THE CRYSTAL STRUCTURE OF $Cu_3(AsO_4)_2$

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By

SANDRA JEAN POULSEN, B.Sc.

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AUTHOR: Sandra Jean Poulsen, B.Sc. (McGill University)

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SCOPE AND CONTENTS:

The crystal structure of $Cu_3(AsO_4)_2$ was determined using a direct method of crystal structure analysis. The crystal structure is described, and its features compared to those of several compounds which have similar molecular formulas. The method used in the structure determination process is described, and an assessment of its general usefulness is attempted.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES (continued)

I. INTRODUCTION

The solution of crystal structures would be a routine procedure if the amplitudes of the X-ray reflections from a single crystal could be determined directly from the observed intensities. If the amplitude (or "structure factor") were known for each reflection, then the electron density could be calculated at any point within the crystal. The atomic positions could then be inferred from the positions of the maxima in the electron density distribution throughout the crystal.

But the structure factor is in general a complex quantity, having both magnitude and phase. The magnitude of the structure factor can be determined directly from the observed intensities (which are proportional to the square of the amplitudes), but the phase of the structure factor cannot be directly determined from the intensities (except in the special case where the X-rays are anomalously dispersed). This is the "phase problem" of X-ray crystallography.

Methods of crystal structure determination have been developed which attempt to derive the phases of the structure factors from the intensity values using statistical techniques. One of these methods, the "correlation method",was developed by de Vries (1965) as a refinement of a procedure described by Woolfson (1961).

In an effort to evaluate the usefulness of the correlation method, an attempt has been made to use this technique to determine the crystal structure of copper ortho-arsenate, $Cu_3(AsO_4)_2$. The compound was expected to provide a non-trivial test of the method as its structure was unknown; furthermore, since chemically related but crystallographically independent structures had been previously resolved by other structure determination methods, an evaluation of the merits of the correlation method might be made.

The correlation method is described in detail in Chapter II. Chapter III deals with the results of its application to the structure determination $Cu_3(AsO_4)_2$. Chapter IV attempts to predict the results that would have been achieved in a Patterson analysis of $Cu_3(AsO_4)_2$, and in a correlation analysis of $(Zn,Cd)_3(PO_4)_2$, β-$Zn_3(PO_4)_2$, and α-$Mg_2P_2O_7$, and compares the predicted results with the results of the structure determination method used. Chapter V is a brief summary of the work.

II. THE CORRELATION METHOD

1. The Phase Problem

The aim of any direct method of crystal structure determination is to derive the phases of the structure factors, F_H, directly from the intensity data. With the phases of a sufficient number of the larger F_H values known, a Fourier synthesis may show the electron density associated with at least the heavier atoms of the crystal.

The electron density ρ at any point $\vec{r}$ in the unit cell having a volume V is

$$\rho(\vec{r}) = \frac{1}{V} \sum_H F_H \exp 2\pi i \, \vec{H}\cdot\vec{r}$$

Here $\vec{H}$ represents the position in reciprocal space of the point (hkℓ) relative to an arbitrary crystal lattice point, and F_H is the structure factor of the X-ray reflection of indices (hkℓ). Every point in the reciprocal lattice corresponds to a possible reflection from the crystal lattice. The electron density can be evaluated if the F_H values are known.

In a crystal having a unit cell containing N atoms located at positions $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N$ the general expression for the structure factor F_H is

$$F_H = \sum_{j=1}^{N} f_j \exp 2\pi i \, \vec{H}\cdot\vec{r}_j ,$$

where f_j is the scattering factor of the j^{th} atom. F_H is a complex quantity, and as such can have any relative phase between 0 and 2π.

The phase determination problem for an arbitrary crystal reduces to a simpler problem when a crystal has a centre of symmetry. In a centrosymmetric crystal, the atoms occur in pairs with coordinates $\pm \vec{r}_j$, and the general expression for F_H is simplified:

$$F_H = \sum_{j=1}^{N} f_j \cos 2\pi \vec{H}\cdot\vec{r}_j .$$

For a centrosymmetric crystal, then, F_H is a real quantity and so can only be either a positive or a negative number. As a result, the phase determination problem in a general structure reduces to a sign determination problem in a centrosymmetric crystal structure.

2. The Sign Relation

Because the signs of the various structure factors are not mutually independent, it has been possible to develop methods of sign determination. The following relationship among the signs of the structure factors proves most useful:

Denoting the sign of the structure factor F_H as s(H), then it can be shown that the product S of the three signs s(H), s(H'), and s(H+H') is probably positive. This is particularly true when F_H, $F_{H'}$, and $F_{H+H'}$ are all large. This "sign relation" is expressed mathematically as

$$S(H)\ s(H')\ s(H+H') = S,$$

and S is probably +.

One derivation of this sign is due to Cochran (1952). He begins with the premise than an electron density map of a crystal structure consists of large, high density positive regions (representing the atomic positions) superposed on a low but non-negative background. Mathematically, this premise can be usefully expressed as $\int_V \rho^3\, dV$ is large and positive.

Now

$$\rho^3 = \frac{1}{V^3} \sum_H \sum_{H'} \sum_{H''} F_H\, F_{H'}\, F_{H''} \exp 2\pi i\ (\vec{H} + \vec{H}' - \vec{H}'')\cdot\vec{r}$$

and in the centrosymmetric case this reduces to

$$\rho^3 = \frac{1}{V^3} \sum_H \sum_{H'} \sum_{H''} F_H\, F_{H'}\, F_{H''} \cos 2\pi\ (\vec{H} + \vec{H}' - \vec{H}'')\cdot\vec{r}$$

The expression $\int_V \rho^3\, dV$ can now be written as

$$\frac{1}{V^3} \sum_H \sum_{H'} \sum_{H''} F_H\, F_{H'}\, F_{H''} \int_V \cos 2\pi\ (\vec{H} + \vec{H}' - \vec{H}'')\cdot\vec{r}\ dV$$

This integral is zero unless the argument of the cosine is zero. When H" = H+H' the integral has the value V. As a result, the condition that $\int_V \rho^3 dV$ is large and positive is equivalent to the condition that

$$\frac{1}{V^2} \sum_H \sum_{H'} F_H\, F_{H'}\, F_{H+H'}$$

is large and positive.

In order for the summation to be large and positive, the individual terms must tend to be positive, particularly when the F's are large. That is, the sign S in the sign relation

$$s(H)\ s(H')\ s(H+H') = S$$

is probably +, as we wished to show. If a particular sign relation can be shown to hold, and if two of the signs involved are known, then the third sign can be determined.

3. The Probability Calculation

In order to use the sign relations as part of a mathematical procedure to determine the signs of structure factors, Cochran and Woolfson (1955) evaluated the probability $P_-(\vec{H},\vec{H}')$ that the sign S will be negative rather than positive. They expressed this probability in terms of the "unitary structure factor", U_H, and the "unitary scattering factor", n_j.

The unitary structure factor is defined as

$$U_H = F_H \Big/ \sum_{j=1}^{N} f_j \ .$$

Since $\sum_{j=1}^{N} f_j$ is the maximum possible value of F_H (which would occur when $\cos 2\pi\vec{H}\cdot\vec{r}_j = 1$ for all j) then U_H gives the structure factor as the fraction of its maximum possible value.

The unitary scattering factor of the j^{th} atom is defined as

$$n_j = f_j / \sum_{j=1}^{N} f_j \; ;$$

n_j bears the same relationship to U_H as f_j bears to F_H. The assumption is made that the values of n_j do not vary with $\vec{H}$. Although rigorously true only for structures with equal atoms, this condition is reasonably well satisfied for general structures in which no excessively heavy atoms are present.

The expression which Cochran and Woolfson derived for the probability that the sign S will be negative is

$$P_-(\vec{H},\vec{H}') = 0.5 \left\{1 + \tanh[(\varepsilon_3/\varepsilon^3)\,|U_H \; U_{H'} \; U_{H+H'}|]\right\}, \quad \text{II.3.1}$$

where

$$\varepsilon_3 = \sum_{j=1}^{N} n_j^3$$

and

$$\varepsilon = \sum_{j=1}^{N} n_j^2 ,$$

provided $\vec{H}$ and $\vec{H}'$ are independent.

If $\vec{H}' = \vec{H}$, then

$$P_-(2\vec{H}) = 0.5 \left\{1 + \tanh[(\varepsilon_3/2\varepsilon^3)\,|U_{2H}|\,(U_H^2 - \varepsilon)]\right\} , \quad \text{II.3.2}$$

For each group of three structure factors F_H, $F_{H'}$, and $F_{H+H'}$, the probability P_- that the sign relation will fail to hold (that is, S will be negative) can be calculated with one or the other of these two expressions.

4. The Correlation Equation

De Vries (1965) extended the calculation of P_- to include the influence that the sign relations have upon each other. His "correlation" method recognizes that different sign relations may have one structure factor (or perhaps even two structure factors) in common. For example, among the list of sign relations for an hk0 projection might be the following three:

$$S_1 = s(4,5,0)\ s(1,0,0)\ s(5,5,0)$$

$$S_2 = s(1,0,0)\ s(5,5,0)\ s(6,5,0)$$

$$\text{and } S_3 = s(1,5,0)\ s(5,0,0)\ s(6,5,0)$$

The signs S have been given arbitrary subscripts, and the indices written as h,k,ℓ rather than H. The sign relations S_1 and S_2 have two factors in common, while S_2 and S_3 have one factor in common. Multiplying the sign relations S_1 and S_2 together we obtain

$$S_1S_2 = s(4,5,0)\ s^2(1,0,0)\ s^2(5,5,0)\ s(6,5,0)$$

$$= s(4,5,0)\ s(6,5,0),$$

since the square of any sign symbol must be +1.

Similarly,

$$S_2S_3 = s(1,0,0)\ s(5,5,0)\ s(1,5,0)\ s(5,0,0)\ .$$

Now it may happen that among the list of sign relations the following two occur:

$$S_4 = s(4,5,0)\ s(2,0,0)\ s(6,5,0)\ ,$$

and $S_5 = s(1,0,0)\ s(1,0,0)\ s(2,0,0)$.

Then

$$S_4S_5 = s(4,5,0)\ s(6,5,0)$$

and therefore

$$S_1S_2 = S_4S_5. \qquad \text{II.4.1}$$

Similarly there might be a pair of sign relations whose product is equal to S_2S_3, resulting in another equation of this form.

De Vries calls such an equation between sign relations a "correlation equation". The power of a correlation equation lies in the fact that because the correlation equation must be valid, the probability that each of its constituent signs S_n will fail decreases.

To demonstrate this, the correlation equation II.4.1 can be rewritten as

$$S_1 = S_2S_4S_5$$

by multiplying both sides of the equation by the sign S_2. Assuming for convenience that each sign relation has a P_- value of 0.20 when considered individually, then the probability P_-^*, which includes the influence of other sign relations, can be calculated.

Because the correlation equation must hold, S_1 can only be negative if the product $S_2S_4S_5$ is also negative.

Mathematically,

$$\frac{P_-^*(S_1)}{P_+^*(S_1)} = \frac{P_-(S_1)}{P_+(S_1)} \; \frac{P_-(S_2S_4S_5)}{P_+(S_2S_4S_5)} \; .$$

Now the product $S_2S_3S_4$ will be negative when all three signs are negative, or when two are positive and one is negative.

That is

$$P_-^*(S_2S_4S_5) = P_-(S_2)P_-(S_4)P_-(S_5) + P_-(S_2)P_+(S_4)P_+(S_5)$$
$$+ P_+(S_2)P_-(S_4)P_+(S_5) + P_+(S_2)P_+(S_4)P_-(S_5)$$
$$= (0.20)^3 + 3(0.20)(0.80)(0.80) = 0.392.$$

Then

$$\frac{P_-^*(S_1)}{P_+^*(S_1)} = \frac{0.20}{0.80} \; \frac{0.392}{0.608} = 0.161$$

and

$$P_-^*(S_1) = 0.14 \; .$$

This is less than the probability $P_-(S_1) = 0.20$ that the sign relation S_1 will fail. The probabilities that the other three sign relations will fail are decreased in the same way.

The greater the number of correlation equations in which a particular sign relation is involved, the smaller its probability P_-^* of failing will become. Some sign relations will be involved in a large number of correlation equations and so have their calculated probabilities of failing greatly decreased. Other sign relations may not be involved in any correlation equations, and their calculated probabilities will be unchanged. As a result, the correlation method can be used as a reliable guide in determining which of the sign relations hold. In effect, the correlation method serves to determine the signs of the sign relations.

5. The Sign Determination Method

The procedure of determining the signs of the structure factors is begun by listing all the sign relations which occur among the signs of the larger structure factors. The probabilities P_- that each sign relation will fail are calculated from the appropriate Cochran and Woolfson equation (II.3.1 or II.3.2).

The correlation method is then used to determine the signs S of the sign relations. The sign relation with the smallest probability of failing is assumed to be correct, and given the sign +. Letter symbols are then substituted for each of the signs of the structure factors involved in that sign relation. For example, the sign relation

$$s(H)\ s(H')\ s(H+H') = S$$

becomes

$$a \cdot b \cdot ab = +$$

Wherever these three structure factors appear in the list of sign relations, the corresponding letter symbol is substituted.

The sign relation with the next lowest P_-^* value is assumed in turn to hold. Letter symbols are again assigned, with as few new symbols as possible being used. The procedure is continued until a significant portion of the structure factors have been assigned letter symbols (or products of letter symbols) for their signs. It then remains to determine whether each of the letter symbols stands for + or −.

Woolfson (1961, p.21) shows that the signs of two of the letter symbols can be chosen arbitrarily for any two-dimensional projection with plane group symmetry p2.

In the hk0 projection, for example, for a structure where the unit cell contains N atoms with coordinates x_j, y_j with respect to an origin at 0,0, the structure factor of index hk is

$$(F_{hk})_{0,0} = \sum_{j=1}^{N} f_j \cos 2\pi (hx_j + ky_j) .$$

If the origin is changed instead to the centre of symmetry at $\frac{1}{2}$,0 the structure factor equation becomes

$$(F_{hk})_{\frac{1}{2},0} = \sum_{j=1}^{N} f_j \cos \{2\pi (hx_j + ky_j) + 2\pi \frac{h}{2}\}$$

$$= (-1)^h (F_{hk})_{0,0} .$$

Similarly

$$(F_{hk})_{0,\frac{1}{2}} = (-1)^{k} (F_{hk})_{0,0}$$

and

$$(F_{hk})_{\frac{1}{2},\frac{1}{2}} = (-1)^{h+k} (F_{hk})_{0,0} .$$

The changes in the signs of the structure factors with a change in origin are summarized in Table 1. In Table 1, + represents no change in sign, while - represents a change in sign, referred to the sign of the structure factor with the origin at 0,0.

Structure factors having both h and k even are the "structure invariants" (group 1). Their signs are independent of the choice of origin. However, structure factors with one or both of h and k odd have signs which may change with a change in origin.

To take a specific case, consider two signs, one from group (2) with the letter symbol a, and another from group (3) with the letter symbol b, both assigned with respect to an origin at 0,0. Then with respect to the alternative origins, their signs are given in Table 2. The four possible origins give the four possible combinations of sign for a and b. As a result, any combination of + and - for a and b is permissible, for it will be the correct combination for one of the four origins. The choice of sign for these two symbols is arbitrary.

TABLE 1

Changes in sign of a structure factor F_{hk}.

ORIGIN	Group 1 h even k even	Group 2 h odd k even	Group 3 h even k odd	Group 4 h odd k odd
$0,0$	+	+	+	+
$\frac{1}{2},0$	+	-	+	-
$0,\frac{1}{2}$	+	+	-	-
$\frac{1}{2},\frac{1}{2}$	+	-	-	-

TABLE 2

Signs of two letter symbols, taken from Groups 2 and 3

ORIGIN	SIGNS
$0,0$	+a, +b
$\frac{1}{2},0$	-a, +b
$0,\frac{1}{2}$	+a, -b
$\frac{1}{2},\frac{1}{2}$	-a, -b

In general, two signs can be allotted freely, one to each of two symbols taken from groups (2), (3), or (4), but not two from the same group. Once the origin of the projection has been fixed in this way, all other signs must be found with respect to this origin.

In addition it is sometimes possible to determine a few signs of structure factors through the use of an inequality relationship. Harker and Kasper (1948) made use of Cauchy's inequality,

$$\left|\sum_{j=1}^{N} a_j b_j\right|^2 \leqslant \left(\sum_{j=1}^{N} |a_j|^2\right)\left(\sum_{j=1}^{N} |b_j|^2\right) ,$$

to derive a number of inequalities holding for the unitary structure factors.

For example, taking

$$a_j = \sqrt{n_j}$$

and

$$b_j = \sqrt{n_j} \cos 2\pi \vec{H}\cdot\vec{r}_j .$$

the Cauchy relation becomes

$$U_H^2 \leqslant 1/2\ (1 + U_{2H}) ,$$

provided n_j is assumed to be independent of $\vec{H}$.

When both U_H and U_{2H} are sufficiently large, this inequality will show that U_{2H} is positive.

Another substitution for a_j and b_j leads to the relation

$$(U_H + U_{H'})^2 \leqslant (1 + U_{H+H'})(1 + U_{H-H'}) .$$

Similarly

$$(U_H + U_{H'})^2 \leqslant (1 - U_{H+H'})(1 - U_{H-H'}).$$

These inequalities may be sufficient to determine the signs s(H+H') or s(H-H').

With as many as possible of the letter symbols determined by fixing the origin and by using the inequality relations, there will still be undetermined symbols. One way of dealing with them is to select the two (or perhaps three) of the remaining letter symbols which occur most frequently among the remaining undetermined signs. Since these two (or three) can each be + or -, there are four (or eight) combinations of possible signs for these structure factors.

Among these combinations should be the one correct set of signs relative to the fixed origin. To find the correct set, each combination of signs can be used in turn to obtain an electron density map; and from the group of maps it should be possible to choose the one giving the actual location in projection of the heavier atoms of the structure.

III THE STRUCTURE DETERMINATION OF $Cu_3(AsO_4)_2$

1. Experimental Work

Crystals of copper ortho-arsenate were prepared by K. Neelakantan by slowly cooling a melt formed from the precipitate recovered from the reaction of Na_2HAsO_4 and $CuCl_2$ in an aqueous solution.

The greenish coloured crystals were obtained usually as needles with a as the needle axis, but sometimes as platelets developed on (001). The Cu content of the crystals was determined to be 40.3%, as compared to the calculated 40.69% Cu content of $Cu_3(AsO_4)_2$. The density measured with a pycnometer is 4.83 gm/cc; it agrees roughly with the calculated density, 5.04 gm/cc, assuming four molecules of $Cu_3(AsO_4)_2$ per unit cell.

The cell parameters b and c were determined from a Weissenberg film of the [100] zone which had superposed upon it for calibration purposes an Al_2O_3 powder pattern exposed through the Weissenberg screen in three equally spaced positions across the film.
The θ values of the high angle powder lines of Al_2O_3 were accurately known from the hexagonal lattice constants $a = 4.75903(3)$ Å and $c = 12.9908(2)$ Å (Cooper, 1962), where

the figure in brackets gives the uncertainty in the last digit. Thus the high angle reflections of $Cu_3(AsO_4)_2$ could be determined accurately on the calibrated film, with errors caused by film shrinkage thereby eliminated. A least squares refinement of the $Cu_3(AsO_4)_2$ reciprocal axes, b* and c*, using the accurate θ values was then carried out.

The a parameter was determined from a rotation photograph about the a axis which had superposed upon it a TiO_2 single crystal rotation pattern. The lattice parameters of TiO_2 were determined by Cromer and Herrington (1955) as $a = 4.5929(5)$ Å and $c = 2.9591(3)$ Å. The camera diameter D could be calculated accurately from the translation distance T along the TiO_2 rotation axis and from the measured spacing Δn between the $\pm$ nth TiO_2 layer lines on the film:

$$D = \frac{\Delta n}{\tan(\sin^{-1} \frac{n\lambda}{T})}$$

The average of the values of D calculated in this way was used along with the measured spacings between the $Cu_3(AsO_4)_2$ layer lines to calculate a.

The monoclinic angle β was measured on an $h0\ell$ precession film to an accuracy limited by the smallest angular division of the measuring instrument.

The lattice constants determined from the Weissenberg

and precession photographs are:
$\underline{a} = 6.327(5)$ Å; $\underline{b} = 8.642(5)$ Å; $\underline{c} = 11.313(5)$ Å; $\beta = 92.04(4)$. The observed systematic absences are 0k0 absent for k odd, and h0ℓ absent for ℓ odd,and these determine the space group of $Cu_3(AsO_4)_2$ uniquely as $P2_1/c$.

Two crystals were used for the single crystal study. The first, needlelike in shape and measuring 0.16 x 0.08 x 0.08 mm^3, was used to obtain the equi-inclination Weissenberg photographs nkℓ (with n = 0,1,2) with Ni-filtered Cu Kα radiation. A NaI(Tℓ) scintillation detector and an electronic counting system were used to record the intensities of the reflections in the three layers.

The observed count rates, N_{obs} of the stronger reflections were corrected for the dead time τ of the detector to give the true count rates, N_{true}:

$$N_{true} = N_{obs} / 1 - N_{obs} \tau \quad \text{(Korff,p.257,1955).}$$

The dead time was determined to be 0.36 μ sec. It was found that the correction was significant for about 25% of the reflections; that is, for those which had N_{obs} greater than 125 counts/sec. The count rates of all the reflections were corrected for the background noise.

A second crystal, platelike in shape and measuring 0.24 x 0.08 x 0.04 mm^3, was used to obtain the integrated photographs containing reflections indexed as h0ℓ and hk0, with Zr-filtered MoKα radiation. For both projections the integrated intensities were measured on a Joyce-Lobell recording microdensitometer on three films exposed for different times. Scaling factors between the films were calculated for both h0ℓ and hk0 by comparing all those reflections which could be measured on more than one of the three films. The average scaling factors between films were used to obtain the (average) integrated intensity value of each reflection.

For both the Weissenberg and precession films, unobserved reflections were assigned an upper limit of intensity by visual comparison with neighbouring observed reflections.

Absorption corrections to the hk0 precession intensities(obtained with a plate-shaped crystal aligned approximately normal to the X-ray beam) were negligible (Buerger, 1960, p.207), but the h0ℓ precession intensities were corrected by using a cylindrical approximation ($\mu R = 0.84$). Absorption corrections to the Weissenberg data (obtained with a needle-shaped crystal) were also made by using a cylindrical approximation ($\mu R = 0.98$).

Lorentz and polarization corrections were made to the precession and Weissenberg intensity data using FORTRAN programs written for this laboratory by I.D. Brown and A. K. Das.

The magnitudes of the structure factors F_H and the unitary structure factors U_H were then calculated using the corrected intensities. The approximate scaling for the structure factors was known from the results of an earlier trial structure for $Cu_3(AsO_4)_2$. Visual measurements had been made of Weissenberg and precession films by C. Calvo and the intensity values had been used to test a model based upon the interpretation of the Patterson projections. Although the model proved unsuccessful, Fehlmann et al. (1964) have shown that the results of a number of random trial structures, when considered together, can yield a scaling of the structure factors which is approximately correct. The visually measured hk0 data was scaled on the basis of the Patterson model, and used in the initial phase of the sign determination process.

The values of the unitary structure factors of the reflections which were used in the sign determining process are given in Tables 3, 4 and 5, along with the correctly scaled values calculated after the structure had been determined. The hk0 values, in particular, were overestimated because of the method of scaling and because of errors in the visual estimation of the original data.

TABLE 3

Comparison of the initially and finally scaled unitary structure factors, U_H, for the hk0 projection.

h	k	ℓ	Initial $\|U_H\|$	Final $\|U_H\|$	h	k	ℓ	Initial $\|U_H\|$	Final $\|U_H\|$
0	8	0	.25	.15	4	2	0	.35	.21
0	10	0	.25	.11	4	6	0	.23	.14
1	5	0	.45	.38	4	8	0	.25	.10
1	7	0	.23	.15	4	9	0	.25	.07
1	8	0	.54	.34	5	3	0	.21	.12
1	10	0	.25	.11	5	7	0	.23	.09
2	1	0	.28	.19	5	8	0	.56	.37
2	3	0	.24	.19	6	0	0	.61	.46
2	6	0	.28	.22	6	3	0	.22	.13
2	9	0	.33	.20	6	4	0	.25	.16
3	1	0	.35	.24	6	5	0	.24	.06
3	5	0	.27	.21	7	3	0	.21	.09
3	7	0	.70	.42	7	4	0	.27	.11
3	8	0	.26	.10	7	5	0	.49	.33
4	0	0	.41	.34	7	6	0	.26	.14
4	1	0	.32	.21					

TABLE 4

Comparison of the initially and finally scaled unitary structure factors, U_H, for the $h0\ell$ projection.

h	k	ℓ	Initial $\|U_H\|$	Final $\|U_H\|$	h	k	ℓ	Initial $\|U_H\|$	Final $\|U_H\|$
0	0	8	.31	.32	6	0	8	.30	.26
0	0	10	.31	.28	7	0	4	.23	.20
0	0	12	.30	.27	8	0	0	.20	.16
0	0	14	.40	.36	-1	0	2	.19	.16
1	0	12	.20	.17	-1	0	8	.41	.39
1	0	14	.26	.21	-1	0	12	.24	.22
2	0	4	.25	.23	-3	0	4	.31	.27
2	0	14	.26	.26	-3	0	6	.25	.22
3	0	2	.19	.17	-3	0	8	.22	.20
3	0	4	.37	.33	-4	0	4	.33	.29
3	0	6	.48	.44	-4	0	14	.36	.34
3	0	8	.36	.32	-5	0	8	.35	.30
3	0	10	.42	.38	-5	0	12	.41	.35
3	0	12	.22	.19	-6	0	4	.36	.32
4	0	0	.41	.34	-6	0	6	.34	.31
5	0	8	.23	.19	-6	0	10	.40	.34
5	0	12	.22	.20	-7	0	2	.20	.16
6	0	0	.60	.46	-7	0	4	.23	.21
6	0	2	.26	.22	-7	0	8	.26	.24
6	0	4	.59	.52	-8	0	4	.29	.23

TABLE 5

Comparison of the initially and finally scaled unitary structure factors, U_H, for the $0k\ell$ projection.

h	k	ℓ	Initial $\lvert U_H \rvert$	Final $\lvert U_H \rvert$	h	k	ℓ	Initial $\lvert U_H \rvert$	Final $\lvert U_H \rvert$
0	0	4	.64	.52	0	4	12	.25	.20
0	0	8	.39	.32	0	5	7	.20	.15
0	0	10	.35	.28	0	5	8	.25	.19
0	0	12	.34	.27	0	5	9	.23	.18
0	1	4	.24	.20	0	5	12	.20	.15
0	2	1	.20	.15	0	6	7	.23	.18
0	2	4	.21	.17	0	6	9	.23	.18
0	2	6	.23	.18	0	6	11	.36	.28
0	2	8	.23	.19	0	7	3	.24	.18
0	2	11	.23	.18	0	7	4	.21	.16
0	3	1	.51	.40	0	7	6	.25	.19
0	3	3	.28	.22	0	7	7	.37	.28
0	3	5	.39	.31	0	7	8	.24	.18
0	3	7	.24	.19	0	7	10	.22	.17
0	3	10	.34	.27	0	8	1	.20	.15
0	3	11	.32	.25	0	8	3	.28	.21
0	3	12	.23	.18	0	8	5	.24	.18
0	4	5	.39	.31	0	8	7	.21	.15
0	4	9	.30	.24	0	9	3	.22	.16
0	4	10	.23	.18	0	9	7	.23	.16

2. The Sign Determination Procedure in $Cu_3(AsO_4)_2$

The reflections listed in Tables 3 to 5 are the strongest in each of the three major projections of $Cu_3(AsO_4)_2$. The thirty-one hk0 reflections have a lower limit of 0.21 on $|U_H|$, while the forty h0ℓ reflections range down to 0.19, and the forty 0kℓ reflections range down to 0.20. Because these $|U_H|$ values were large, it was expected that among these reflections, sign relations of the form

$$s(H)s(H')s(H+H') = S$$

would have relatively small probabilities of failing. A FORTRAN program was written to determine all the sign relations occurring among the selected reflections, and to compute the probability P_- from the Cochran and Woolfson equations. A second program was written to determine all correlation equations holding among the sign relations, and to compute the probability P_-^* which included the influence of the correlation equations upon the individual sign relations. The sign relations found are listed with their probabilities in Tables 6, 7 and 8.

The probabilities P_-^* determined the order in which the sign relations could safely be assumed to hold. Letter symbols were substituted for the signs of the reflections occurring in "accepted" sign relations, with as many signs as possible being expressed in terms of a small number of letter symbols.

TABLE 6. SIGN RELATIONS AND PROBABILITIES FOR THE HKO PROJECTION.

SIGN RELATION			P-	P-*
0, 8	2, 1	2, 9	.120	.00011
	4, 0	4, 8	.099	.01947
	4, 1	4, 9	.149	.00424
1, 5	2, 3	3, 8	.085	.00000
	3, 1	4, 6	.042	.00000
	4, 2	5, 7	.043	.00000
	6, 0	7, 5	.001	.00000
-1, 5	2, 3	1, 8	.008	.00000
	3, 1	2, 6	.022	.00000
	4, 0	3, 5	.016	.00000
	4, 2	3, 7	.001	.00000
	5, 3	4, 8	.117	
	6, 3	5, 8	.010	.00000
1, 7	2, 1	3, 8	.193	.00453
	3, 1	4, 8	.146	.00067
	4, 0	5, 7	.133	.00001
	4, 1	5, 8	.028	.00000
-1, 7	2, 1	1, 8	.048	.00000
	4, 0	3, 7	.004	.00000
	4, 1	3, 8	.162	.07401
	6, 0	5, 7	.057	.02110
1, 8	3, 1	4, 9	.017	.00000
	4, 0	5, 8	.001	.00000
-1, 8	3, 1	2, 9	.006	.00000
	4, 0	3, 8	.009	.00382
	6, 0	5, 8	.001	.00001
2, 1	3, 7	5, 8	.001	.00000
	4, 2	6, 3	.134	.00000
	5, 3	7, 4	.203	
-2, 1	2, 9	0,10	.119	
	3, 7	1, 8	.001	.00000
	4, 2	2, 3	.115	
	4, 8	2, 9	.119	.02952
	5, 7	3, 8	.194	.04832
	6, 0	4, 1	.010	
	6, 5	4, 6	.211	
	7, 6	5, 7	.193	.00997
2, 3	2, 6	4, 9	.186	.01081
	3, 5	5, 8	.044	.00000
	4, 0	6, 3	.134	.00000
	4, 1	6, 4	.160	
	4, 2	6, 5	.152	.00003
-2, 3	3, 5	1, 8	.049	.00000
	3, 7	1,10	.025	.00004
	4, 6	2, 9	.168	.01156
2, 3	7, 5	5, 8	.004	.00004
2, 6	3, 1	5, 7	.123	.03834
-2, 6	3, 1	1, 7	.122	.00195
	6, 0	4, 6	.032	.00002
	6, 3	4, 9	.207	
2, 9	3, 1	1,10	.074	
-2, 9	6, 0	4, 9	.013	
3, 1	4, 2	7, 3	.099	.00044
-3, 1	3, 7	0, 8	.006	.00000
	4, 6	1, 7	.164	.00180
	4, 9	1,10	.127	
	5, 8	2, 9	.005	.00000
	6, 4	3, 5	.119	.00191
	7, 5	4, 6	.032	.00000
3, 5	4, 0	7, 5	.011	.00000
	4, 1	7, 6	.129	.06265
-3, 5	4, 2	1, 7	.133	.00000
	6, 3	3, 8	.213	.00038
	7, 4	4, 9	.172	.03905
-3, 7	4, 1	1, 8	.001	.00000
-3, 8	4, 2	1,10	.123	.01645
-4, 1	4, 9	0,10	.148	
	5, 7	1, 8	.032	.00812
	6, 5	2, 6	.138	
	7, 4	3, 5	.118	
	7, 6	3, 7	.008	.00218
-4, 2	4, 6	0, 8	.146	.00000
	4, 8	0,10	.128	
	5, 3	1, 5	.056	.00000
	5, 8	1,10	.015	
	6, 4	2, 6	.108	.04681
	7, 3	3, 5	.157	.05721
	7, 5	3, 7	.001	.00000
	7, 6	3, 8	.119	.05872
-4, 6	6, 3	2, 9	.188	.00137
-5, 3	6, 5	1, 8	.093	.02437
	7, 6	2, 9	.177	
-6, 3	7, 5	1, 8	.008	.00000
-6, 4	7, 4	1, 8	.043	.01543
	7, 6	1,10	.199	
-6, 5	7, 3	1, 8	.095	.04010
	7, 5	1,10	.075	.01634
-7, 3	7, 5	0, 8	.101	.00045
-7, 4	7, 6	0,10	.180	

TABLE 7. SIGN RELATIONS AND PROBABILITIES FOR THE OKL PROJECTION.

SIGN RELATION			P-	P-*
0, 4	0, 4	0, 8	.002	.00000
	0, 8	0,12	.001	.00000
	2, 4	2, 8	.056	.00000
	3, 1	3, 5	.001	.00000
	3, 3	3, 7	.023	.00000
	3, 7	3,11	.014	.00000
	4, 5	5, 9	.002	.00000
	5, 8	5,12	.058	.00044
	6, 7	6,11	.008	.00000
	7, 3	7, 7	.007	.00000
	7, 4	7, 8	.051	.00000
	7, 6	7,10	.039	.00000
	8, 1	8, 5	.054	.02361
	8, 3	8, 7	.033	.00000
	9, 3	9, 7	.047	.00021
0, 8	3, 3	3,11	.044	.00000
0,10	3, 1	3,11	.007	.00000
1, 4	2, 1	3, 5	.159	.00526
	2, 6	3,10	.157	.00087
	3, 1	4, 5	.014	.00000
	3, 5	4, 9	.073	.00000
	4, 5	5, 9	.122	.07044
	5, 7	6,11	.173	.00269
	7, 3	8, 7	.254	
	8, 3	9, 7	.195	
	-1, 4	0, 8	.002	
	7, 7	-6,11	.051	.02162
	-8, 3	7, 7	.093	.02635
2, 1	2, 4	4, 5	.191	.01308
	4,10	6,11	.190	
	-4, 5	2, 6	.175	
	-6,11	4,12	.169	.05337
	7, 7	-5, 8	.167	.09645
2, 4	3, 5	5, 9	.151	.00235
	4, 5	6, 9	.155	
	2, 4	0, 8	.002	.00000
	2, 6	0,10	.181	
	2, 8	0,12	.185	.00020
	8, 7	6,11	.193	.04772
	9, 3	7, 7	.170	.09779
2, 6	3, 1	5, 7	.114	.00175
	4, 5	6,11	.054	.00023
	4, 5	2,11	.144	
	8, 5	6,11	.141	
2, 8	3, 1	5, 9	.078	.01955
	8, 3	6,11	.106	.00137
2.11	3, 1	5,12	.116	
3, 1	3,10	6,11	.004	.00000
3, 1	4, 5	7, 6	.013	.00000
	4, 9	7,10	.045	.00000
	3, 3	0, 4	.001	.00000
	3, 7	0, 8	.015	.00000
	3,11	0,12	.008	.00000
	5, 7	2, 8	.109	.03501
	6, 9	3,10	.027	
	6,11	3,12	.023	.00377
	7, 4	4, 5	.025	.00000
	7, 8	4, 9	.035	.00000
	8, 7	5, 8	.088	.00034
3, 3	4, 5	7, 8	.087	.00000
	3, 5	0, 8	.023	.00000
	3, 7	0,10	.111	.00000
	6, 7	3,10	.119	.00176
	7, 6	4, 9	.137	.00000
	7, 7	4,10	.110	
	8, 5	5, 8	.183	
3, 5	4, 5	7,10	.045	.00000
	3, 7	0,12	.058	.00000
	6, 7	3,12	.132	.00493
	7, 4	4, 9	.102	.00000
	7, 7	4,12	.038	.00021
	8, 3	5, 8	.080	.00033
	8, 7	5,12	.194	.00165
4, 5	-7, 6	3,11	.061	.01456
	7, 7	-3,12	.050	.01248
	-8, 5	4,10	.125	
	-8, 7	4,12	.141	
	9, 3	-5, 8	.126	.07627
	9, 7	-5,12	.171	
4, 9	7, 3	-3,12	.188	.01407
	-8, 3	4,12	.131	.03179
5, 7	8, 3	3,10	.153	.04176
5, 8	-8, 3	3,11	.122	
5, 9	8, 1	3,10	.190	
6, 7	9, 3	-3,10	.164	
7, 3	7, 7	0,10	.058	.00014
7, 4	-7, 4	0, 8	.002	
	-7, 6	0,10	.164	.01876
	-7, 8	0,12	.178	
7, 8	9, 3	-2,11	.247	
8, 1	-8, 7	0, 8	.186	.00017
8, 3	-8, 5	0, 8	.081	.00007
	-8, 7	0,10	.135	
8, 5	-8, 7	0,12	.177	.05734
9, 3	9, 7	0,10	.162	.00086

TABLE 8. SIGN RELATIONS AND PROBABILITIES FOR THE HOL PROJECTION.

SIGN RELATION			P-	P-*
0, 8	3, 2	3,10	.090	.00086
	3, 4	3,12	.092	.00001
	6, 0	6, 8	.007	.00000
0,10	2, 4	2,14	.129	.00000
	3, 2	3,12	.232	.00000
	-1, 2	-1,12	.209	.00008
	-4, 4	-4,14	.032	.00000
1,12	4, 0	5,12	.151	.00000
	-1, 2	0,14	.190	.02295
2, 4	3, 4	5, 8	.120	.00000
	3, 8	5,12	.133	.00000
	4, 0	6, 4	.004	.00000
	-1, 8	1,12	.123	.00000
	-3, 4	-1, 8	.050	.00000
	-3, 8	-1,12	.219	.00000
	-6,10	-4,14	.032	.00000
	-7, 4	-5, 8	.134	.00000
	-7, 8	-5,12	.078	.00000
3, 2	3, 6	6, 8	.076	.00000
	-1, 2	2, 4	.298	.00411
	-1,12	2,14	.244	.00041
	-3, 6	0, 8	.206	.00277
	-3, 8	0,10	.228	.00419
	-6, 4	-3, 6	.168	.00000
	-6, 6	-3, 8	.204	.00003
	-7, 2	-4, 4	.236	.00454
3, 4	4, 0	7, 4	.038	.00000
	-3, 4	0, 8	.039	.01302
	-3, 6	0,10	.069	.00000
	-3, 8	0,12	.095	.00024
	-4, 4	-1, 8	.011	.00000
	-6, 4	-3, 8	.059	.00000
	-8, 4	-5, 8	.029	.00000
3, 6	-1, 8	2,14	.009	.00000
	-3, 4	0,10	.015	.00000
	-3, 6	0,12	.038	.00000
	-3, 8	0,14	.019	.00000
	-7, 8	-4,14	.016	.00000
3, 8	-3, 4	0,12	.047	.00000
	-3, 6	0,14	.037	.00000
	-4, 4	-1,12	.067	.00000
	-8, 4	-5,12	.019	.00000
3,10	-3, 4	0,14	.009	.00000
	-7, 4	-4,14	.039	.00000
3,12	-1, 2	2,14	.265	.00185
	-7, 2	-4,14	.184	.01345
4, 0	-1, 2	3, 2	.201	.00055
	-1, 8	3, 8	.005	.00000
	-1,12	3,12	.119	.00000
	-4,14	0,14	.005	.00000
	-5, 8	-1, 8	.005	.00000
	-5,12	-1,12	.024	.00000
	-7, 4	-3, 4	.068	.00000
4, 0	-7, 8	-3, 8	.103	.00000
	-8, 4	-4, 4	.027	.00000
5, 8	-3, 6	2,14	.198	.00000
	-4, 4	1,12	.191	.00001
	-6, 4	-1,12	.130	.00070
6, 0	-1, 8	5, 8	.006	.00000
	-1,12	5,12	.046	.00000
	-3, 4	3, 4	.003	.00000
	-3, 6	3, 6	.002	.00000
	-3, 8	3, 8	.012	.00000
	-4, 4	2, 4	.010	.00000
	-4,14	2,14	.006	.00000
	-5,12	1,12	.010	.00000
	-6,10	0,10	.002	.00000
	-7, 2	-1, 2	.103	.00469
	-7, 8	-1, 8	.004	.00000
6, 2	-3, 4	3, 6	.030	.00000
	-3, 6	3, 8	.109	.00030
	-3, 8	3,10	.095	.00027
	-5,12	1,14	.075	
	-6, 6	0, 8	.075	.03411
	-6,10	0,12	.056	.00010
6, 4	-1, 8	5,12	.007	.00000
	-3, 4	3, 8	.003	.00000
	-3, 6	3,10	.004	.00000
	-3, 8	3,12	.064	.00000
	-5, 8	1,12	.019	.00000
	-6, 4	0, 8	.003	.00000
	-6, 6	0,10	.004	.00000
	-6,10	0,14	.001	.00000
	-7, 4	-1, 8	.007	.00000
	-7, 8	-1,12	.032	.00000
6, 8	-3, 4	3,12	.138	.00007
	-6, 4	0,12	.050	.01634
	-6, 6	0,14	.023	.00814
	-7, 4	-1,12	.183	.07355
7, 4	-4, 4	3, 8	.073	.00000
	-6,10	1,14	.095	
	-7, 4	0, 8	.181	.03251
	-7, 8	0,12	.161	.00203
	-8, 4	-1, 8	.069	.00000
8, 0	-3, 8	5, 8	.277	.02858
	-5, 8	3, 8	.088	
	-5,12	3,12	.159	
	-6, 4	2, 4	.152	.01177
-1, 2	-5, 8	-6,10	.074	.01987
	-6, 6	-7, 8	.173	.00727
	-7, 2	-8, 4	.259	.15878
-1, 8	-3, 6	-4,14	.032	.00000
	-4, 4	-5,12	.007	.00000
-3, 4	-3, 6	-6,10	.055	.00000
	-4, 4	-7, 8	.084	.00000

The hk0 projection had thirty-one sign relations with a calculated P_* value of zero (to five figures). All thirty-one relations were accepted. The process of assigning letter symbols to the signs of the reflections was begun by assigning the letter symbols "a" and "b" to the large and frequently occurring signs s(-1,5,0) and s(3,7,0). With the sign s(5,8,0) next taken as "c", a total of fifteen signs could be expressed in terms of the three letter symbols by means of the thirty-one accepted sign relations. The assignment of the letter "d" to s(3,1,0) permitted a total of twenty-three signs to be expressed in terms of four letter symbols.

Sign relations having the next lowest P_* values were then accepted, and five more expressions for signs were obtained. The final sign relation to be accepted had P_* = 0.00218. The process was terminated then because new letter symbols would have been necessary in order to continue.

After the structure had been determined, it was found that seventeen of the eighty-nine sign relations were in fact incorrect. Through the use of the correlation method, only two of these seventeen incorrect sign relations were among the fifty-one accepted relations. (One sign was predicted incorrectly as a result.) The other fifteen were among the thirty-eight unaccepted relations.

TABLE 9

Predicted and correct signs of the structure factors in the hk0 projection.

h	k	ℓ	Letter Symbol	Predicted Sign	Correct Sign
0	8	0	-d	-	-
1	5	0	-a	+	+
1	7	0	+	+	+
1	8	0	-	-	-
1	10	0	a	-	-
2	1	0	+	+	+
2	3	0	-a	+	+
2	6	0	ad	-	-
2	9	0	-d	-	-
3	1	0	d	+	+
3	5	0	-a	+	+
3	7	0	+	+	+
3	8	0	+	+	+
4	0	0	-	-	-
4	1	0	+	+	+
4	2	0	a	-	-
4	6	0	-ad	+	+
4	8	0	d	+	+
4	9	0	-d	-	-
5	3	0	-	-	-
5	7	0	-	-	-
5	8	0	+	+	+
6	0	0	-	-	-

TABLE 9 (continued)

Predicted and correct signs of the structure factors in the hk0 projection.

h	k	ℓ	Letter Symbol	Predicted Sign	Correct Sign
6	3	0	a	-	-
6	5	0	-	-	+
7	3	0	ad	-	-
7	5	0	a	-	-
7	6	0	-	-	-

The origin of the hk0 projection was fixed by taking the two signs s(3,7,0) and s(5,8,0) as +. The twenty-eight signs could then be expressed in terms of two unknown sign symbols. The predicted signs (with a = - and d = +) are shown in Table 9 along with the signs eventually found to be correct.

With two possibilities (+ or -) for each of the letter symbols, there were four possible sets of signs. For each possibility an electron density map was computed using a Fourier synthesis program written for this laboratory by J. S. Rutherford.

Three of the four electron density maps had peaks on the glide plane at 1/4 b. In two of these maps, however, the glide plane peak was not even the largest of the peaks which appeared and certainly not of double weight as required by the space group symmetry. Although the third electron density had a peak on the glide plane which was sufficiently strong, there were five other single weight peaks in the asymmetric unit, rather than the expected four. This possible electron density distribution did not refine, and the remaining electron density was selected as the most probable of the four.

The remaining electron density map (calculated with a = - and d = +) is illustrated in Figure 1. Contour lines are drawn at arbitrary but regular intervals, with the

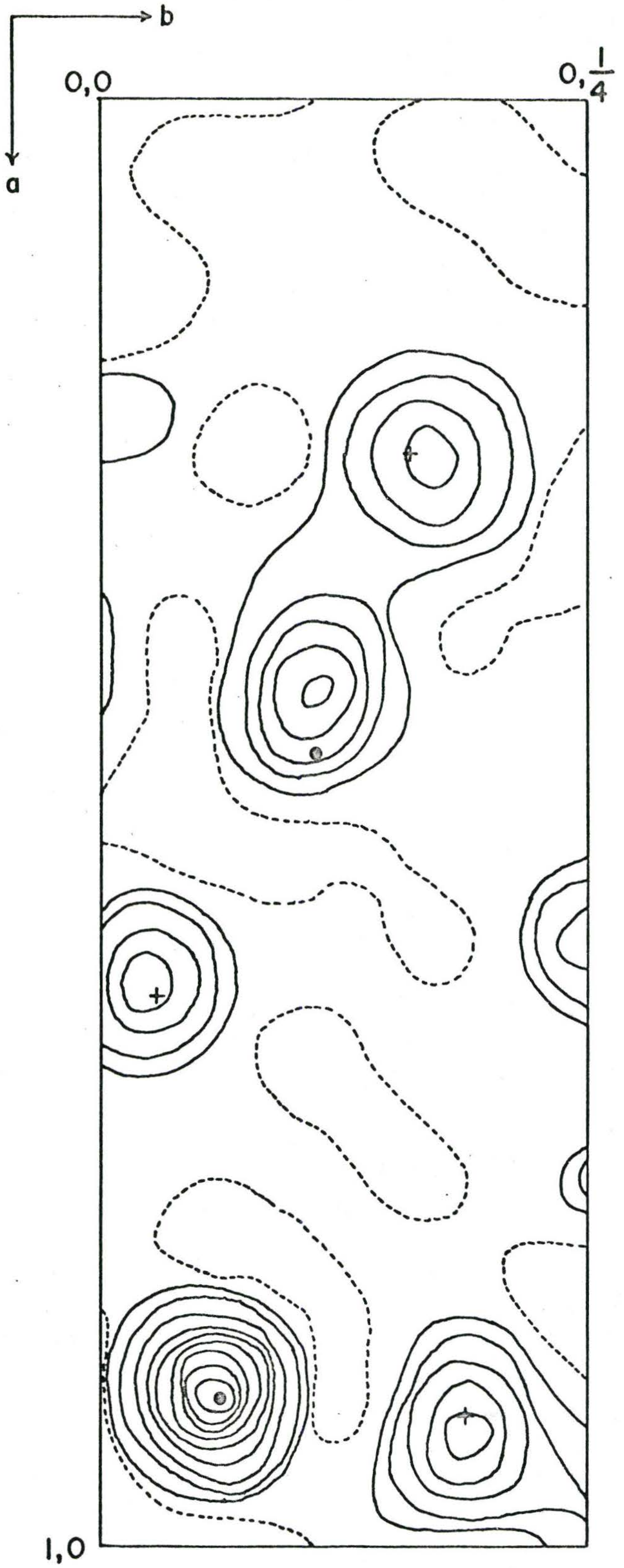


Figure 1

The electron density map of the hk0 projection with the final atomic positions superimposed zero level contours appearing as dashed lines.

Five distinct peaks are apparent. Since copper and arsenic atoms have very similar scattering factors, the peak positions were taken temporarily as the location of five copper atoms. Structure factors were calculated, using these x and y coordinates and compared to the observed structure factors. A reliability index, R, was computed, where

$$R = \sum_H ||F_H\ (\text{obs})| - |F_H\ (\text{calc})|| \;/\; \sum_H F_H(\text{obs}).$$

R was found to be 0.31 after one cycle of least squares refinement of the atomic positions (using a program written by J. S. Stephens). With none of the eight oxygens yet being included in the calculation, this was considered an encouraging figure.

In the $0k\ell$ projection, thirty-two sign relations having effectively zero P_* values were accepted immediately. The sign s(0,0,4) was given the letter symbol a, s(0,3,1) was given the symbol b, and s(0,4,5) the symbol c. It was possible to express fifteen signs in terms of these three letter symbols. Since only four more signs could be obtained by assigning a fourth symbol, only the three symbols were used. A sixteenth sign, s(0,0,8) was shown to be + by applying the Harker-Kasper inequality

$$U_H^{\ 2} \leqslant 1/2\ (1 + U_{2H})$$

with H = 0,0,4.

TABLE 10

Predicted and correct signs of the structure factors in the 0kℓ projection .

h	k	ℓ	Letter Symbol	Predicted Sign	Correct Sign
0	0	4	a	-	-
0	0	8	+	+	+
0	0	10	a	-	-
0	0	12	a	-	-
0	0	4	+	+	+
0	3	1	+	+	+
0	3	3	a	-	-
0	3	5	a	-	-
0	3	7	+	+	+
0	3	11	a	-	-
0	4	5	+	+	+
0	4	9	a	-	-
0	7	4	+	+	+
0	7	6	+	+	+
0	7	8	a	-	-
0	7	10	a	-	-

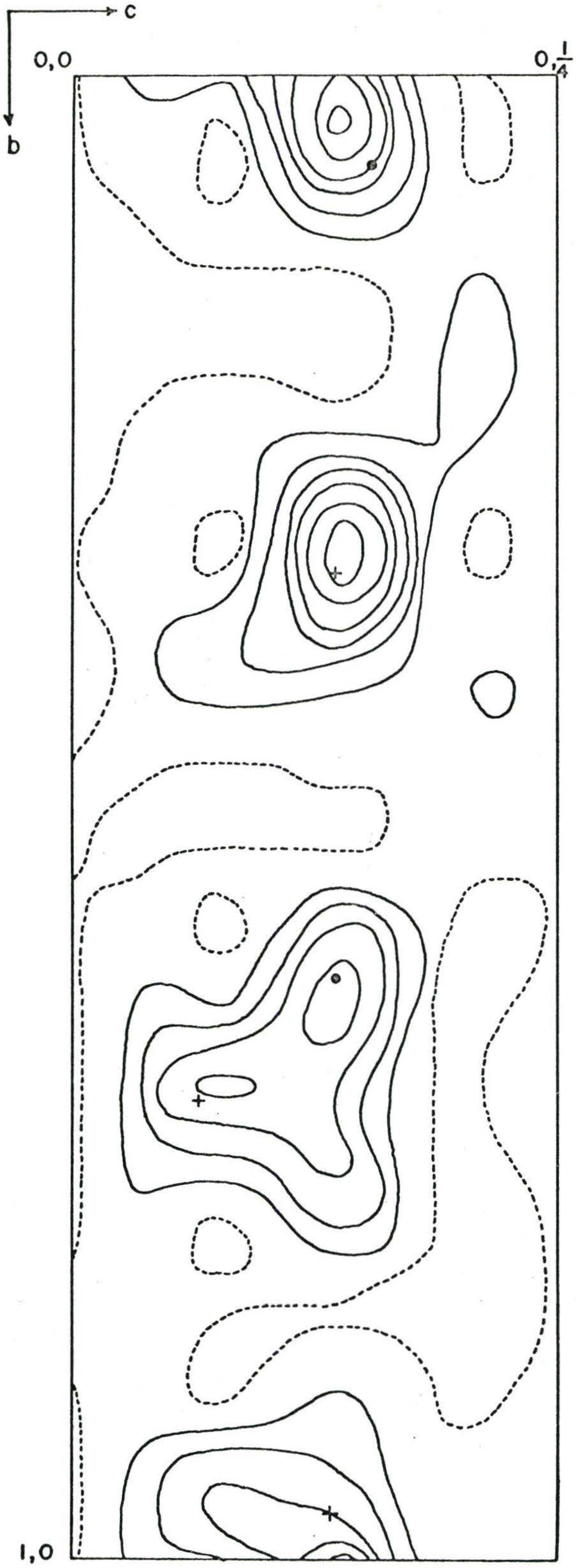
With the sign s(0,0,8) known to be +, two of the sign relations were known to be incorrect. None of the ten other sign relations later found to be incorrect was included among the thirty-two sign relations which were accepted.

To fix the origin of the projection, s(0,3,1) and s(0,4,5) were taken as +. The predicted signs of the $0k\ell$ projection are listed in Table 10.

With sixteen signs expressed in terms of the single letter symbol a, two sets of signs were possible. Because one set (a = +) had all signs positive and was therefore unlikely to be correct, only the electron density map corresponding to a = - was calculated (Figure 2).

Just four of the five heavy atom peaks of the asymmetric unit could be positively located from the electron density map. However, after two cycles of least squares refinement, the sign of the calculated structure factor could safely be accepted as the sign of the observed structure factor for fifteen additional strong reflections where the calculated and observed magnitudes agreed closely. An electron density map calculated with thirty-one reflections showed the fifth peak clearly. The R factor then calculated was 0.28.

Only eleven of the $h0\ell$ reflections could be expressed in terms of two letter symbols (Table 11.) Instead of at-



+ Cu
● As

Figure 2

The electron density map of the $0k\ell$ projection with the final atomic positions superimposed

TABLE 11

Predicted and correct signs of the structure factors in the h0ℓ projection.

h	k	ℓ	Letter Symbol	Predicted Sign	Correct Sign
0	0	12	-ac	+	-
1	0	12	-a	+	+
2	0	4	a	-	-
3	0	8	c	+	+
4	0	0	-c	-	-
5	0	12	ac	-	-
6	0	4	-ac	+	+
-1	0	8	-	-	-
-3	0	4	-a	+	+
-5	0	8	c	+	+
-7	0	4	ac	-	-

tempting a Fourier synthesis with these few signs, the x and z coordinates were found by the pairing of the common y coordinates of the atomic positions found in the hk0 and 0kℓ projections. The calculated R factor for the h0ℓ projection using these coordinates was 0.30.

3. Refinement of the Trial Structure

The approximate y and z coordinates of six of the eight oxygen atoms were found from a sequence of difference syntheses, computed from the equation

$$\rho(\mathrm{obs})-\rho(\mathrm{calc}) = \frac{1}{bc} \sum_{k,\ell} \left\{F(\mathrm{obs})-F(\mathrm{calc})\right\} \cos 2\pi\ (ky+\ell z).$$

During this sequence it became possible to distinguish between the two arsenic peaks and the three somewhat weaker copper peaks.

The x coordinates of the six oxygen atoms found from the difference syntheses, and the x,y,z coordinates of the remaining two oxygens,were found by using the following two postulates about the chemical bond arrangement:

(1) The arsenic atom would be at the centre of a regular tetrahedron, with four oxygens at the corners at a distance of about 1.7 Å.

(2) Groups of one arsenic and two copper atoms bonded to the same oxygen atom would be found in an electrostatically plausible planar arrangement having the arsenic-to-oxygen vector as the right

bisector of the copper-to-copper vector.

The remaining unknown oxygen coordinates were readily found through the use of these postulates, except in the case of two of the oxygens. These were initially assumed to be bonded to the wrong arsenic atom, and so had their postulated x coordinates interchanged.

The Mo Kα radiation data ($h0\ell$ and $hk0$) and the Cu Kα radiation data ($nk\ell$) were at first used independently for the refinement of the atomic parameters; the computer program used for the least squares refinement was designed to accept only one set of scattering curves for each atomic species. To permit refinement of the two sets of data together, the Mo Kα radiation data was converted to "pseudo" Cu Kα radiation data by applying the following reasoning:

The calculated structure factors for molybdenum and copper radiation differ because of anomalous dispersion by the copper and arsenic atoms of the structure. The scattering factor f can be represented as

$$f = f_o + \Delta f' + i\Delta f''$$

(International Tables, 1962, p.213), where $\Delta f'$ and $\Delta f''$ are the real and imaginary dispersion corrections. Setting $\Delta f''' = \Delta f' + (\Delta f''^2/2(f_o + \Delta f'))$, the difference δ_F between the calculated structure factors is given by

$$\delta_F = F_{Cu}^{calc} - F_{Mo}^{calc}$$

$$= \sum_{j=1}^{N} \{f_j + \Delta f_j''(\mathrm{Cu})\}\cos 2\pi\vec{H}\cdot\vec{r}_j - \sum_{j=1}^{N} \{f_j + \Delta f_j''(\mathrm{Mo})\}\cos 2\pi\vec{H}\cdot\vec{r}_j$$

$$= \sum_{j=1}^{N} \{\Delta f_j''(\mathrm{Cu}) - \Delta f_j''(\mathrm{Mo})\} \cos 2\pi \vec{H}\cdot\vec{r}_j.$$

The difference δ_F could be calculated with good accuracy for each reflection since the atomic parameters $\vec{r}_j$ were known to a good approximation when the conversion was made (R = 0.08 for the Mo data, and R = 0.13 for the Cu data).

The assumption was then made that

$$|F^{obs}_{\text{pseudo-Cu}}| - |F^{obs}_{\text{Mo}}| = |F^{calc}_{\text{Cu}}| - |F^{calc}_{\text{Mo}}|.$$

That is,

$$|F^{obs}_{\text{pseudo-Cu}}| = |F^{obs}_{\text{Mo}}| + \delta_F .$$

Table 12 lists the F^{obs}_{Mo} values at the time of the conversion, and the δ_F value corresponding to each. The sign of F^{calc} was used in making the conversion.

With the correction δ_F applied to the h0ℓ and hk0 structure factors, the final refinement of the atomic parameters was made, using all the data with the Cu Kα scattering curves.

After several cycles of least squares refinement, the final unweighted R factor for all 647 reflections was 0.09, while the R factor calculated with $1/\sigma^2$ weighting was 0.11.

TABLE 12. CORRECTIONS APPLIED TO MOK$_\alpha$ OBSERVED STRUCTURE FACTORS.

H	K	L	FOBS	δ	H	K	L	FOBS	δ	H	K	L	FOBS	δ
0	2	0	90.16	-1.46	6	0	0	200.16	18.40	5	0	8	77.06	-11.11
0	4	0	51.14	2.09	6	1	0	37.34	3.41	5	0	10	58.80	-4.40
0	6	0	27.18	-3.82	6	2	0	*19.34	-2.88	5	0	12	59.65	6.56
0	8	0	76.52	8.46	6	3	0	47.21	-1.39	6	0	0	224.91	18.40
0	10	0	41.17	1.33	6	4	0	62.37	-4.60	6	0	2	93.63	9.83
1	1	0	39.89	1.90	6	5	0	25.28	-4.35	6	0	4	205.95	-16.12
1	2	0	80.25	7.38	6	6	0	*22.17	5.92	6	0	6	56.89	-9.06
1	3	0	*11.03	-1.01	6	7	0	*20.05	-1.03	6	0	8	87.46	7.62
1	4	0	41.09	0.17	6	8	0	42.12	-6.15	6	0	10	33.62	-0.31
1	5	0	207.31	-11.34	7	0	0	42.18	5.61	7	0	0	30.34	5.61
1	6	0	*19.09	-1.12	7	1	0	*19.82	0.68	7	0	2	21.35	-6.33
1	7	0	73.48	-4.58	7	2	0	*19.26	-1.18	7	0	4	70.90	-8.21
1	8	0	134.34	10.28	7	3	0	32.43	1.91	7	0	6	16.63	1.11
1	9	0	25.70	1.23	7	4	0	38.55	3.16	7	0	8	30.46	1.92
1	10	0	31.82	-1.13	7	5	0	107.83	10.38	8	0	0	55.99	-9.17
1	11	0	*24.49	-6.07	7	6	0	44.86	5.32	-1	0	2	141.96	-13.21
2	0	0	48.24	0.57	7	7	0	73.68	6.48	-1	0	4	106.01	-8.98
2	1	0	149.34	-7.53	8	0	0	59.25	-9.17	-1	0	6	18.73	8.24
2	2	0	37.13	-2.78	8	1	0	44.59	5.28	-1	0	8	194.56	13.04
2	3	0	111.30	0.16	8	2	0	28.72	-3.08	-1	0	10	*24.06	-0.61
2	4	0	32.71	-2.60	8	3	0	63.42	1.42	-1	0	12	82.45	-6.04
2	5	0	*18.53	4.31	8	4	0	25.88	-1.78	-1	0	14	21.39	3.02
2	6	0	113.75	5.79	0	0	2	*16.88	-2.42	-2	0	2	*18.78	-0.47
2	7	0	19.48	2.91	0	0	6	*15.94	-0.16	-2	0	4	41.13	-10.26
2	8	0	*19.26	-0.29	0	0	8	147.73	-10.39	-2	0	6	45.60	-5.16
2	9	0	94.09	11.06	0	0	10	125.02	9.81	-2	0	8	50.00	8.71
2	10	0	37.25	-5.37	0	0	12	100.96	9.39	-2	0	10	37.45	7.02
2	11	0	*23.45	1.17	0	0	14	117.27	-11.85	-2	0	12	*21.76	0.10
3	0	0	*13.56	-0.43	1	0	2	68.70	7.22	-2	0	14	33.92	0.90
3	1	0	166.61	-11.66	1	0	4	29.44	-0.37	-3	0	2	101.29	3.55
3	2	0	*13.92	-4.02	1	0	6	21.00	-2.99	-3	0	4	166.11	-8.98
3	3	0	15.47	-0.51	1	0	8	53.13	9.78	-3	0	6	119.10	-9.14
3	4	0	60.87	-3.14	1	0	10	71.93	8.91	-3	0	8	94.87	5.33
3	5	0	102.99	-1.15	1	0	12	68.85	-11.57	-3	0	10	41.29	6.07
3	6	0	35.86	-0.66	1	0	14	74.69	-13.35	-3	0	12	57.48	0.19
3	7	0	188.95	-18.61	2	0	0	52.31	0.57	-3	0	14	95.54	4.59
3	8	0	54.10	-2.70	2	0	2	19.08	-3.46	-4	0	2	43.57	0.21
3	9	0	*22.94	1.57	2	0	4	151.18	4.34	-4	0	4	155.39	-10.36
3	10	0	*24.89	0.31	2	0	6	61.63	10.67	-4	0	6	18.55	-5.59
3	11	0	83.81	4.19	2	0	8	34.86	2.59	-4	0	8	17.48	1.11
4	0	0	177.25	9.53	2	0	10	17.23	-7.41	-4	0	10	51.90	1.19
4	1	0	120.50	-8.09	2	0	12	20.60	-8.03	-4	0	12	24.70	3.21
4	2	0	119.57	8.02	2	0	14	74.19	-1.01	-4	0	14	95.54	4.59
4	3	0	66.16	-1.78	3	0	0	*22.09	-0.43	-5	0	2	*12.86	0.56
4	4	0	53.63	6.27	3	0	2	110.47	-3.28	-5	0	4	25.99	5.86
4	5	0	22.86	2.92	3	0	4	194.81	12.28	-5	0	6	*15.78	-2.50
4	6	0	58.48	-3.70	3	0	6	225.65	10.49	-5	0	8	121.39	-14.90
4	7	0	21.57	-1.65	3	0	8	147.14	-11.98	-5	0	10	*16.62	-3.45
4	8	0	35.15	-3.01	3	0	10	149.91	-10.81	-5	0	12	113.31	14.20
4	9	0	27.10	4.65	3	0	12	67.07	6.27	-6	0	2	56.59	-5.91
4	10	0	*22.70	3.48	4	0	0	208.95	9.53	-6	0	4	129.35	-9.33
5	0	0	*25.36	-0.37	4	0	2	36.18	4.69	-6	0	6	114.86	9.04
5	1	0	44.94	5.61	4	0	4	34.76	0.34	-6	0	8	24.48	1.98
5	2	0	*16.90	-6.20	4	0	6	*20.20	0.41	-6	0	10	113.47	-15.28
5	3	0	58.40	4.31	4	0	8	*17.21	-3.36	-7	0	2	64.61	10.51
5	4	0	39.99	0.67	4	0	10	17.70	-5.25	-7	0	4	69.84	3.09
5	5	0	24.42	-2.55	4	0	12	19.09	-2.26	-7	0	6	21.74	-6.02
5	6	0	*19.44	-1.01	5	0	0	*12.82	-0.37	-7	0	8	70.69	-4.21
5	7	0	33.26	4.57	5	0	2	*12.91	5.69	-8	0	2	30.78	5.17
5	8	0	124.49	-10.03	5	0	4	56.07	6.12	-8	0	4	79.40	14.53
5	9	0	29.75	4.50	5	0	6	*21.12	-3.34	-8	0	6	27.84	-0.71
5	10	0	14.37	2.20										

TABLE 13. OBSERVED AND CALCULATED STRUCTURE FACTORS OF $Cu_3(AsO_4)_2$ (x10).
Reflections marked * were unobserved.

		|FØBS|	FCAL
K	L		H = 0
0	2	182	205
0	4	3432	-4038
0	6	*145	-34
0	8	1475	1477
0	10	1065	-1048
0	12	879	-777
0	14	971	883
1	2	475	434
1	3	559	-533
1	4	1270	1342
1	5	207	-216
1	6	616	631
1	7	388	382
1	8	332	-342
1	9	* 95	2
1	10	433	-405
1	11	229	188
1	12	* 89	-92
1	13	401	255
2	0	803	814
2	1	1119	-957
2	2	843	-797
2	3	394	-328
2	4	1052	-1033
2	5	326	-345
2	6	968	1000
2	7	528	-460
2	8	836	840
2	9	161	-150
2	10	209	-216
2	11	624	575
2	12	252	-269
2	13	342	300
3	1	2663	2680
3	2	355	337
3	3	1349	-1311
3	4	* 74	70
3	5	1686	-1664
3	6	599	-635
3	7	877	897
3	8	440	-450
3	9	* 76	-37
3	10	988	911
3	11	841	-757
3	12	559	518
4	0	434	-463
4	1	411	-399
4	2	335	313
4	3	614	607
4	4	349	263
4	5	1531	1543
4	6	588	-546
4	7	330	-375
4	8	583	-589
4	9	881	-857
4	10	615	532
4	11	* 86	107
4	12	579	481
5	1	* 83	40
5	2	* 85	-55
5	3	498	-513
5	4	* 93	84
5	5	*196	-195
5	6	*145	-112
5	7	617	683
5	8	718	-740
5	9	631	618
5	10	464	421
5	11	307	-302
5	12	426	387
6	0	*141	110
6	1	170	180
6	2	300	303
6	3	257	234
6	4	233	244
6	5	491	-495
6	6	573	-565
6	7	663	-661
6	8	182	-152
6	9	571	597
6	10	126	118
6	11	785	708
7	1	288	-330
7	2	438	-502
7	3	712	732
7	4	601	651
7	5	*121	86
7	6	656	708
7	7	930	-979
7	8	580	-629
7	9	169	99
7	10	473	-486
8	0	551	-559
8	1	546	624
8	2	* 88	98
8	3	734	827
8	4	160	191
8	5	597	-629
8	6	213	-242
8	7	465	-491
8	8	280	280
8	9	338	398
9	1	283	-325
9	2	215	222
9	3	511	542
9	4	247	-277
9	5	* 71	62
9	6	364	-390
9	7	458	-556
10	0	312	-306
10	1	* 97	-55
10	2	269	308
K	L		H = 1
0	-2	1186	1131
0	-4	893	874
0	-6	*187	-157
0	-8	1762	-1888
0	-10	*167	-33
0	-12	703	730
0	-14	169	-214
0	2	566	-539
0	4	267	311
0	6	165	171
0	8	399	-458
0	10	580	-538
0	12	526	566
0	14	565	465
1	-2	941	1029
1	-3	875	-1013
1	-4	212	-231
1	-5	*119	107
1	-6	1333	-1510
1	-7	710	777
1	-8	461	-511
1	-9	*150	-90
1	-10	725	696
1	-11	*107	42
1	-12	625	558
1	-13	291	275
1	0	344	-354
1	1	569	469
1	2	256	-226
1	3	1049	-1066
1	4	786	854
1	5	190	-150
1	6	712	699
1	7	1684	1669
1	8	1165	-1124
1	9	455	-469
1	10	330	-377
1	11	1149	-997
1	12	538	434
2	-1	1472	1406
2	-2	1408	-1440
2	-3	943	-978
2	-4	258	301
2	-5	370	-412
2	-6	688	748
2	-7	1862	2031
2	-8	403	-423
2	-9	*214	-129
2	-10	*154	73
2	-11	1367	-1243
2	-12	823	756
2	0	748	-754
2	1	1095	986
2	2	*107	95
2	3	1633	-1626
2	4	719	777
2	5	971	-1008
2	6	683	682
2	7	986	1021
2	8	165	136
2	9	537	538
2	10	561	-510
2	11	254	-241
2	12	311	-229
3	-1	372	381
3	-2	563	549
3	-3	1329	1366
3	-4	573	-552
3	-5	*137	-96
3	-6	266	-279
3	-7	957	-1007
3	-8	857	830
3	-9	539	-521
3	-10	237	190
3	-11	287	248
3	-12	573	-486
3	-13	240	197
3	0	*103	77
3	1	269	-258
3	2	1601	-1535
3	3	426	-409
3	4	* 74	12
3	5	676	693
3	6	1221	1271
3	7	292	-139
3	8	595	-512
3	9	876	-797
3	10	392	-344
3	11	*143	-29
3	12	411	613
4	-1	1336	1255
4	-2	*124	64
4	-3	610	-566
4	-4	196	-173
4	-5	1279	-1359
4	-6	*159	79
4	-7	*168	57
4	-8	375	468
4	-9	321	313
4	-10	*159	-34
4	-11	*146	-79
4	-12	179	-196
4	0	406	404
4	1	* 85	-44
4	2	670	-599
4	3	109	90
4	4	524	-488
4	5	835	800
4	6	448	402
4	7	*175	-62
4	8	299	238
4	9	931	-833
4	10	257	-378
4	11	*163	-90
4	12	328	-228
5	-1	1826	-1738
5	-2	432	439
5	-3	*149	94
5	-4	1184	-1104
5	-5	678	663
5	-6	251	200
5	-7	251	-289
5	-8	947	935
5	-9	*144	-62
5	-10	451	-521
5	-11	451	578
5	-12	437	-599
5	0	1957	1980
5	1	878	-833
5	2	1145	-1097
5	3	1567	1540
5	4	1369	-1338
5	5	874	841
5	6	582	594
5	7	516	-552
5	8	601	663
5	9	*174	53
5	10	395	-247
5	11	457	420
6	-1	1180	1108
6	-2	1435	1393
6	-3	621	633
6	-4	*168	-126
6	-5	798	-758
6	-6	911	-949
6	-7	*144	92
6	-8	*141	121
6	-9	583	646
6	-10	175	369
6	0	*156	-80
6	1	1491	-1480
6	2	798	-736
6	3	1293	-1269
6	4	369	366
6	5	853	840
6	6	434	406
6	7	610	627
6	8	561	-563
6	9	474	-468
6	10	515	-444
6	11	161	119
7	-1	*168	29
7	-2	246	-270
7	-3	549	549
7	-4	716	-698
7	-5	*198	78
7	-6	*196	-58
7	-7	268	-244
7	-8	230	228
7	0	629	608
7	1	630	-595
7	2	501	461
7	3	476	477
7	4	*126	22
7	5	*126	43
7	6	124	127
7	7	584	-647
7	8	214	-161
7	9	*135	-36
7	10	230	-192
8	-1	740	746
8	-2	399	-361
8	-3	*174	98
8	-4	342	349
8	-5	725	-714
8	0	1249	-1217
8	1	*168	-12
8	2	333	314
8	3	629	-629
8	4	1118	1058
8	5	*154	85
8	6	*146	-109
8	7	501	498
8	8	294	-276
9	-1	754	753
9	-2	507	479
9	-3	367	364
9	-4	290	290
9	-5	812	-883
9	-6	175	-166
9	0	220	-215
9	1	454	-430
9	2	635	-629
9	3	372	-362
9	4	441	-429
9	5	442	428
9	6	230	235
10	-1	225	-211
10	-2	*155	48
10	-3	*104	-66
10	-4	421	440
10	0	307	-295
10	1	365	359
10	2	374	376
10	3	318	320
10	4	291	309
11	0	*166	-31
K	L		H = 2
0	-2	*168	71
0	-4	237	202
0	-6	410	414

TABLE 13 (continued). STRUCTURE FACTORS OF $Cu_3(AsO_4)_2$.

		|FØBS|	FCAL
0	-8	468	-495
0	-10	280	-274
0	-12	*201	74
0	-14	304	-336
0	0	487	483
0	2	143	143
0	4	1352	-1287
0	6	469	-510
0	8	345	415
0	10	90	96
0	12	115	150
0	14	674	599
1	-2	1083	-981
1	-3	1106	-1077
1	-4	632	-595
1	-5	1666	1552
1	-6	507	446
1	-7	659	597
1	-8	*148	-5
1	-9	1277	-1004
1	-10	893	-718
1	-11	*127	8
1	-12	290	260
1	0	1283	1504
1	1	2154	2135
1	2	790	812
1	3	627	742
1	4	478	-548
1	5	1198	-1430
1	6	513	-593
1	7	*139	-32
1	8	*150	83
1	9	987	931
1	10	*148	-124
1	11	139	-170
2	-1	293	200
2	-2	1567	-1394
2	-3	844	785
2	-4	509	-481
2	-5	174	-172
2	-6	1202	1145
2	-7	198	-167
2	-8	*150	15
2	-9	303	176
2	-10	389	-354
2	-11	169	107
2	-12	254	163
2	-13	260	-88
2	0	359	332
2	1	1236	-1282
2	2	585	597
2	3	673	-715
2	4	435	-461
2	5	1259	1454
2	6	*158	-31
2	7	369	473
2	8	951	1048
2	9	676	-736
2	10	208	-218
2	11	223	181
2	12	649	-643
3	-1	241	-184
3	-2	839	-730
3	-3	651	561
3	-4	870	-804
3	-5	1026	919
3	-6	1257	1169
3	-7	454	-452
3	-8	740	666
3	-9	560	-458
3	-10	1016	-812
3	-11	172	-134
3	-12	250	-203
3	0	1130	1133
3	1	320	-255
3	2	595	-491
3	3	*130	-72
3	4	863	-874
3	5	528	-589
3	6	340	366
3	7	256	-306
3	8	266	280
3	9	118	153
3	10	172	-184
3	11	337	400
4	-1	*220	71
4	-2	1335	-1140
4	-3	800	-684
4	-4	*136	92
4	-5	206	79
4	-6	1209	1070
4	-7	319	250
4	-8	223	-177
4	-9	1173	-964
4	-10	740	-572
4	0	304	309
4	1	1109	966
4	2	1407	1304
4	3	644	580
4	4	*127	-80
4	5	192	-206
4	6	1086	-1218
4	7	259	-253
4	8	*187	167
4	9	702	-764
4	10	535	574
5	-1	349	292
5	-2	724	670
5	-3	855	-773
5	-4	242	-208
5	-5	1121	-956
5	-6	*185	28
5	-7	512	585
5	-8	*190	-16
5	-9	1009	771
5	-10	*181	18
5	-11	314	-248
5	0	*128	-97
5	1	119	-99
5	2	1347	-1264
5	3	325	-331
5	4	297	308
5	5	596	603
5	6	1148	1329
5	7	539	635
5	8	357	-404
5	9	163	-174
5	10	472	-606
6	-1	*119	-70
6	-2	465	423
6	-3	707	-661
6	-4	1202	1081
6	-5	485	436
6	-6	*202	-6
6	-7	1203	1120
6	-8	427	-446
6	-9	439	-362
6	-10	450	-363
6	0	977	-987
6	1	*112	115
6	2	*114	-113
6	3	617	-670
6	4	510	533
6	5	307	-384
6	6	429	-407
6	7	518	648
6	8	647	-732
6	9	*103	104
6	10	594	716
7	-1	483	448
7	-2	* 90	-80
7	-3	250	240
7	-4	491	466
7	-5	259	-223
7	-6	272	-219
7	-7	403	399
7	-8	891	-807
7	0	150	-158
7	1	141	-138
7	2	367	362
7	3	119	-172
7	4	825	871
7	5	* 83	49
7	6	143	-183
7	7	220	-328
7	8	852	-978
8	-1	* 87	64
8	-2	348	329
8	-3	*122	73
8	-4	871	-825
8	-5	* 81	-81
8	-6	698	-674
8	-7	* 70	17
8	-8	1030	876
8	0	* 87	-45
8	1	* 87	-125
8	2	510	-560
8	3	*121	-102
8	4	450	461
8	5	292	353
8	6	602	754
8	7	*120	70
8	8	242	-264
9	-1	*147	-101
9	-2	252	-240
9	-3	464	488
9	-4	617	611
9	-5	264	260
9	-6	308	319
9	0	642	-659
9	1	545	-637
9	2	194	-238
9	3	483	490
9	4	172	165
10	-1	349	-374
10	-2	728	816
10	0	243	232
10	1	248	-264
10	2	654	-778
11	0	*201	-79
K	L		H = 3
0	-2	900	-856
0	-4	1447	1454
0	-6	1013	1030
0	-8	824	-938
0	-10	324	-432
0	-12	531	496
0	-14	179	-195
0	0	*126	32
0	2	987	1003
0	4	1681	-1569
0	6	1982	-2163
0	8	1245	1406
0	10	1281	1203
0	12	560	-534
1	0	1402	1647
2	0	* 89	-40
3	0	135	152
4	0	522	517
5	0	922	898
6	0	318	281
7	0	1542	1645
8	0	465	488
9	0	*193	-128
10	0	*228	69
11	0	720	-634
K	L		H = 4
0	-2	403	405
0	-4	1336	1228
0	-6	119	162
0	-8	150	-119
0	-10	489	516
0	-12	197	-281
0	-14	837	-693
0	0	1685	-1698
0	2	290	-290
0	4	323	414
0	6	*182	-66
0	8	*127	-0
0	10	114	73
0	12	155	175
1	0	1017	1120
2	0	1010	-1096
3	0	582	626
4	0	428	-396
5	0	180	-152
6	0	495	471
7	0	210	-174
8	0	290	277
9	0	203	-234
10	0	*174	-25
K	L		H = 5
0	-2	*113	48
0	-4	185	-260
0	-6	*168	-104
0	-8	981	987
0	-10	*121	140
0	-12	913	-769
0	0	*121	-62
0	2	*171	72
0	4	460	-528
0	6	*225	-78
0	8	607	623
0	10	501	547
0	12	489	-497
1	0	356	-407
2	0	* 96	-80
3	0	489	-502
4	0	355	-326
5	0	197	178
6	0	*166	90
7	0	259	-157
8	0	1036	1091
9	0	228	-170
10	0	150	157
K	L		H = 6
0	-2	466	523
0	-4	1105	1039
0	-6	974	-926
0	-8	207	-239
0	-10	904	791
0	0	1645	-1677
0	2	771	-766
0	4	1748	1616
0	6	440	399
0	8	735	-796
0	10	306	318
1	0	307	-300
2	0	*148	33
3	0	440	-423
4	0	523	521
5	0	189	121
6	0	*254	31
7	0	*190	-113
8	0	325	252
K	L		H = 7
0	-2	498	-448
0	-4	614	-641
0	-6	144	176
0	-8	612	644
0	0	227	-245
0	2	138	93
0	4	577	561
0	6	163	199
0	8	262	-296
1	0	*173	-81
2	0	*163	70
3	0	276	-227
4	0	320	-240
5	0	882	-720
6	0	358	-299
7	0	608	-503
K	L		H = 8
0	-2	235	-299
0	-4	597	-650
0	-6	249	256
0	0	431	437
1	0	355	-317
2	0	232	191
3	0	561	-512
4	0	218	190

The values of σ were taken as one-tenth of the F_H value for those reflections having F_H greater than 40, and as one-third of the F_H value for all weaker reflections.

Table 13 lists the observed and calculated structure factors of $Cu_3(AsO_4)_2$.

4. Description of the Structure

Table 14 lists the final atomic coordinates in the asymmetric unit and the isotropic temperature factors for each atom, together with their estimated standard deviations. Bond lengths and bond angles are listed in Table 15.

Figure 3 illustrates the structure of $Cu_3(AsO_4)_2$, projected along the a axis. The copper atoms are represented by the dark circles, the arsenic atoms by the double circles, and the oxygen atoms by the open circles. The illustration is intended to represent one unit cell about the point (1/2,0,0), and bonds to atoms outside this unit cell are shown as broken bonds.

The arsenic of the AsO_4 groups shows the usual tetrahedral coordination. The average As-O bond length between As(1) and O(1), O(3), O(5), and O(7) is 1.68 Å, while the average between As(2) and O(2), O(4), O(6), and O(8) is 1.69 Å. The tetrahedral angles subtended by As(1) range from 102.9° to 116.2°, a larger variation than for As(2) where the range is from 105.6° to 113.8°.

TABLE 14

Atomic Coordinates and Isotropic Temperature Factors of $Cu_3(AsO_4)_2$

Atom	Atomic Coordinates			Temperature Factor
	x	y	z	
Cu(1)	0.2415(8)	0.1641(4)	0.6322(3)	1.01(8)
Cu(2)	0.6162(9)	0.0211(4)	0.8778(4)	1.25(8)
Cu(3)	0.9082(8)	0.1900(4)	0.4315(3)	1.03(8)
As(1)	0.4143(6)	0.1134(3)	0.3680(2)	0.77(6)
As(2)	0.8960(6)	0.0602(3)	0.1506(2)	0.78(6)
O(1)	0.6065(33)	0.2381(20)	0.4188(14)	0.79(27)
O(2)	-0.0322(35)	0.2403(21)	0.1061(13)	0.86(28)
O(3)	0.2076(38)	0.1311(21)	0.4568(15)	1.21(32)
O(4)	0.0858(40)	-0.0731(21)	0.1207(15)	1.33(35)
O(5)	0.3377(37)	0.1539(19)	0.2286(14)	0.84(28)
O(6)	0.6707(43)	-0.0050(23)	0.0840(17)	1.47(34)
O(7)	0.4815(38)	-0.0706(17)	0.3602(14)	0.82(29)
O(8)	-0.1314(41)	0.0526(19)	0.2977(16)	1.25(31)

TABLE 15

Bond Lengths and Bond Angles in $Cu_3(AsO_4)_2$

In the Cu(1) trigonal bipyramid:

	Bond lengths	
Cu(1)	- O(3)	2.01(3) Å
	- O(5)	2.00(4)
	- O(8)	2.16(4)
	- O(2)	1.93(4)
	- O(7)	1.93(4)

Angles (average error is 1.6°)			
O(3)-	Cu(1)	-O(5)	132.2°
O(5)-		-O(8)	125.3
O(8)-		-O(3)	102.5
O(2)-		-O(7)	173.7
O(2)-		-O(3)	81.1
O(2)-		-O(5)	90.1
O(2)-		-O(8)	97.4
O(7)-		-O(3)	92.8
O(7)-		-O(5)	92.7
O(7)-		-O(8)	85.6

In the Cu(2) octahedron:

	Bond lengths	
Cu(2)	- O(1)	2.05(3) Å
	- O(4)	1.92(4)
	-O(5)	2.03(3)
	-O(6)II	1.89(5)
	-O(6)I	2.37(3)
	-O(7)	2.77(3)

Angles (average error is 1.5°)			
O(1)-	Cu(2)	-O(4)	81.4°
O(4)-		-O(5)	89.5
O(5)-		-O(6)II	101.5
O(6)II-		-O(1)	91.7
O(6)I-		-O(7)	175.4
O(6)I-		-O(1)	84.8
O(6)I-		-O(4)	84.7
O(6)I-		-O(5)	117.5
O(6)I-		-O(6)II	82.4
O(7)-		-O(1)	95.4
O(7)-		-O(4)	99.9

TABLE 15 (Continued)

Bond Lengths and Bond Angles in $Cu_3(AsO_4)_2$

O(7)-Cu(2)-O(5)	63.3°
O(7)- -O(6)II	93.0
O(1)- -O(5)	155.2
O(4)- -O(6)II	165.9

In the Cu(3) trigonal bipyramid:

Bond lengths		Angles (average error is 1.6°)	
Cu(3)-O(2)	2.09(3) Å	O(2)-Cu(3)-O(4)	88.9°
-O(4)	2.13(3)	O(4)- -O(8)	112.0
-O(8)	1.93(3)	O(8)- -O(2)	158.9
-O(1)	1.95(3)	O(1)- -O(3)	175.0
-O(3)	1.97(4)	O(1) -O(2)	98.8
		O(1)- -O(4)	78.7
		O(1)- -O(8)	88.4
		O(3)- -O(2)	78.2
		O(3)- -O(4)	105.1
		O(3)- -O(8)	93.2

In the As(1) tetrahedron:

Bond lengths		Angles (average error is 1.8°)	
As(1)-O(1)	1.71(4) Å	O(1)-As(1)-O(3)	107.4°
-O(3)	1.69(4)	O(1)- -O(5)	111.4
-O(5)	1.67(3)	O(1)- -O(7)	116.2
-O(7)	1.65(3)	O(3)- -O(5)	109.8
		O(3)- -O(7)	109.1
		O(5)- -O(7)	102.9

TABLE 15 (Continued)

Bond Lengths and Bond Angles in $Cu_3(AsO_4)_2$

In the As(2) tetrahedron

Bond lengths			Angles (average error is 1.8°)	
As(2)	- O(2)	1.70(4) Å	O(2)-As(1)-O(4)	111.2°
	- O(4)	1.71(2)	O(2)- -O(6)	113.8
	- O(6)	1.68(4)	O(2)- -O(8)	111.4
	- O(8)	1.68(3)	O(4)- -O(6)	106.1
			O(4)- -O(8)	105.7
			O(6)- -O(8)	108.2

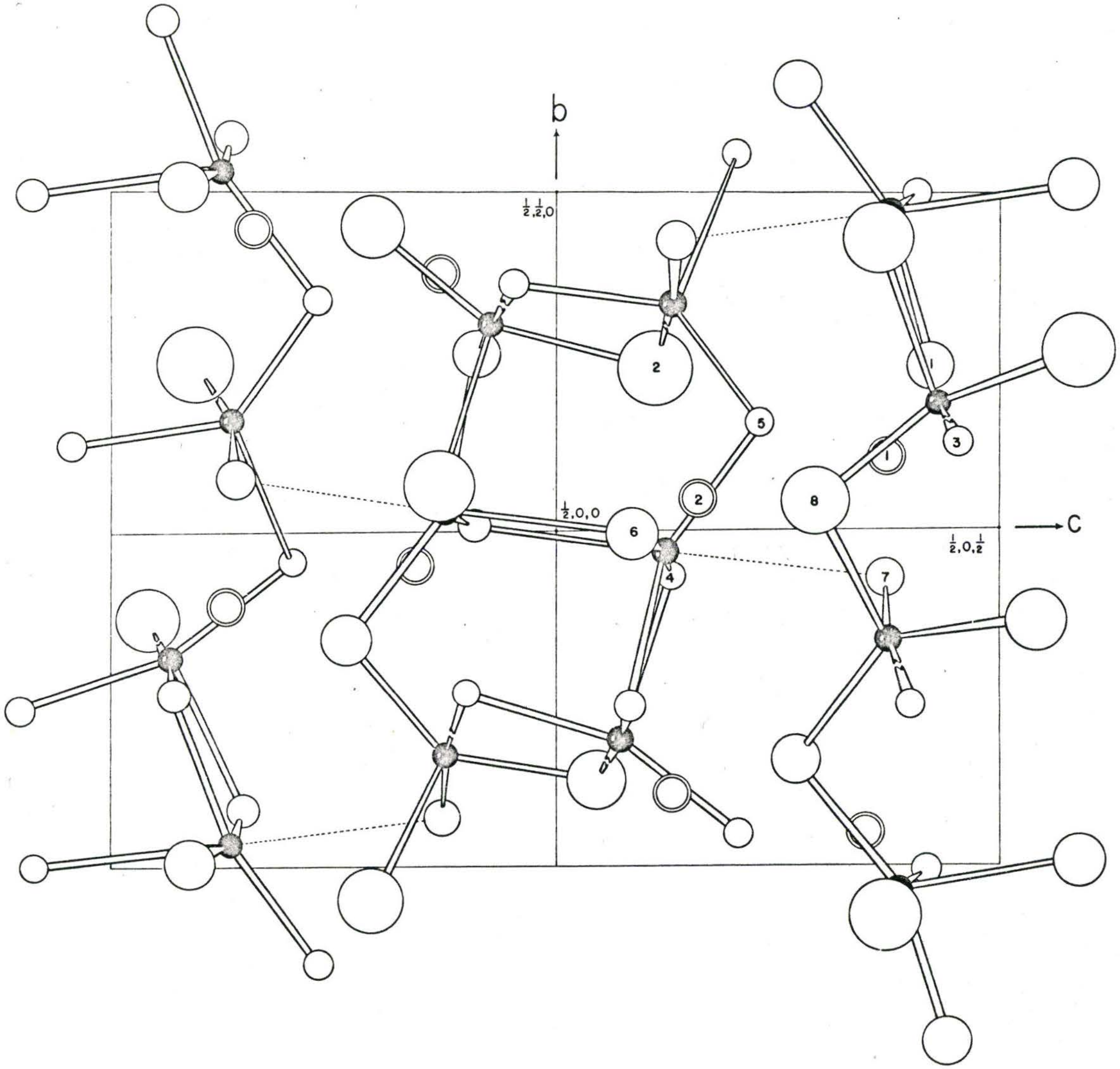


Figure 3

The structure of $Cu_3(AsO_4)_2$ projected down the x-axis

The Cu(1) atom is bound to five oxygen atoms in a fairly regular trigonal bipyramidal arrangement. The equatorial oxygens O(3), O(5), and O(8) are at an average distance of 2.08 Å from the Cu(1), while the axial oxygens O(2) and O(7) are at a distance of 1.93 Å.

The Cu(2) atom is surrounded by six oxygen atoms in a distorted octahedral arrangement. The equatorial oxygens O(1), O(4), O(5), and O(6) average 1.97 Å from Cu(2). One axial oxygen atom, O(6), is at a distance of 2.37 Å; a long bond of 2.77 Å from the copper atom to O(7) completes the octahedron.

The Cu(3) atom is bound to five oxygens in a trigonal bipyramidal arrangement less regular than that about Cu(1). The equatorial oxygens O(2), O(4), and O(8) are at an average distance of 2.05 Å from the copper atom with O-Cu-O angles ranging from 88.9° to 158.9° instead of the ideal value of 120° for the angles in the plane. The axial oxygens O(1) and O(3) average 1.96 Å from the Cu(3) atom.

The framework of $Cu_3(AsO_4)_2$ consists of sheets of copper coordination polyhedra along the a and b axes, connected together along the c direction by discrete AsO_4 tetrahedra and by a long (2.77 Å) Cu-O bond. The AsO_4 tetrahedra share three oxygens with one sheet, and one with the adjacent sheet.

The sheets themselves consist of zig-zag chains formed by cations which edge and corner-share oxygen atoms. In alternate sheets the chains descend and climb the a axis. In each sheet a chain is bound to the one below by O(5) atoms corner-shared between a Cu(1) cation of one chain and a Cu(2) cation of the chain below.

As can be seen from Figure 3, in each chain equivalent Cu(2) cations edge-share equivalent O(6) atoms across a centre of symmetry. The Cu(2) cations each have a long bond to an O(7) in the adjacent sheet, and each corner-share an O(5) with a Cu(1) in an adjacent chain. The Cu(2) cations also edge-share O(4) and O(1) atoms with Cu(3).

Continuing the chain, the Cu(3) cation in turn edge-shares O(3) and O(2) atoms with one Cu(1) cation and corner-shares an O(8) atom with another Cu(1) cation, related to the first by a centre of symmetry. The O(7) atom is strongly bonded only to Cu(1), and does not link cations of the same chain.

The interatomic angles of the arsenic, oxygen, and two copper groups (which had been expected to be planar) are listed in Table 16. Except for the group containing the long Cu(2) - O(7) bond, the sum of the angles is close to 360°.

TABLE 16

Interatomic Angles of the Arsenic, Oxygen and Two Copper Groups

Atoms	Angle (degrees)	Sum
Cu(2)-O(1)-Cu(3)	100.7	
Cu(2)-O(1)-As(1)	124.2	
As(1)-O(1)-Cu(3)	125.1	
		350.0
Cu(1)-O(2)-Cu(3)	98.7	
Cu(1)-O(2)-As(2)	126.4	
As(2)-O(2)-Cu(3)	120.1	
		345.2
Cu(1)-O(3)-Cu(3)	100.2	
Cu(1)-O(3)-As(1)	123.0	
As(1)-O(3)-Cu(3)	134.3	
		357.5
Cu(2)-O(4)-Cu(3)	99.0	
Cu(2)-O(4)-As(2)	124.8	
As(2)-O(4)-Cu(3)	136.2	
		360.0
Cu(1)-O(5)-Cu(2)	110.1	
Cu(1)-O(5)-As(1)	139.1	
As(1)-O(5)-Cu(2)	110.5	
		359.7
Cu(2)-O(6)-Cu(2)	97.6	
Cu(2)-O(6)-As(2)	119.2	
As(2)-O(6)-Cu(2)	137.8	
		354.6
Cu(1)-O(7)-Cu(2)	105.4	
Cu(1)-O(7)-As(1)	129.7	
As(1)-O(7)-Cu(2)	83.2	
		318.3
Cu(1)-O(8)-Cu(3)	106.2	
Cu(1)-O(8)-As(2)	116.3	
As(2)-O(8)-Cu(3)	137.5	
		360.0

5. Arsenate Structures

The structure of $Cu_3(AsO_4)_2$ is similar in several respects to that of the mineral clinoclase, $Cu_3AsO_4(OH)_3$ (Ghose et al., 1965), which also has space group symmetry $P2_1/c$.

While both structures show a cross-linking of cation chains to form a sheet structure, the environment of the cations of the two structures differs considerably. Two of the three copper ions of clinoclase are octahedrally coordinated, each with one medium length axial bond and one long axial bond (2.30 Å and 2.99 Å for one cation and 2.31 Å and 2.84 Å for the other). The single cation of $Cu_3(AsO_4)_2$ which shows octahedral coordination, Cu(2), has axial bond lengths of 2.37 Å and 2.77 Å.

The remaining copper ion of clinoclase shows five-fold coordination, with the oxygen atoms in a distorted tetragonal pyramidal arrangement. The two cations of $Cu_3(AsO_4)_2$ which are five-fold coordinated have the oxygen atoms arranged about them to form a trigonal bipyramid.

In clinoclase the AsO_4 groups are found in the usual tetrahedral arrangement, although the tetrahedron deviates somewhat from regularity. A difference in length among the As-O bonds has been attributed (Ghose et al., 1965) to the fact that the shorter bonds are of higher bond order as the oxygen is less strongly bonded to a second cation.

However, the difference between the two "long" As-O bonds, 1.746 Å and 1.716 Å, is nearly as large as the difference between the average of the "short" As-O bonds, 1.678 Å, and the "long" 1.716 Å bond. In $Cu_3(AsO_4)_2$, O(7) has a "short" 1.647 Å As-O bond. O(7) is strongly bonded to only one copper ion, and the same phenomena of varying bond orders within the AsO_4 group may be occurring.

The mineral stranskiite, $CuZn_2(AsO_4)_2$ has a molecular formula similar to that of $Cu_3(AsO_4)_2$, but the two structures differ considerably (Plieth and Sanger, 1965). Stranskiite is triclinic, with space group symmetry $P\bar{1}$. The copper ion is located at a centre of symmetry, and is octahedrally coordinated, having the axial oxygens at a distance of 2.96 Å. The zinc ions show five-fold coordination, with an average Zn-O distance of 2.05 Å.

The AsO_4 groups again show a tetrahedral arrangement, but with longer As-O bond lengths (ranging from 1.74 Å to 1.78 Å) than are found in either clinoclase or copper ortho-arsenate. The longest of the As-O bonds in stranskiite is formed with an oxygen which is corner-shared between a zinc ion and the copper ion. However, the Cu-O bond is long (2.96 Å), and so the oxygen is strongly bound only to the Zn cation. This distinctly differs from the situation in both copper ortho-arsenate and clinoclase, where an oxygen bound strongly to only one cation seems to form the shortest As-O bond, not the longest as in stranskiite,and may reflect a primitive stage of refinement of the structure of stranskiite.

Stranskiite has one pair of the equatorial oxygen atoms about the copper ion bonding to each zinc cation. The zinc cations in turn edge-share oxygen atoms across a centre of symmetry, thus forming a sheet structure with the cations in a centred, planar array having a Cu ion at the centre and paired Zn ions at four corners. The AsO_4 groups link the cation sheet structures, with two oxygen atoms lying in each sheet.

Only a few other arsenate structures have been determined. Ag_3AsO_4 has an average As-O bond length of 1.75 Å, while in KH_2AsO_4 the average bond length is 1.74 Å (Helmholz and Levine, 1942). $Mg_2As_2O_7$ has terminal As-O bonds averaging 1.64 Å and internal (As-O-As) bonds averaging 1.68 Å (Calvo and Neelakantan, 1967). In $NaAsO_3$ the terminal bond lengths are 1.68 Å and the internal bond lengths 1.77 Å (Liebau, 1956).

It thus appears that the arsenates with the more electro-positive elements have larger average As-O bond lengths than is the case for the less electro-positive divalent metal ions.

IV. EVALUATION OF THE CORRELATION METHOD

1. The Patterson Analysis of $Cu_3(AsO_4)_2$.

An attempt was made to evaluate the relative usefulness of the correlation method as a means of solving a crystal structure. A definitive comparison of the method with the traditional use of Patterson functions is not possible, although it seems clear that the application of the correlation method requires a minimum of experience on the part of the crystallographer.

A criterion for the ease with which a structure might be expected to yield to direct methods was given by Woolfson (1961,p.42) who shows that a structure having fewer than sixteen equal atoms (or an equivalent number of non-equal atoms) should be soluble. In $Cu_3(AsO_4)_2$ there are twenty heavy scatterers in the unit cell. Using this number as the number of "equal" atoms, Woolfson's criterion implies that $Cu_3(AsO_4)_2$ has a structure approaching the limit in complexity which direct methods might reasonably be expected to solve.

The Patterson function is a three-dimensional radial distribution giving the vectorial separation of electron density within a crystal. The Patterson function is defined by

$$P(\vec{U}) = V \int \rho(\vec{r})\, \rho(\vec{r} + \vec{U})\, dV$$

where $\vec{U}$ and $\vec{r}$ are vectors in the unit cell (Patterson, 1934). Because the value of the integral (for a given $\vec{U}$) is small when the electron densities at the positions $\vec{r}$ and $\vec{r} + \vec{U}$ are small, a large $P(\vec{U})$ value implies that there are atoms in the unit cell which are separated by the vector $\vec{U}$. From the information which the Patterson function $P(\vec{U})$ yields about interatomic vectors, it is sometimes possible to derive the atomic positions.

$P(\vec{U})$ can be written

$$P(u,v,w) = \frac{1}{V} \sum_{h,k,\ell} |F_{hk\ell}|^2 \cos 2\pi\, (hu + kv + \ell w)$$

where u, v, and w are the components of $\vec{U}$. The $|F_{hk\ell}|^2$ coefficients are known since they are directly related to the measured intensity values.

Fourier syntheses can also be devised using data from the n^th^ level of the reciprocal lattice only. For example, the function

$$P_n\, (v,w) = \frac{1}{bc} \sum_{k,\ell} \left|F_{nk\ell}\right|^2 \cos 2\pi\, (kv + \ell w)$$

(a "generalized Patterson projection") can be used in conjunction with $P_o(v,w)$ to provide a measure of the u coordinate of the Patterson peak (Clews and Cochran, 1949).

The three Patterson projections were computed for $Cu_3(AsO_4)_2$. In each of these there was considerable superposition of peaks. The h0ℓ Patterson projection indicated that the heavy scatterers would be found separated in the c direction by 1/4 of the unit cell length. The structure as determined by the correlation method did, in fact, show that the heavy scatterers were located at positions $\frac{1}{8}, \frac{3}{8}, \frac{5}{8}$, and $\frac{7}{8}$ of the c axis.

The first and second layer generalized Patterson functions $P_1(v,w)$ and $P_2(v,w)$ were also computed, but again because of much overlap the projections could not be readily solved. It is of course possible that higher layer data might have led to a solution of the structure by the Patterson method, but the intensity data available proved sufficient to permit a successful correlation analysis of the structure.

2. The Correlation Analysis of β-$Zn_3(PO_4)_2$ and $(Zn,Cd)_3(PO_4)_2$.

An attempt was made to apply the correlation method to β-$Zn_3(PO_4)_2$ and $(Zn,Cd_3)(PO_4)_2$, two phosphate compounds whose structures had been determined by Patterson functions. Both compounds had molecular formulas of the same $M_3(XO_4)_2$ type (with the XO_4^{-n} group being tetrahedral) as $Cu_3(AsO_4)_2$.

Unitary structure factors were calculated for both compounds from the final F_H values, which were correctly scaled since the structures were known. Sign relations and then correlation equations were computed.

Table 17 summarizes the results of the correlation method for the two compounds.

TABLE 17

Results of a Correlation Analysis of β-$Zn_3(PO_4)_2$ and $(Zn,Cd)_3(PO_4)_2$

Structure	Projection	Number of Signs Predicted	Number of Letter Symbols Used	Results
β-$Zn_3(PO_4)_2$	hk0	32	1	29 correct signs
	h0ℓ	17	2	16 correct signs
	0kℓ	37	1	20 correct signs
$(Zn,Cd)_3(PO_4)_2$				
	hk0	20	1	all signs correct
	h0ℓ	17	2	all signs correct
	0kℓ	18	2	12 correct signs

The h0ℓ projection of β-$Zn_3(PO_4)_2$ had been easily solved from the Patterson projection (Stephens and Calvo, 1967); but the correlation method predicted four possible electron density distributions. These four were computed from only seventeen structure factors, and the correct solution might not have been obvious. There were, however, many possible solutions to the hk0 Patterson projection, whereas one of only two solutions obtained by the correlation method had twenty-nine of thirty-two signs correct. The proper electron density map could probably have been recognized from R factor calculations. The 0kℓ projection resisted solution by either method.

For β-$Zn_3(PO_4)_2$, the use of the correlation and the Patterson methods in conjunction would probably have led to the solution of the structure more quickly than the independent use of either.

The graftonite-like structure $(Zn,Cd)_3(PO_4)_2$ was not soluble in projection, but instead was solved with generalized hkn Patterson functions (Stephens, 1967). The correlation method predicted the correct set of signs among the possible sets for each of the hk0 and h0ℓ projections. It seems likely that both correct solutions would have been recognizable from among the electron density maps, and from the subsequent R factor calculations.

For this compound, both the Patterson and the correlation methods would probably have worked equally well.

According to Woolfson's criterion, one might have expected both the β-$Zn_3(PO_4)_2$ and $(Zn,Cd)_3(PO_4)_2$ structures to yield to direct methods. The β-$Zn_3(PO_4)_2$ unit cell contains twelve heavy scatterers, while the $(Zn,Cd)_3(PO_4)_2$ has the equivalent of about ten equal atoms in the unit cell. Both these numbers are fewer than the limit of sixteen which Woolfson uses as a criterion for solubility of structures by direct means.

3. The Correlation Analysis of α-$Mg_2P_2O_7$

The structure of α-$Mg_2P_2O_7$ was determined after the structure of a higher temperature phase was known (Calvo, 1967). In passing from the high temperature phase to the low temperature phase, the $\underline{a}$ and $\underline{c}$ axes of the monoclinic cell doubled, and weak reflections were introduced. The correlation method would have been of particular value in the structure determination of the α-phase if it were able to determine the signs of the reflections which were unique to the α-phase, and not observed in the higher symmetry high temperature phase.

The correlation method is designed to express as many signs as possible in terms of a few letter symbols. Because signs known from the high temperature form of $Mg_2P_2O_7$ might be included among the signs of the low temperature form for which letter symbols would be assigned, it was hoped that the number of possible sets of signs for the unknown α-phase might be reduced.

Unfortunately, because of the very nature of the sign relation which requires the sum of the indices of two of the signs to be equal to the indices of the third, few of the signs unique to the low temperature phase were involved in the sign relations. As a result, few of these unique signs could be assigned letter symbols.

The correlation method did predict twenty-two correct signs in the hk0 projection, for example (Table 18), but none of these signs was unique to the low temperature α-phase.

The actual structure determination was made by postulating trial structures based upon the known β-phase.

TABLE 18

Predicted and Correct Signs of the Structure Factors in the hk0 Projection of α-$Mg_2P_2O_7$

h	k	ℓ	$\lvert U_H \rvert$	Letter Symbol	Predicted Sign	Correct Sign
2	5	0	.27	b	+	-
2	11	0	.25	-b	-	+
4	0	0	.18	-a	+	+
4	2	0	.24	a	-	-
4	6	0	.19	a	-	-
4	8	0	.41	-a	+	+
4	10	0	.16	a	-	+
6	1	0	.18	-ab	+	+
6	3	0	.19	ab	-	+
6	5	0	.28	-ab	+	+
6	7	0	.20	ab	-	-
8	0	0	.28	+	+	+
8	6	0	.17	-	-	-
8	8	0	.22	+	+	-
10	1	0	.34	b	+	+
10	3	0	.39	-b	-	-
10	5	0	.15	b	+	+
10	7	0	.25	-b	-	-
10	9	0	.24	b	+	+
14	1	0	.28	-ab	+	+
14	3	0	.28	ab	-	-
14	5	0	.31	-ab	+	+
14	7	0	.27	ab	-	-
16	4	0	.15	a	-	-
20	0	0	.19	-	-	-
24	0	0	.25	a	-	-
24	2	0	.17	-a	+	+

V. SUMMARY

The structure of $Cu_3(AsO_4)_2$ was determined through the use of the deVries correlation method. The crystal has space group symmetry $P2_1/c$ with the unit cell dimensions $\underline{a} = 6.327(5)$ Å; $\underline{b} = 8.642(5)$ Å; $\underline{c} = 11.313(5)$ Å; $\beta = 92.04(4)$. Two of the copper atoms are found in trigonal bipyramidal arrangements while the third copper atom is octahedrally coordinated. The arsenate groups are somewhat distorted tetrahedra.

The correlation method used in the structure determination process minimizes the time and effort involved between the acquiring of scaled structure factors and the production of the electron density maps of the structure in projection. The sequence of three computer programs (which calculate the unitary structure factors, the sign relations, and the correlation equations) requires a minimum of personal intervention. The assignment of letter symbols is a mathematical problem, and could probably be programmed for the computer as well, and the final step of computing the possible electron density maps is again performed by the computer.

The correlation method can be applied with speed and simplicity during the preliminary stages of a structure determination with the possibility that useful information might be gained. Its use, in conjunction with other methods, could speed the structure determination process considerably.

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