In the case of KHC_2O_4, $l=5\cdot1$ Å $(=a_3/2)$, $F=20$ Å^2, and $s=1\cdot3\cdot10^{-12}$ cm^2 dyne^{-1}. These values yield a force constant $f=0\cdot30\cdot10^5$ dyne cm^{-1}, which is in reasonable agreement with the value f derived from force constants as determined from optical measurements.

The actual value of f should be somewhat lower because the influence of some force constants, which contribute to an increase of the compliance of the whole unit, was neglected. On the other hand, f, as derived from the elastic constants, is not only caused by the forces given in Fig. 6 but also, to a smaller extent, by some ionic forces due to the cation.

Cauchy relations

According to Haussühl (1967), the deviations from Cauchy relations constitute a second-rank tensor g_{rs} which represents information about bonding characteristics. In the case of KHC_2O_4 the components of the reduced tensor $g_{rs}^* = g_{rs}\cdot K$ (with $K=$ volume compressibility) have the following values:

$$g_{11}^* = -0\cdot024; g_{22}^* = 0\cdot318; g_{33}^* = 0\cdot746; g_{13}^* = 0\cdot014.$$

The principal axes of this tensor nearly coincide with the Cartesian system. Here also an appreciable anisotropy is observed. Characteristically, g_{11}^*, which represents the forces in the cleavage plane (100), is found to have the lowest value. A similar behaviour is found in gypsum (Haussühl, 1967).

The author is deeply indebted to Professor Dr S. Haussühl for making experimental arrangements available and for critical remarks. Thanks are also due to Dr H. Siegert whose computer program was used and to Professor Dr H. Pettersen for reading the manuscript.

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An Automated Deconvolution of the Patterson Synthesis by Means of a Modified Vector-Verification Method. Its Application to Some Heavy-Atom Patterson Functions

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A general scheme for the deconvolution of the Patterson-vector map is discussed, in which no structural information is needed. It appears to be possible to overcome the difficulties arising from vector overlap and vector coincidence. The vector-verification method is extended so as make it possible to locate every configuration of a small, fixed number of atoms, for which the complete corresponding vector set is present in the Patterson function. A criterion is defined which expresses the reliability of each configuration, making it possible to recognize the correct one.

1. Introduction

We employed the Patterson superposition method to develop an automated structure-determination proce-

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dure, in which no *a priori* structural information is needed (Lenstra, 1969). Having but restricted computer facilities available it was not possible to handle the symmetry minimum function (Simpson, Dobrott & Lipscomb, 1965) adequately. For this reason we have used the vector-verification method (Mighell & Jacobsen, 1963).

If the method of vector verification, illustrated in Fig. 1, is used *ab initio* in the deconvolution of the Patterson function, the first result will be a symmetry map (Raman, 1966), which shows the space-group symmetry [Fig. 1(c)], and in the case of a non-centrosymmetric space group an additional inversion centre at the origin. Therefore the first atom can be chosen relative to any of the symmetry centres of, for instance, the space group $P\bar{1}$ [Fig. 1(d)]. This means that the first atom to be located can be found in the asymmetric part of the symmetry map, which is smaller than the asymmetric part of the unit cell. Its dimensions can be determined beforehand from the known symmetry.

The asymmetric part of the symmetry map shows in the 'ideal' case as many 'atomic positions' as there are atoms in the asymmetric part of the unit cell, and in practice it may show spurious ones too. Consequently, the 'density' of the distribution of these 'atomic positions' will be much higher than that of the real-atom distribution.

At this stage it is impossible to decide whether a cluster of 'atomic positions' indicates the positions of one or more atoms or none. The usual interpretation criteria for this purpose, *e.g.* the frequency check (Gorres & Jacobson, 1964), are not sufficiently strict, because of the considerable overlap of structure images in the symmetry map.

To overcome these difficulties we have to take into account the vectors between crystallographic non-equivalent atoms (Corfield & Rosenstein, 1966). From the outset applying these vectors too, we determined what the locations of any combination of a small, fixed number of atoms might be, instead of determining the positions allowed for any single atom. This partial structure solution is described in the next section.

The procedure of the partial structure solution often yields many possible locations for the mentioned fixed number of atoms. From these we select a correct one by means of two criteria, namely a 'set reliability', which is discussed in detail in §3, and the common residual, to be discussed in our next paper (Lenstra, 1973).

The results obtained by the application of our Patterson-deconvolution procedure are given in §4.

2. The partial structure solution

Because of the limited computer facilities available we were forced to store the Patterson function in a one-bit code. Depending on the kind of interatomic vectors we were interested in, a certain height in the Patterson function was chosen as the level of significance. All values in the Patterson synthesis above this level are essential (in the one-bit code represented by the value unity); the rest was of no direct use for the structure determination (value zero in the one-bit code). The crystal space is represented in this one-bit code too.

The one-bit code representation of the Patterson function on the one hand decreases the required computing time considerably, but on the other hand it is responsible for a big loss of valuable information. How far this use of the one-bit code affects, for instance, the interpretation of the crystal space in terms of atoms has been shown by Jacobson (1966).

Starting the Patterson deconvolution we only know the space-group symmetry. Let x, y and z be the co-ordinates of the first searcher position. In general x, y and z are fully determined by the interatomic vectors produced by the space-group symmetry. In other cases, such as in the space group $P2_1$, the undetermined co-ordinates of the first searcher position are fixed at the value zero.

We assume that the structure sought contains N atoms in the asymmetric part of the unit cell. The deconvolution of the Patterson function is started by locating a small, fixed number of, say n atoms ($n < N$).

The method applied for checking every combination of n atoms was a vector test. A combination of n atomic positions was accepted only as probably correct when the complete related vector set occurs in the Patterson synthesis.

The independent variables chosen were the n searcher positions; so all related vectors are dependent variables. The searcher positions were assumed to coincide with the grid points in the crystal space.

The area which one has to scan with the first searcher position can be restricted to the asymmetric part of the symmetry map; for any other searcher position an area equal to the asymmetric part of the unit cell should be scanned.

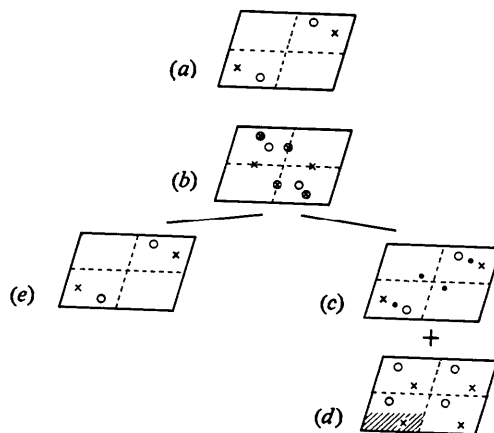Once the grid is fixed and the limited scanning areas for each searcher position are known it is quite easy to

Fig. 1. The illustration of the vector-verification method. (a) The original unit cell (plane group *p*2) containing two atoms in the asymmetric part. (b) The corresponding vector map, from which the origin peak is substracted. (c) The first atom distribution function derived by vector verification, knowing only the space-group symmetry. For clarity the origin shifts are removed. (d) Each possible position for the first atom is found relative to any of the symmetry centres (implication diagram). The shaded area is the asymmetric part of the symmetry map. (e) The distribution for the second atom derived by vector verification, knowing not only the space-group symmetry, but also the position of the first atom, say ⊃.

generate all combinations of n atomic positions. In practice each combination is built up of one searcher position after another, applying the criterion that each addition of a possible atom will correspond to a number of vectors that all have to occur in the Patterson function.

If this is not the case the added searcher position is incorrect and therefore must be replaced by another. Every time a location for the nth searcher position is accepted the whole set of n atomic positions was stored as a possibly correct one. Our procedure ends when the required areas have been scanned completely.

The result of the n-atom search is a list of all possibly correct sets. Of each different set we now know that all interatomic vectors are present in the one-bit code Patterson function. This vector map, however, permits an arbitrary number of coinciding vectors, which number may be contradicted by the height information in the original Patterson synthesis. This suffices to show that some of the obtained sets will be correct, and others will be false.

3. The set reliability; choice of a correct set

The more additional Patterson vectors that can be explained, starting from the n atomic positions of a set, the more likely the set is to be a correct one. The distribution function A_n of the presumable positions for the $(n+1)$th atom was therefore calculated by vector verification of each set. The search for the $(n+1)$th atom is illustrated in Fig. 1(e).

The number (T) of the possibilities for the $(n+1)$th atom, which was adopted as a reliability criterion, was expected to have a maximum value for a correct set. The set reliability was defined as:

$$S \equiv w_{vec} \times w_{sym} \times T,$$

where w_{vec} and w_{sym} are correction factors.

w_{vec}: A_n was calculated by testing the vectors corresponding to the $(n+1)$th atom. If the n atoms of the set are located in general positions we called the number of tested vectors B. If, however, one or more atoms of the set are located at special positions the number of tested vectors will be lower, say C.

We state: $w_{vec} = C/B$.

w_{sym}: A_n can be m-fold ($m > 1$), owing to pseudosymmetry of a set. The value of w_{sym} is approximated by $w_{sym} = 1/m$.

The choice of the first atoms in a structure analysis is very important, since it will influence all further conclusions. So we decided not to rely on the set reliability only. The S function we defined is not an exact criterion. A great drawback of S is the impossibility of obtaining a theoretical S value for a correct set that can be compared with the experimental values.

Consequently, we decided to make use also of the residual, which is a quantitative 'difference-Patterson' criterion (Lenstra, 1973). The theoretical values of the

residual for a correct set and that of an incorrect one can be calculated, and so can be compared with the experimental values. This provides a sounder basis for the use of the residual as a means to distinguish among correct and incorrect sets.

The use of both the residual and S is, of course, proper only if both functions are based on a different principle. Whereas the residual only gives information about the n atoms of the set, the S function is related to a tentative crystal structure, including the n atoms of the tested set. This important difference between these functions is illustrated in the following example.

Suppose that by deconvolution of a Patterson function we have found two sets of n atoms, which are crystallographically non-equivalent but which result in exactly the same interatomic vectors. In this case both sets will show the same value for the residual; therefore it is impossible to decide by means of this residual which set is the correct one. The S values of these two sets, however, will be different. They are determined by introducing the $(n+1)$th searcher position, so that both sets in general will no longer be homometric.

We therefore proceeded as follows to select a correct set. For all sets obtained by means of the partial structure solution we calculated the related S values; the necessary information – the one-bit code Patterson function – is directly available. We selected a number of these sets, say 15, which were the most promising because of their S values. Only for these sets did we calculate the corresponding residual; the lowest value of the residual should then correspond to a correct solution.

4. Experimental results

The procedure for the automated deconvolution of the Patterson function was tested on several heavy-atom compounds. We confined ourselves to the positioning of the heavy atoms only. For convenience n was taken equal to the number of independent heavy atoms in the asymmetric part of the unit cell.

To determine the S values we now had to use a searcher position for a light atom in the derivation of A_n. The vectors, which all have to occur in the calculated one-bit code Patterson function, were restricted to the vectors between the 'light-searcher position' and the heavy atoms of the set. Therefore the level of significance had to be lowered compared with the original significance level we used to find all possible locations for the heavy atoms looked for.

The calculated Patterson syntheses were slightly sharpened in the usual way. The grid distances were chosen ~ 0.25 Å for both the Patterson map and the crystal space. We made use of the following compounds.

Zinc malate (space group $P2_1$) contains two Zn^{2+} ions in the unit cell. The heavy-atom vectors appeared to be hardly influenced by other interatomic vectors. Our procedure yielded the correct zinc atom positions.

Nickel hydrogen malate (space group $P4_12_12$ or

$P4_32_12$) has four Ni^{2+} ions per unit cell. The Ni^{2+} was known to be located at a special position of the space group. The heavy-atom vectors did not show overlap. The nickel atom positions came out properly.

Potassium hydrogen monofluormalonate (space group $Pca2_1$) contains four K^+ ions in the unit cell, located at general positions. Some of the K vectors show a slight mutual overlap. The K^+ positions were correctly found from the vector map.

The fourth test compund was (+)-benzeetimide hydrobromide, space group $P\bar{1}$. The unit cell contains two independent molecules. Both Br^- ions were properly placed by means of our routine.

Potassium hydrogen mesotartrate, space group $P\bar{1}$ (Kroon & Kanters, 1972), contains two molecules in the asymmetric part of the unit cell. Some of the K vectors show such an amount of mutual overlap that some of the highest Patterson maxima do not correspond to real K vectors. The heavy-atom positions were correctly calculated in our deconvolution procedure.

Bis(hydrazinecarboxylato-N'-O)manganese dihydrate, space group $Pba2$ (Braibanti, Tiripicchio, Manotti Lanfredi & Camellini, 1967), served as the final test compound. The structure contains four Mn ions per unit cell; the atoms, however, are located at two crystallographically non-equivalent, special positions of the space group. Most of the heavy-atom vectors coincide; some occur separately in the Patterson map. In this situation too the heavy atoms obtained by the application of our procedure were correctly placed.

In the six test cases unfortunately no homometric sets for the n-atom part of the structure were met with, which could have proved the indispensability of the set reliability. In every case the set of n atomic positions with the highest set reliability was correct. This set also showed the lowest value of the residual.

In view of this it seems a pity to spend computer time for the calculation of both the set reliability and the residual.

However, the fact remains that the residual is not effective for homometric sets in contrast to the set

reliability; on the other hand, excepting homometric sets, the residual is theoretically an absolute criterion and it is therefore the best we have. So we decided to maintain both criteria, but naturally we tried to reduce the computing time. In the case of, for instance, potassium hydrogen mesotartrate the time required to compute the set reliability is nearly equal to the time needed to calculate the residual. It appeared that the time to compute S could be reduced to $\sim 15\%$ of its original computing time by simply using a doubled grid spacing (~ 0.5 Å) for the ($n+1$)th searcher position. We thus found that the correct set of heavy atoms for all six crystal structures mentioned still showed the highest S value.

We accept a drawback of this doubled-scan step which is, of course, a higher inaccuracy of the obtained S values. Table 1 shows that this is, for instance, responsible for a greater spreading in the S values belonging to sets that differ only in the choice of the origin, namely set numbers 3, 4 and 7. The 15 sets given in this table were found by the deconvolution of the Patterson function of potassium hydrogen mesotartrate, and these sets showed the highest S values. The other sets found are not mentioned in this Table. The rather small variations in S are the result of the levelling effect of the one-bit code representation of the crystal space.

Some of the given sets only differ from others by 0·028 in one fractional coordinate. This corresponds to a single grid spacing. The procedure followed gives them separately, because it cannot discriminate between correct and nearly correct positions because of the grid spacing and of the use of the one-bit code Patterson function.

From Table 1 we also see that because of the spreading in S values, it is not any longer necessarily justified to select a correct set only by means of its S value. In our selected table, however, each correct set occurs. This is our main purpose, since we applied the set reliability as an initial criterion, not least because it is calculated about eight times faster than the residual. The correct set is then obtained with the residual – a quanti-

Table 1. *Potassium hydrogen mesotartrate; results of the automated deconvolution procedure*

Set number	Fractional coordinates ($\times 10^3$)						S	R	Remarks
	Searcher position I			Searcher position II					
1	222	167	222	278	556	389	13	62·92	
2	250	306	278	222	944	111	12	63·61	
3	250	167	222	278	556	389	17	60·93	$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$−set 7
4	222	444	111	278	833	278	14	62·92	$(0\frac{1}{2}0)$+set 7
5	222	444	139	278	833	278	16	62·16	
6	222	139	194	000	500	500	10	67·19	
7	250	333	278	222	944	111	18	60·92	correct set.
8	250	194	222	278	556	389	13	63·61	
9	028	167	222	278	111	389	17	68·02	
10	028	167	222	333	056	722	16	69·25	
11	028	472	167	500	500	000	9	67·38	
12	250	139	194	000	500	500	10	66·14	
13	250	361	306	500	000	000	10	66·14	
14	194	111	000	500	000	500	10	67·48	
15	222	111	194	000	500	500	15	66·30	
	255	329	272	223	934	129	K^+ positions refined		

tative criterion – as the final and most accurate criterion.

The authors are grateful to Professor A. F. Peerdeman for critical reading of the manuscript.

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X-ray Structural Damage of Triglycine Sulphate (TGS)

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The complete spectrum emitted by a conventional X-ray diffraction Cu target produces damage in a small TGS crystal which is evident from the variation of integrated intensities of X-ray reflexions with irradiation time. An interpretation of the data is proposed which assumes that the trapping of irradiation products causes an exponential decrease of mosaic-block diameters. An empirical correction of the Zachariasen extinction factor for crystals belonging to type II is suggested, since the TGS crystal is of this type.

Introduction

Structure analysis requires the accurate determination of both integrated intensities and structure factors. It is well known that X-rays used to collect data have undesirable effects on the crystals. These effects are ascribed to material instability, or to defects produced by X-ray damage. Young (1969) and Milledge (1969) have made detailed reviews of the different problems concerning the precise determination of integrated X-ray reflexion intensities, emphasizing how to avoid the effects of damage rather than explaining the production mechanism.

There is a copious bibliography covering the topic of irradiation damage with special reference to X-ray diffraction effects. Examples are Lonsdale, Nave & Stephens (1966), Kolontsova & Telegina (1969), Krueger, Cook, Sartain & Yockey (1963), Telegina & Kolontsova (1970), Larson & Young (1972) and Baldwin & Dunn (1972). Work on X-irradiated TGS crystals has been carried out by Petroff (1971), who detected planar defects, and Mendiola & Alemany (1970), who pointed out large variations in the intensities of X-ray reflexions with cumulative doses.

In this paper we study the variation of integrated intensities of X-ray reflexions with time when a single crystal is irradiated by the complete spectrum emitted from a conventional X-ray diffraction Cu target. For reflexions with $F \geq 16$, a continuous increase in intensity is observed until a maximum is reached, followed by a decrease; but for reflexions with $F < 16$ the intensities diminish from the beginning. This behaviour is fairly well explained by an empirical correction to the Zachariasen extinction factor for crystals belonging to type II, as we suggest for TGS crystals, and assuming an exponential decrease of mosaic-block radius as well.

The TGS lattice parameters and the observed and calculated structure factors of the reflexions used in this paper are the early ones reported by Hoshino, Okaya & Pepinsky (1959). The results obtained there are substantially the same as those deduced from the fractional atomic coordinates x, y, z and temperature factors B_{ij} given by Itoh & Mitsui (1971). However we do not follow the latter paper because no extinction correction is made. In this paper we show that the inclusion of an extinction correction is necessary.

Theory

The concepts that are used in discussing the results have been exhaustively developed by Zachariasen (1967a,b; 1968a,b,c,d; 1969). According to his theory, the integrated intensity of a reflexion from a symmetrically shaped crystal of volume v, assumed to consist of nearly spherical domains of radius r, is given by

$$I = I_k \cdot y \tag{1}$$