char predict an intensity of diffuse scattering along the rekha $[1\bar{1}0]_{220}$ some 40% greater than was observed during a careful search for this large intensity.

We must note further that the elastic constants as measured from diffuse-scattering experiments predict a much smaller difference between the velocities of the two transverse waves travelling along a diad axis. This is consistent with the observations of Chandrasekharan (1950) that there is only one transverse Brillouin component in the light scattered by waves travelling in that direction.

It may therefore be concluded, concerning the values of the elastic constants published by Bhagavantam & Bhimasenachar, that c_{44} is acceptable, that c_{11} is probably too low, as it differs by more than the experimental value from our value, and that c_{12} is too high.

References

Adams, L. H. (1921). *J. Wash. Acad. Sci.* **11**, 45.

Bhagavantam, S. & Bhimasenachar, J. (1946). *Proc. Roy. Soc.* A, **187**, 381.

Brillouin, L. (1922). *Ann. Phys., Paris,* **17**, 88.

Chandrasekharan, V. (1950). *Proc. Indian Acad. Sci.* A, **32**, 379.

Cole, H. & Warren, B. E. (1952). *J. Appl. Phys.* **23**, 335.

Compton, A. H. & Allison, S. K. (1935). *X-rays in Theory and Experiment.* New York: van Nostrand.

Grenville-Wells, H. J. (1952). *Proc. Phys. Soc.* B, **65**, 313.

Hargreaves, C. M., Prince, E. & Wooster, W. A. (1952). *J. Sci. Instrum.* **29**, 82.

James R. W. (1948). *The Optical Principles of the Diffraction of X-rays.* London: Bell.

Pisharoty, P. R. (1940). *Proc. Indian Acad. Sci.,* A, **12**, 208.

Ramachandran, G. N. & Wooster, W. A. (1951*a*). *Acta Cryst.* **4**, 335.

Ramachandran, G. N. & Wooster, W. A. (1951*b*). *Acta Cryst.* **4**, 431.

Williamson, E. D. (1922). *J. Franklin Inst.* **193**, 491.

Acta Cryst. (1953). **6**, 454

An Extension of the 'Difference Patterson' to Facilitate the Solution of Order-Disorder Problems

By Alfred J. Frueh, Jr.

Department of Geology, University of Chicago, Chicago 37, Illinois, U.S.A.

(*Received* 29 *October* 1952)

In both the ordered and disordered phases of those minerals based upon close packed anions (chalcopyrite, bornite, stannite, etc.) it is often difficult to locate the specific cation positions from among the symmetrically distributed possible sites. Because of the identity of many of the interatomic distance vectors, the Patterson projections, or sections, of such structures cannot be readily solved.

If it can be shown, or assumed, that the non-superstructure, or fundamental, X-ray reflections do not change in intensity when these structures are disordered, then Patterson projections, or sections, made using the superstructure reflections alone, represent vector maps where all the vectors are suppressed except those between like atoms that change position during the disordering process. Positive peaks represent vectors between sites, both of which have gained or both lost in atomic number through disordering. Negative peaks represent vectors between sites where one has gained and the other has lost in atomic number during disordering. Chalcopyrite is used as a known example to show the advantages and shortcomings of the method.

Introduction

The crystallographer often encounters difficulty in attempting to solve structures exhibiting a high degree of symmetry, or pseudo symmetry, that are based upon close-packed anions with two or more species of cations distributed in the interstitial openings. Although anion positions and positions of unspecified cations are relatively easily determined, the determination of the exact distribution of the specific cations among the cationic positions presents a problem.

The major difficulties that stand in the way of the solution of this problem are the similarity in the scattering factor of the different cations involved, and the identity in both direction and magnitude of many of the interatomic distance vectors. Because of this identity, which is brought about by the high symmetry of the close-packed cell, the Patterson projections or Patterson–Harker sections, cannot be readily interpreted.

Perhaps the best example of this is illustrated by some of the highly symmetrical sulphide minerals such as bornite (Cu_5FeS_4) and some forms of stannite (Cu_2FeSnS_4). The diffraction record of these minerals is quite similar to that of sphalerite (ZnS), indicating a cubic close-packed sulphur cell. In addition, there appear weaker but nevertheless sharp reflections that increase the f.c.c. sulphur cell by a rational whole multiple along one or more of the axes. Thus it is evident that a unit of more than one sulphur cell is required to contain the well ordered unit pattern of metal atoms.

Bornite is known to exist in at least two different ordered forms. For one of these an approximate statistical arrangement was determined which did not account for the weak superstructure reflections (Tunell & Adams, 1949). The arrangement of the metal atoms has never been determined in the other known form of this mineral but an order–disorder relationship with temperature was established (Frueh, 1950).

Stannite is known to exist in at least four different forms (Ramdohr, 1944), only one of which has been exactly determined (Brockway, 1934). The possibility of disorder occurring at elevated temperatures in stannite has also been established (Frueh, 1949).

In order to overcome the difficulties of solving these and similar structures the following method is proposed:

Derivation of the method

The technique of applying 'difference Fourier diagrams' to the Patterson method was developed by Buerger (1942). He showed that for two crystals having the same structure but having a different species of atom occupying the same position in the two crystals, as in compounds *MABCD* and *NABCD* where *M* and *N* occupy the same position in the two structures, the 'difference Patterson' projection could be expressed by:

$$P(u, v)_{MABCD}-P(u, v)_{NABCD}$$
$$=\sum_h \sum_k (|F_{MABCD}|^2-|F_{NABCD}|^2)_{hk0} \exp [2\pi i(hu+kv)]\,. \quad (1)$$

With a cell of one formula weight, the resulting map consists of peaks corresponding to the ends of vectors $(M-N)A$; $(M-N)B$; $(M-N)C$; $(M-N)D$; plus peaks corresponding to the reverse vectors plus a peak $(M-N)$ $(N-M)$ at the origin.

In the general case this would differ from the Patterson projection of a hypothetical 'difference structure' (i.e. a hypothetical structure whose electron-density distribution in space is determined by the difference between the electron density of crystal *MABCD* and that of *NABCD* at every point) expressed by:

$$P(u, v)_{MABCD-NABCD}$$
$$=\sum_h \sum_k (|F_{MABCD}-F_{NABCD}|^2)_{hk0} \exp [2\pi i(hu+kv)]\,. \quad (2)$$

With a cell of one formula weight this map will contain only the peak $(M-N)^2$ at the origin. However, when there is more than one formula weight per cell there will be a peak $(M-N)^2$ at the end of each vector between the various *M* and/or *N* positions and their reverses.

The 'difference Patterson' and the Patterson of the 'difference structure' will become equal, i.e.

$$P(u, v)_{MABCD}-P(u, v)_{NABCD} = P(u, v)_{MABCD-NABCD}\,,$$

when either

$$F_{NABCD} = 0; \text{ or } F_{MABCD} = F_{NABCD}\,. \quad (3)$$

Assume an ordered crystal *ABCD* in which atoms *A* and *B* will substitute for each other forming a randomly disordered phase $\{A, B\}CD$. This disordered phase shall be considered from the point of view of the relative intensities of its Bragg and Laue reflections to be a crystal isostructural with the ordered crystal in which an atom $\frac{1}{2}(A+B)$ has been substituted for both *A* and *B*. If it is further assumed that when crystal *ABCD* is disordered its superstructure reflections disappear from its X-ray diffraction record and the fundamental or non-superstructure reflections remain the same in intensity, then for the superstructure spots $F_{\{A,B\}CD} = 0$, and for the fundamental spots $F_{\{A,B\}CD} = F_{ABCD}$, fulfilling the conditions defined in (3) above. Thus if a Patterson projection, or section, is made from the superstructure spots alone, it may be interpreted either as a 'difference Patterson' or as a Patterson of a 'difference structure'.

If in the ordered crystal *ABCD*, *A* is of greater atomic number than *B*, then in the difference crystal $(ABCD-\{A, B\}CD)$ all positions occupied in the ordered crystal by *A* would be areas of positive electron density; those positions occupied by *B* would be areas of negative electron density; and all other positions would be areas of zero electron density. Consequently, the Patterson of this difference crystal would have positive peaks corresponding with the ends of all the vectors *AA* and *BB* in the ordered crystal and their reverse vectors, and negative peaks corresponding with the ends of all vectors *AB* in the ordered crystal and their reverse vectors. The signs of the peaks are due to the fact that in any Patterson map the amplitudes of the peaks are proportional to the product of the electron density at the ends of the vectors in the crystal.

Example

The mineral chalcopyrite ($CuFeS_2$) was chosen as a sulphide, of known structure, on which to illustrate further, and to test, this method. The diffraction record of chalcopyrite is very close to that of sphalerite (cubic ZnS) with the addition of very faint, sharp superstructure reflections that double the length of one of the axes. The structure was determined by Pauling & Brockway (1932) and is illustrated in Fig. 1. Although chalcopyrite has been shown to disorder (Buerger & Buerger, 1934; Frueh, 1949) the exact nature of the disorder has never been determined. Let it be assumed that complete substitutional disorder between the iron and the copper atoms take place. Structure-factor calculations show that as a result of this disordering the superstructure spots will completely disappear and there will be no change in the fundamental relative intensities. Intensities (F^2) were calculated for the superstructure spots of the ordered crystal out to the 17th order of l and the 13th order of h and k. From these a Harker section $(x, y, 0)$ shown in Fig. 2 and a Patterson projection on (100) shown in Fig. 3 were computed.

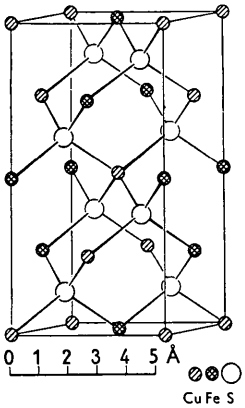

Fig. 1. The structure of chalcopyrite after Pauling & Brockway (1932).

Fig. 2, with a positive peak at the origin and a negative peak at the center, shows very simply that like metal atoms lying on the same plane perpendicular to the base form a simple square arrangement with the other species of metal atom at the center, that is, in an interpenetrating simple square net. Fig. 3 shows that the projection of the crystal on (100) is an interpenetrating rectangular centered net. This accounts for only half the required number of metal atoms. The peaks at the ends of the vectors with a vertical component of $\frac{1}{4}$ and $\frac{3}{4}$ seem to be missing from this latter projection. Upon inspection of Fig. 1 it becomes obvious that these peaks cancel out because of the equal number of positive and negative interactions.

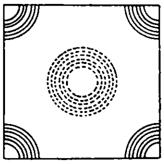

Fig. 2.

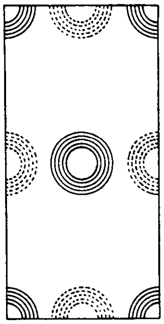

Fig. 3.

Fig. 2. Harker section $(x, y, 0)$ of chalcopyrite 'difference structure'.

Fig. 3. Patterson projection on (100) of chalcopyrite 'difference structure'.

Conclusions

Patterson projections and Patterson–Harker sections of 'difference structures' will greatly aid in the location of metal atoms in the structures based upon close-packed anions, as well as in any structure where an order–disorder phenomenon is known to occur. Information may also be gained by this method without regard to the possibility of actual disorder. Thus it should prove useful in determining the arrangements of atoms that do not follow the higher symmetry of a structure that shows a marked degree of pseudo-symmetry (i.e. in cases where weak X-ray reflections have a lower symmetry or indicate a larger cell than the stronger reflection). In some of these instances, holes (atoms of atomic number zero) may have to be considered as being involved in substitutional disorder. In interpreting these maps one should always be aware of the possibility of peaks of opposite sign cancelling out each other.

The writer wishes to thank Prof. Martin J. Buerger for reading and commenting on this paper.

References

Brockway, L. O. (1934). *Z. Krystallogr.* **89**, 434.
Buerger, M. J. (1942). *Proc. Nat. Acad. Sci., Wash.* **28**, 281.
Buerger, N. W. & Buerger, M. J. (1934). *Amer. Min.* **19**, 303.
Frueh, A. J., Jr. (1949). Thesis, Massachusetts Institute of Technology.
Frueh, A. J., Jr. (1950). *Amer. Min.* **35**, 185.
Pauling, L. & Brockway, L. O. (1932). *Z. Krystallogr.* **82**, 188.
Ramdohr, P. (1944). *Abh. preuss. Akad. Wiss.* No. 4.
Tunell, G. & Adams, C. E. (1949). *Amer. Min.* **34**, 824.