{2}$, there is no ordered structure which will preserve the correct titanium-beryllium distances 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 distance is to be maintained. A



Figure 8. A schematic representation of the titanium positions in the final structure. The titaniums occur over the indicated positions at z = 0 or $z = \frac{1}{2}$, and the fractions are the probabilities that the atom at that xy position occur 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 elimination of the ordered structures containing this forbidden grouping of titanium atoms in the same layer. All of the possible ordered structures could not be examined in such detail but if this grouping occurs in all of them the structure is disordered because no ordered structure will preserve the correct interatomic distances.

We may conjecture that the various probabilities in the partially disordered cell arise through a partial ordering of some completely disordered structure. Indeed, the sharp reflections alone (the even layers and (401), (801), etc. 7 can be explained by a disordered structure in which the titanium 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 factors of all absent reflections zero and, in addition, yields a zero structure factor for (501), (221), and the reflections related to these. The final structure might, then, represent the greatest amount of ordering the system could achieve while maintaining the proper interatomic distances.

In Table 14 are given the numbers and distances of atoms within the true cell. Some of the distances found may be explained very nicely if the bond orders are chosen properly. Each titanium is bonded to eight berylliums, two at 2.18 A and six at 2.55 A. The sum of the titanium and beryllium coordination number twelve metallic radii is 2.59, while the sum of their single bond radii 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 distance. There is also the one titanium at the single bond distance, 2.13 A, so this beryllium has a valency of two.

Table 14

Neighboring atoms and interatomic 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; etc.) at 2.55 A; 12 Be (at 1,0,1/4; etc.) at 2.80 A. Each Be at 0,0,0.29 has: 1 Ti at 2.13 A; 6 Be (at 1/2,0,1/4; etc.) at 2.13 A; 12 Be (near 1/3,2/3,0; etc.) at 3.34 A. Each 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; etc.) at 3.34 A; 2 or 4 Be (at 1/2,0,1/4; etc.) at 2.2 A; 4 or 2 Be (at 1/4; etc.) at 2.3 A. Each Be at 1,0,1/4 has: 2 Be (at 0,0,0.29; etc.) at 2.13 A; 2 Be (near 1/3,2/3,0; etc.) at 2.2 A; 2 Be (near 1/3,2/3,0; etc.) at 2.3 A; 4 Be (at 1,1,1/4; etc.) at 2.12 A; 2 Ti at 2.8 A.

*The positions given refer to the pseudo cell.

The berylliums at $\frac{1}{2}01/4$, etc., lie in a haxagonal net perpendicular to c_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 distances are compatible with this.

Finally, the berylliums near 1/3, 2/3, 0 seem to be less strongly bound. It is possible, since the direction of the shift of these berylliums with respect to the titanium atoms is not determined by the data but is merely assumed, that some of these berylliums are bound more strongly to one of the adjacent titanium atoms. This again is pure conjecture.

SUMMARY

The structure of the metallic compound TiBe_{12} has been investigated. The compound was found to crystallize in the hexagonal system with lattice constants, $a_0 = 29.44 \pm .01$ A, $c_0 = 7.33 \pm .01$ A. The Laue diffraction class is D_{6h} and the space group of the postulated disordered structure is D_{6h}^1 (C6/mmm).

The intensities of reflections with even \mathcal{L} index have been used to establish a pseudo cell structure from which the various interatomic distances have been determined. The pseudo cell contained an ambiguity, since it did not distinguish between the points x,y,z, and $x,y,z + \frac{1}{2}$. This ambiguity is only partially resolved in the final structure, for it was found that only a partially disordered structure would explain the absence of the large number of extinct reflections. All possible ordered structures in any of the possible space groups were systematically eliminated and only one disordered structure was found which would explain the absences in D_{SD}^1 .

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

A study of Fourier transforms was of help in the structural determination. The most important result of this study was the development of a new method of Fourier synthesis, using data obtained from a single layer line,

71

other than the zeroth. The interpretation of such syntheses was found to be quite simple in the present structural determination and is used to find the postulated structure.

LITERATURE CITED

Baenziger (1947). Iowa City, Iowa. /Frivate Communication.7

Baensiger and Rundle (1948). Acta Cryst. 1, 274.

- Booth (1948). "Fourier Technique in X-ray Organic Structure Analysis". Cambridge University Press, Cambridge, Eng.
- Bragg (1915). Phil. Trans. Roy. Soc., A, 215, 253.

Clews and Cochran (1947). Acta Cryst. 2, 46.

Duane (1925). Proc. Nat. Acad. Sci. 11, 489.

Harker (1948a). Am. Miner. 33, 762.

- Harker (1948b). Am. Miner. 33, 764.
- James (1948). "The Optical Principles of the Diffraction of X-rays". G. Bell and Sons, London.
- Konobeevskii (1948). Doklady Akad. Nauk. S.S.S.R. 59, 53.
- Lu (1943). <u>Rev. Sci. Inst. 14</u>, 331.
- Patterson (1935). Z. Kristallogr. 90, 517.
- Pauling (1947). J. Am. Chem. Soc. 69, 542.
- Robertson (1943). J. Sci. Inst. 20, 165.
- Wrinch (1946). "Fourier Transforms and Structure Factors". A.S.X.R.E.D. Monograph Number 2.
- Zachariasen (1945). "Theory of X-ray Diffraction in Crystals". John Wiley and Sons, New York.

ACKNOWLEDGMENTS

The author is indebted to Dr. N. C. Baenziger for suggesting an investigation of the structure of titanium-beryllium compound.

The author is greatly indebted to Dr. R. E. Rundle for his guidance and inspiration throughout the course of the investigation.

The author is also grateful to the Ames Laboratory of the Atomic Energy Commission for providing the facilities and funds for this investigation.