The authors wish to acknowledge financial support from the National Institute of Health under Grants A-858 and CY-4082 and to thank the University of Washington Research Computer Laboratory for the gift of unsupported computer time.

References

Ashley, J. N., Hobbs, B. C. & Raistrick, H. (1937). *Biochem. J.* **31**, 385.

Busing, W. R. & Levy, H. A. (1959). *A Crystallographic Least Squares Refinement Program for the IBM* 709, Oak Ridge National Laboratories.

Cochran, W. (1952). *Acta Cryst.* **5**, 65.

Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.

Hauptman, H. & Karle, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal.* A. C. A. Monograph No. 3. Brooklyn: Polycrystal Book Service.

Lonsdale, K. & Grenville-Wells, H. J. (1954). *Acta Cryst.* **7**, 490.

Lund, N. A., Robertson, A. & Whalley, W. B. (1953). *J. Chem. Soc.*, p. 2434.

Mull, R. R. & Nord, F. F. (1944). *Arch. Biochem.* **4**. 419.

Sayre, D. (1952). *Acta Cryst.* **5**, 60.

Stout, G. H., Dreyer, D. & Jensen, L. H. (1961). *Chem. and Ind.*, p. 289.

Zachariasen, W. H. (1952). *Acta Cryst.* **5**, 69.

Acta Cryst. (1962). **15**, 457

Principle of Maximum Superposition. A Method for Determining the Positions of replaceable Atoms in Isomorphous Crystals

By V. Raghupathy Sarma and R. Srinivasan

Department of Physics, University of Madras, Madras-25, India

(*Received* 24 *April* 1961 *and in revised form* 28 *July* 1961)

This paper describes a new method for the location of replaceable atoms in a pair of isomorphous crystals and is useful when the replaceable atoms are of low atomic number. The method uses what is known as the principle of maximum superposition in the difference-Patterson diagram of the two compounds. The application of the method to an actual case is also given.

1. Introduction

As is well known the use of the technique of isomorphous replacement requires first the determination of the position of the replaceable atoms. The problem is comparatively simple if the replaceable atoms happen to be heavy, since the peaks corresponding to the vectors between them would then stand out prominently in the individual Patterson diagrams. It becomes even easier if the difference Patterson (D.P.) is used. (Kartha & Ramachandran, 1955).

However, the problem becomes rather difficult if the contribution of the replaceable atoms to the intensity is only a small fraction of the total intensity scattered by the whole structure, as, for example, for compounds in which the difference in the scattering factors of the replaceable atoms is of the same order as those of the other atoms in the structure; or the molecule in one crystal may have an atom more than in the other, this additional atom having nearly the same scattering factor as the other atoms in the molecule. An example of the latter type would be the pair morellin ($C_{33}H_{38}O_7$) and its monomethyl ether ($C_{34}H_{39}O_7$) which are at present under investigation in this laboratory.

The determination of the replaceable atom position also becomes difficult when the replaceable atom, although 'heavy', occurs in a structure of high molecular weight, as in the complexes of heavy metals with proteins which are often isomorphous with the free compound. Perutz (1956) has suggested a method for the determination of the replaceable-atom positions in such crystals, making use of the possibility of preparing isomorphous specimens with partial replacement of the heavy atoms. Such a method obviously cannot be used with just a pair of crystals. However, there is a simple and very general method which can be used for the location of the replaceable atom in a pair of isomorphous crystals and the present paper deals essentially with this method, which makes use of what may be called the 'Principle of Maximum Superposition' applied to the difference–Patterson (D.–P.) diagram. The principle is described in the next section and it is applied to an actual case in section 3.

2. The principle of maximum superposition

Let P and Q denote respectively the number of replaceable and the remaining non-replaceable atoms in the unit cell, the total number of atoms being $P+Q=N$. We shall also use indices P and Q to indicate the two types of atoms. Let $f_P^{(1)}$ and $f_P^{(2)}$ be the scattering factors of the replaceable atoms in the two structures and f_Q that of the non-replaceable atoms, which, for convenience, are all assumed to be alike. The D.–P. obtained from the synthesis using $(|F^{(1)}|^2-|F^{(2)}|^2)$ as coefficients would contain peaks corresponding only to the (PP) and (PQ) types of interactions* (Kartha & Ramachandran, 1955) but, the (QQ) type of peaks of the ordinary Patterson would be supressed.

Consider the general case when the structure is non-centrosymmetric. Suppose the D.–P. diagram is given a vector shift corresponding to one of the (PP) vectors and the coincidences are marked out. Indicating the vector from an atom P_i in the structure to another atom P_j by (P_iP_j) and the class of all such vectors from a definite atom P_1 by $\{P_1P_j\}$ and similarly by (P_iQ_j) and $\{P_1Q_j\}$, the superposition of peaks in the D.–P. when it is shifted by a vector (P_1P_2) may be given by the following equations:

$$\left.\begin{aligned}\{P_jP_1\}+(P_1P_2)&=\{P_jP_2\}\\ \{P_2P_j\}+(P_1P_2)&=\{P_1P_j\}\end{aligned}\right\}\qquad 1(a)$$

$$\left.\begin{aligned}\{Q_jP_1\}+(P_1P_2)&=\{Q_jP_2\}\\ \{P_2Q_j\}+(P_1P_2)&=\{P_1Q_j\}\end{aligned}\right\}\qquad 1(b)$$

On the other hand, if a vector (P_1Q_2) is used for the shift, the only coincidences are given by

$$\{P_jP_1\}+(P_1Q_2)=\{P_jQ_2\};\ \{Q_2P_j\}+(P_1Q_2)=\{P_1P_j\}.\quad (2)$$

It is seen from the above equations that the coincidences for a (PP) vector contain the complete image of the structure plus its inverse about the midpoint of the shift vector. On the other hand, if a (PQ) vector is used for vector shift, (2) shows that the coincidences contain only an image of the P group and its inverse. This arises essentially because the (QQ) type of interactions are completely absent in the D–P.

Thus the number of coincidences will be much larger when a shift is made corresponding to a (PP) vector than for any (PQ) vector. In fact, equations (1) and (2) show that the ratio of the number of coincidences of the former to the latter type is $(P+Q)/P$. When the number of replaceable atoms is small compared with that of the non-replaceable atoms, the above ratio has a large value. This fact may be made use of for finding the (PP) vector provided a suitable method could be devised for estimating the amount of superposition corresponding to any vector shift.

The need for this arises because we are dealing not with point atoms but with atoms of finite size. The following procedure may be used. Corresponding to any shift vector, the minimum function is first drawn. (We shall consider a projection for convenience, although the argument is applicable equally well to three dimensions). Then the integral of this function is determined over the unit cell. We shall call this integral the 'superposition' (S). It is obvious that the superposition would be a maximum whenever the vector used for the shift is a (PP) vector, while for any other vector it would be much less. This we may call 'The Principle of Maximum Superposition'. The vector corresponding to the replaceable atom interactions can be determined by systematically calculating the magnitude of the superposition corresponding to various shift vectors and finding those for which it reaches maximum values.

Instead of the minimum function one could use the product function which also has the property of having a large value only if there is a coincidence of peaks and a low value otherwise. However, the minimum function is simpler to manipulate.

3. Test of the method

The above method of applying the principle of maximum superposition was actually tried out in the following case. The two structures L-tyrosine hydrochloride (Srinivasan, 1959*a*) and L-tyrosine hydrobromide (Srinivasan, 1959*b*) are isomorphous and belong to the space group $P2_1$ with two molecules per unit cell. The co-ordinates of the atoms of the tyrosine molecule were taken from the two structures and two hypothetical isomorphous structures were obtained, (1) having only the tyrosine molecule ($C_9H_{11}NO_3$) as found in the hydrochloride and (2) having atoms at the coordinates corresponding to the tyrosine molecule as found in the hydrobromide and an additional oxygen atom at the position of the bromine atom. In this way the additional atom in the second structure had nearly the same scattering factor as the 13 other atoms in the tyrosine molecule. By choosing co-ordinates as in the two isomorphous crystals, small changes in the position of the molecule between the two were included.

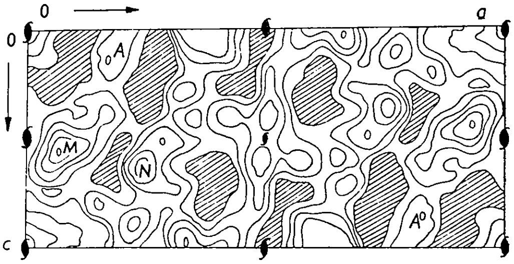

Fig. 1. Sharpened difference Patterson of tyrosine and tyrosine + O, projected down the *b* axis. Contours are at arbitrary intervals. Shaded regions correspond to troughs.

The structure factors $F^{(1)}$ and $F^{(2)}$ of the above two structures were calculated and the sharpened difference Patterson diagram of the *b* projection was obtained (Fig. 1). The sharpening was done by dividing the intensities by $\hat{f}^2$ and then multiplying them with a damping factor, $\exp[-2B\sin^2\theta/\lambda^2]$ with $2B=7$. The peak marked A in Fig. 1 corresponds to a (PP) vector. This is known in the present case since we

---

* The notation used here follows closely that used in the paper cited.

are dealing with a known structure. However, it will be noticed that it is of the same order of magnitude as the other peaks in the diagram and is not marked out in any way.

Vector shifts were made to various points as indicated in Table 1. In each case, the minimum function was obtained. Instead of obtaining its integral, the superposition *S* was calculated as a sum over the net of points at which the Patterson data were available and these are tabulated in Table 1 for a number of points around the peak *A* (60°, 42°) (values without brackets). It will be seen from the table that the superposition exhibits a fairly sharp maximum at the expected position.

Table 1. *Values of superpositions* (*S*) *corresponding to various vector shifts in Fig.* 1

The coordinates are given with respect to the top left corner of Fig. 1 as origin. Values given in brackets correspond to superposition for the product function

$c\downarrow$ \ $\vec{a}$	24°	48°	60°	72°	84°
24°			48900		
36°		42600 (2471×10^4)	50200 (2608×10^4)	46500 (2573×10^4)	
42°		43800	50600 (2624×10^4)	44700	
48°		45100	50300	43200	
60°			49300		
204°	40500				
240°					36700 (2401×10^4)

It is interesting to note that the value of the superposition has nothing to do with the strength of the corresponding peak in the D.–P. synthesis itself. In fact, the superposition corresponding to two strong peaks in the D.–P. [those at (24°, 204°) and (84°, 240°) (marked *M* and *N* respectively in Fig. 1) with strengths of 202 and 173 in arbitrary units] is much less than that for vectors in the neighbourhood of the replaceable atom interaction (60°, 42°) although the peak height of this interaction is only 48 in terms of the same unit.

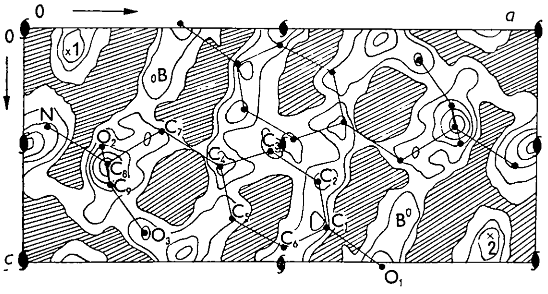

Fig. 2. The minimum function corresponding to the peak *A* in Fig. 1.

Having thus shown that the principle of maximum superposition works satisfactorily in this case, a minimum function was drawn corresponding to this vector shift. The resultant diagram is shown in Fig. 2 in which the mean atomic positions of the assumed molecule (mean of the structures (1) and (2)) are also marked. It will be noticed that, in spite of the fact that the replaceable atom is only of the same strength as the other atoms, the molecule is clearly discernible in Fig. 2. The small shifts of some of the atoms is obviously due to lack of complete isomorphism. The only spurious peak is the one marked *B* in Fig. 2, which is a strong peak in the original diagram and has a chance coincidence.

4. Discussion

The above test has clearly proved the power of the new method for finding the replaceable atom positions in isomorphous compounds. The method will be particularly effective when used with the three-dimensional D.–P. Also from the computational point of view, the method should not offer any particular difficulty since, with the modern facilities of digital computers, programming can be done for a point-by-point scanning of the three dimensional D.–P. to obtain the superposition. This process would completely extract the Patterson of the replaceable atom.

It would, probably, be of interest to examine the relative merits of the different image-seeking functions for applying the principle of maximum superposition. It is an interesting fact that the sum function cannot be used for this purpose since the superposition *S* in such a case will be a constant for all points in the cell. The product function can, however, be used instead of the minimum function. This was, in fact, tried in the present case and the values of the superposition for selected points are given in brackets in Table 1. Although the value of *S* near the correct (*PP*) vector is larger than that at other places, the superposition maximum at the correct vector (60°, 42°) is not as sharp as that obtained in the case of the minimum function. Also, the ratio (ϱ) of the value of *S* for a (*PP*) and a non-(*PP*) vector is larger for the minimum function than for the product functions. Actually, in the use of the latter, another difficulty is also likely to arise; when the D.–P. has negative values (which might arise due to inaccuracy in scaling or when the coefficients are sharpened) the function will give positive values even for a negative–negative coincidence. However, the difficulty can be overcome by initially adding a suitable value to make the function positive everywhere and then obtaining the product function. This, on the other hand, has an effect of increasing the general background and thus reducing the ratio ϱ. The values given in brackets in Table 1 were in fact calculated only in this way. Thus it appears that the product function is not so useful for applying the principle of maximum superposition.

Finally, it may be worthwhile comparing the present method with another method which has been suggested for finding the replaceable atom position, namely, the one which uses the coefficients

$$(|F^{(1)}|-|F^{(2)}|)^2$$

for a Fourier synthesis.

This synthesis, which we may call the $(MD)^2$ synthesis [$(MD)^2$ stands for modulus difference squared], can be shown to give approximately the Patterson of the replaceable atoms both in centrosymmetric and non-centrosymmetric crystals, although it should be more effective for the former.* Rossmann (1960) has used the method to determine the position of the replaceable atoms in protein crystals. However, the method is reported to have been a failure when applied to the case of caffeine and theophylline (Sutor, 1956), where the replaceable 'atom' is just a methyl group. The synthesis was actually tried in the present case also and is shown in Fig. 3. Although there is a broad peak at the required position of the (PP) vector (marked by a cross in Fig. 3), there are also other strong peaks in the map. A similar feature was also observed by Sutor (1956). Thus, the $(MD)^2$ synthesis is not likely to prove useful in such cases, where the replaceable atom is of the same strength as the other atoms in the structure, although, it might work when the replaceable atom itself is heavy (Perutz, 1956).

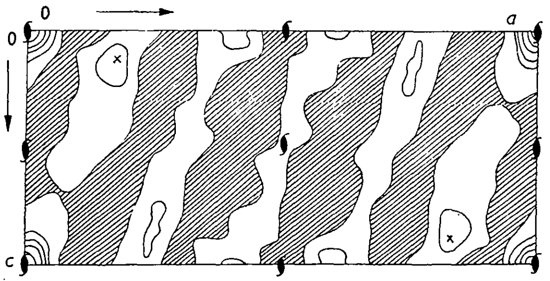

Fig. 3. The $(MD)^2$ synthesis of tyrosine and tyrosine+O, projected down the b axis. Contours are at arbitrary intervals. Shaded areas correspond to troughs.

The authors are deeply indebted to Prof. G. N. Ramachandran for his valuable guidance and encouragement during the progress of this work. One of the authors (V. R. S.) is grateful to the Government of India for the award of a Research Scholarship which made this work possible.

References

Kartha, G. & Ramachandran, G. N. (1955). *Acta Cryst.* **8**, 195.

Perutz, M. F. (1956). *Acta Cryst.* **9**, 867.

Rossmann, M. G. (1960). *Acta Cryst.* **13**, 221.

Srinivasan, R. (1959*a*). *Proc. Indian Acad. Sci.* A, **49**, 340.

Srinivasan, R. (1959*b*). *Proc. Indian Acad. Sci.* A, **50**, 19.

Sutor, D. J. (1956). *Acta Cryst.* **9**, 969.

---

* The details will be published in a later paper from the aboratory.

Acta Cryst. (1962). **15**, 460

The Crystal Structure of Chromium(II) Iodide

By Joseph W. Tracy, N. W. Gregory, J. M. Stewart and E. C. Lingafelter

Department of Chemistry, University of Washington, Seattle 5, U.S.A.

(*Received* 2 *May* 1961)

CrI_2 crystallizes with a monoclinic (pseudo hexagonal) unit cell, $C2/m$, with

$$a_0=7\cdot545,\ b_0=3\cdot929,\ c_0=7\cdot505\ \text{Å};\ \beta=115°\ 31'.$$

The structure consists of infinite parallel planar ribbons formed by chromium atoms bridged by pairs of iodine atoms. The ribbons stack together so as to form a 'sandwich' layer structure in which the iodine atoms are approximately in a close-packed array and each chromium atom is at the center of a distorted octahedron of iodine atoms.

The crystal structures of chromium(II) fluoride (Jack & Maitland, 1957) and chromium(II) chloride (Tracy *et al.*, 1961) have been reported previously. These two substances are not isostructural; the fluoride is monoclinic and the chloride orthorhombic, and both are also structurally different from chromium(II) bromide and chromium(II) iodide (Handy & Gregory, 1951). Continuing a study of this series of compounds, we now wish to report the structure of chromium(II) iodide.

Experimental

CrI_2 was prepared by reaction of iodine (Mallinckrodt, AR) with chromium metal (Fischer Scientific, 98%