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Some Critical Tests of the Use of Mixed Projections in Crystal-Structure Determination

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In view of the present activity in the development of methods for deciphering Patterson structures, and especially in view of the apparent success of several authors along theoretical lines, it seems worthwhile to test at least one of these methods upon carefully chosen structures whose solutions are known. Without correlating the various methods or pointing out wherein they differ, the method of mixed projections is tested upon (*a*) a hypothetical structure of chlorine atoms, (*b*) hexamethylene-diamine dihydrobromide, (*c*) hexamethylene-diamine dihydrochloride, and (*d*) K_2CuCl_3.

This work illustrates the two facts that are anticipated on theoretical grounds: (1) Ambiguities occur because of accidental coincidences, as well as near coincidences. (2) Difficulties in interpretation arise when one component of the translation vector is one-half or one-quarter of a cell translation, owing either to space group conditions or the characteristics of the structure.

However, it is apparent that in any case the method is a very effective aid in simplifying the solution of complicated structures.

Introduction

Since the original paper of Patterson (1935) a number of papers have been written on the various methods of obtaining crystal structures from 'Patterson structures'. Among the earliest of these papers are those by Harker (1936) and Wrinch (1939). More recently works by Buerger (1946, 1947, 1948*a*, *b*, *c*, 1950*a*, *b*), Garrido (1950*a*, *b*), Clastre & Gay (1950*a*, *b*, *c*), Beevers & Robertson (1950) and McLachlan (1950, 1951) have promised substantial encouragement to crystallographers in the deciphering of Patterson structures. It is possible to prove that the more recent methods are based on a similar theoretical foundation; however, since the workers have made their contributions independently and have, therefore, devised their own individual nomenclatures, it is difficult to discuss them all in a single publication. The following discussion, consequently, is based on the methods with which the present authors are most familiar, i.e. the method of mixed projections. The purpose of this paper is to illustrate* the use of mixed projections on a number of structures and, from the results, to point out certain difficulties or ambiguities which are encountered.

The treatment of a hypothetical structure

To clarify the procedure used in the method of mixed projections, a hypothetical structure is treated stepwise so that all the operations may be followed by the reader. The symmetrical plane structure shown in Fig. 1 is taken for illustration. In order that the hypothetical structure may behave somewhat as a practical structure, point atoms are avoided and the atoms are assumed to scatter X-rays in a manner characteristic of chlorins atoms with a Debye–Waller temperature factor $B \times 10^{16} = 1$.

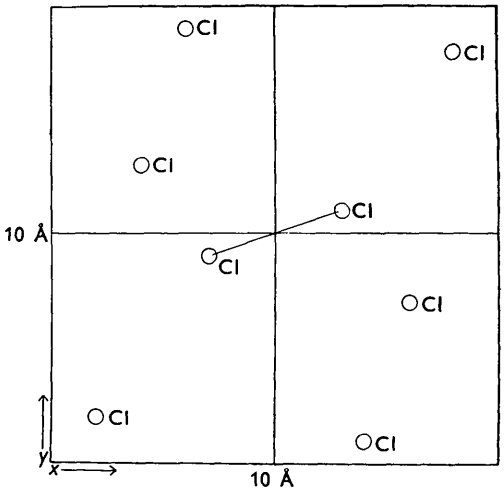

Fig. 1. A hypothetical structure of chlorine atoms symmetrically located on a plane.

Following the nomenclature of a preceding paper (McLachlan, 1951) a structure of eight atoms is represented by the symbols

$$|1\,2\,3\,4\,5\,6\,7\,8|,$$

where 3, for example, means that there exists in the structure an atom at the position x_3, y_3 having an

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* A very practical illustration of the Vector Convergence method has been given by Robertson (1951).

atomic scattering factor f_3. Since the structure is symmetrical the symbols may be written

$$|1\,2\,3\,4\,\bar{1}\,\bar{2}\,\bar{3}\,\bar{4}|\,,$$

in which $\bar{3}$, for example, means an atom at the position $\bar{x}_3$, $\bar{y}_3$ having an atomic scattering factor f_3.

The theoretical Patterson projection (McLachlan, 1950, 1951) of the hypothetical structure is shown in Fig. 2, wherein single peaks are represented by circles and double peaks by two concentric circles. The symbolic Patterson projection is indicated by Table 1. This table indicates 64 points, but since $i\bar{j} = j\bar{i}$ there are many double points (this is easily shown by writing $i\bar{j}$ and $j\bar{i}$ out in full: $i\bar{j} = x_i - \bar{x}_j = x_i + x_j$ and $j\bar{i} = x_j - \bar{x}_i = x_i + x_j$). The double points are not only located at the same place in the cell, $x_i + x_j$, but have the same scattering factors f_if_j. All the points in Table 1 are thus in pairs except those for which $i = j$, as indicated by the diagonals AA', BB' and CC'. The points along AA' are at the origin, since $x_i - x_i = 0$ and their factors are f_i^2; the points along BB' are through-center vectors in the positive sense since $x_i - \bar{x}_i = 2x_i$; and those along CC' are through-center vectors in the negative sence, since $\bar{x}_i - x_i = -2x_i$. These eight (or n) vectors are shown by single circles in Fig. 2 while the $\frac{1}{2}n^2 - n = 24$ double peaks are shown by double circles.

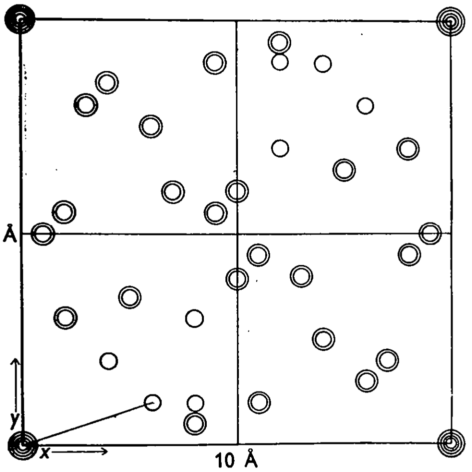

Fig. 2. A 'theoretical' Patterson projection of the structure shown in Fig. 1. The single circles represent through-center vectors.

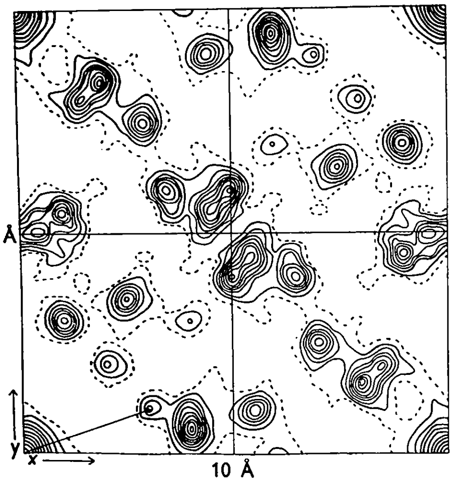

Fig. 3. A computed Patterson projection of the structure shown in Fig. 1, using the F^2 values shown in Table 2.

Table 1. *Symbolic Patterson projection*

A					B				
	11	12	13	14	$1\bar{1}$	$1\bar{2}$	$1\bar{3}$	$1\bar{4}$	
	21	22	23	24	$2\bar{1}$	$2\bar{2}$	$2\bar{3}$	$2\bar{4}$	
	31	32	33	34	$3\bar{1}$	$3\bar{2}$	$3\bar{3}$	$3\bar{4}$	
C	41	42	43	44	$4\bar{1}$	$4\bar{2}$	$4\bar{3}$	$4\bar{4}$	
	$\bar{1}1$	$\bar{1}2$	$\bar{1}3$	$\bar{1}4$	$\bar{1}\bar{1}$	$\bar{1}\bar{2}$	$\bar{1}\bar{3}$	$\bar{1}\bar{4}$	B'
	$\bar{2}1$	$\bar{2}2$	$\bar{2}3$	$\bar{2}4$	$\bar{2}\bar{1}$	$\bar{2}\bar{2}$	$\bar{2}\bar{3}$	$\bar{2}\bar{4}$	
	$\bar{3}1$	$\bar{3}2$	$\bar{3}3$	$\bar{3}4$	$\bar{3}\bar{1}$	$\bar{3}\bar{2}$	$\bar{3}\bar{3}$	$\bar{3}\bar{4}$	
	$\bar{4}1$	$\bar{4}2$	$\bar{4}3$	$\bar{4}4$	$\bar{4}\bar{1}$	$\bar{4}\bar{2}$	$\bar{4}\bar{3}$	$\bar{4}\bar{4}$	
					C'				A'

Fig. 3 shows a Patterson projection of the hypothetical structure obtained from the $|F_{hk0}|^2$ values calculated from the assumed atomic positions shown in Fig. 1. These $|F_{hk0}|^2$ values are given in Table 2. A comparison of Fig. 3 with Fig. 2 indicates that the Patterson summation has resolved nearly all the peaks that are expected to appear. Also, the maxima of Fig. 3 which are weakest are easily associated with the single circles in Fig. 2.

If the through-center vector shown by the diagonal line in Figs. 2 and 3 is used as a translation distance, a mixed projection (McLachlan, 1951) may be made either by the method of sums or by the method of products. In the method of sums the following equation is illustrative of the principle in one dimension:

$$A(u+\tfrac{1}{2}\Delta\chi_{jt})+A(u-\tfrac{1}{2}\Delta\chi_{jt}) = \sum_{h} (F_h)_M \cos 2\pi hu\,, \qquad (1)^*$$

where $(F_{hk0})_M = 2|F_{hk0}|^2 \cos 2\pi(\tfrac{1}{2}h\Delta x_{jt})$, and Δx_{jt} is the x component of the chosen through-center vector. If the method of products is used

$$A(u)A(u+\Delta\chi_{jt}) = \sum_{h''} (F_{h''})_p e^{-2\pi i h'' u}\,, \qquad (2)^*$$

where

$$(F_{h''})_p = \sum_{h'} |F_{h''-h'}|^2 |F_{h'}|^2 e^{-2\pi i h' \Delta\chi_{jt}}\,.$$

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* The volume correction is not included in these equations. Also, equation (2) is not converted to the symmetrical form by decomposing a shift of magnitude Δx_{jt} into two shifts of magnitude, $+\tfrac{1}{2}\Delta x_{jt}$ and $-\tfrac{1}{2}\Delta x_{jt}$.

Table 2. $F^2_{hk0}/10$ *values for hypothetical structure* (see Fig. 1)

h ↓ k →	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
20	3	–	1	–	–	–	–	–	–												
19	–	–	–	–	2	–	2	–	–	–											
18	1	–	1	–	1	–	–	–	–	–	–										
17	–	1	2	1	3	–	–	–	3	–	–	–									
16	1	1	3	2	–	–	–	1	2	1	–	1	1								
15	1	7	1	–	–	–	6	–	1	–	–	–	–	–							
14	1	5	2	–	–	11	–	2	–	–	3	–	2	–	–						
13	3	1	1	1	1	–	1	–	–	4	–	3	1	–	–	–					
12	2	2	3	23	–	10	–	2	1	2	2	–	–	1	1	1	–				
11	5	1	2	1	1	–	1	8	–	13	–	–	–	3	1	1	–	1			
10	0	14	0	10	7	2	–	12	1	1	–	–	–	4	–	–	1	1	–		
9	8	3	2	–	24	–	25	2	1	1	–	13	–	4	–	–	–	–	–	–	
8	5	1	24	5	15	–	–	–	2	–	4	3	1	1	–	3	–	4	–	–	–
7	9	59	2	24	19	2	–	–	6	12	1	9	1	–	1	–	–	–	–	–	–
6	3	1	3	4	–	1	2	–	38	–	11	–	1	4	–	7	–	–	–	–	–
5	9	43	34	16	10	23	5	2	–	3	2	–	3	1	8	–	–	–	–	2	–
4	12	7	3	4	5	30	30	–	27	11	1	3	8	2	–	–	–	1	–	–	–
3	7	24	15	73	1	–	6	5	1	2	5	–	18	1	1	–	5	1	1	1	–
2	55	2	144	34	27	2	8	30	–	7	15	2	3	–	–	–	2	–	2	–	1
1	1	35	20	–	6	24	42	–	15	12	6	1	–	4	9	–	7	–	1	–	–
0	–	1	55	7	12	9	3	9	5	8	13	5	2	3	1	1	1	–	1	–	3
– 1	–	2		2	106	–	52	16	1	1	6	8	6	–	7	2	–	1	3	–	–
– 2	–	1	55	7	31	–	–	1	8	3	15	5	–	8	2	–	2	–	–	–	1
– 3	–	30	55	12	62	–	5	5	40	1	5	1	–	1	1	–	–	–	–	–	–
– 4	–	17	4	28	1	3	–	–	18	5	1	8	12	–	6	4	–	1	1	–	–
– 5	–	64	6	–	3	2	41	3	7	1	2	2	–	1	1	3	1	1	–	1	–
– 6	–	27	8	3	–	–	2	12	1	–	11	–	11	2	–	2	1	1	–	–	–
– 7	–	4	4	5	4	53	4	–	1	14	1	9	2	–	–	–	3	1	–	–	–
– 8	–	4	8	51	1	2	1	4	2	4	4	–	–	2	3	2	–	–	1	–	–
– 9	–	1	4	2	1	21	1	12	–	19	–	–	–	4	1	1	–	1	–	–	
–10	–	14	0	10	7	–	–	12	1	1	–	–	–	4	–	–	1	1	–		
–11	–	5	8	6	3	2	4	8	–	–	–	9	–	3	–	–	–	–			
–12	–	–	3	–	–	5	6	3	–	–	2	1	–	1	–	–	–				
–13	–	14	1	4	10	5	–	–	1	4	–	3	–	–	–	2					
–14	–	1	–	4	2	–	–	1	5	–	3	–	–	8	–						
–15	–	4	4	2	1	3	1	–	–	–	–	–	1	–							
–16	–	–	–	–	–	3	3	–	3	1	–	–	1								
–17	–	1	1	3	–	2	–	–	–	–	–	–									
–18	–	3	1	1	–	–	–	1	–	–	–										
–19	–	–	–	–	–	–	–	–	–	–											
–20	–	–	1	–	–	–	–	–	–												

Since the method of products is the most desirable (McLachlan, 1951) this method is illustrated; but since the Utah calculator does not accommodate high enough values of h'' and k'' for the Fourier summation, another procedure was followed in accomplishing the operation stipulated by the left-hand side of equation (2). A transparent template was made with two small circles inscribed on it so that the two circles are located in the same direction and distance with respect to one another as are the two terminations of the chosen vector in Fig. 3. Before Fig. 3 had the contour lines marked on it, and while numbers representing the Fourier sums were visible, the template was moved over the Patterson projection at intervals of $a/60$ along the x axis and $b/60$ along the y axis, and, at each interval, the two numbers which appeared simultaneously within the two inscribed circles were multiplied together. The products obtained at each interval are recorded on a chart in the same sequence in which they were obtained and a new contour diagram is drawn. Fig. 4 shows the mixed projection by the method of products obtained in this manner. It may be seen by comparison with Fig. 1 that the original structure has been reproduced. There are two ghosts marked F in Fig. 4. These ghosts occur frequently in this work. The original vector terminations show up as extra strong peaks C, C' (Fig. 4), but they belong to the structure.

The treatment of hexamethylenediamine dihydrobromide

This compound was chosen as a first effort because Binnie & Robertson (1949*a*) in this original paper show a Patterson projection and a theoretical vector map which are in total agreement with one another and in which the through-center vectors can be identified by the relative weakness of their corresponding maxima. It is understood that these maxima are associated with the Br–Br distances while the Br–C as well as the C–C distances are not resolved on the Patterson projection. This structure was used to test both the method of sums and the method of products. It was not expected that the method of sums should resolve any atoms except the bromines. Fig. 5, which was computed on the Utah calculator using equation (1), clearly shows all the bromine atoms in a configuration agreeing with the structure given by Binnie & Robertson. The terminations of chosen vector distance for translation is shown by the heavier bromine peaks in Fig. 5, while the diffused background represents the sum of all the non-coincident peaks obtained by the addition of two translated Patterson projections. Using the method of sums, the non-coincidences are not eliminated.

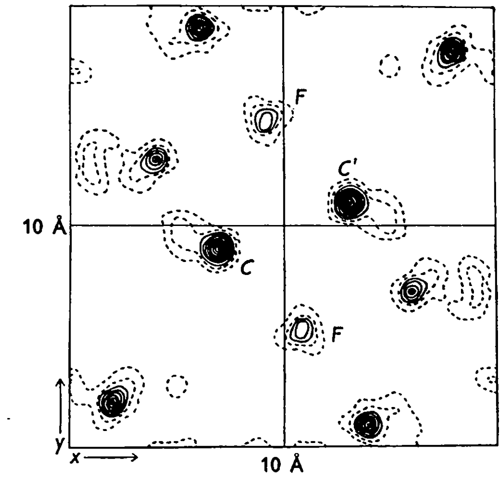

Fig. 4. A mixed projection by the method of products to produce maxima agreeing with Fig. 1. The two maxima marked *F* are accidental ghosts.

The method of products, however, does eliminate the non-coincident maxima and therefore may be expected to resolve the carbon atoms as well as the bromine atoms in this structure. Fig. 6 shows the results of the use of the method of products as applied to the same structure. This map was obtained by the use of the template, as was described in connection with Fig. 4. It is first to be noted that the bromine maxima have the same configuration in Fig. 6 as is shown in Fig. 5, although the chosen translation vector is different. The positions of the carbon atoms, as found by Binnie & Robertson, are represented in this figure by black dots, and those belonging to the same molecule are connected by lines. It may be seen by comparing Fig. 5 with Fig. 6 that greater information is produced by use of the method of products. However, Fig. 6 shows one set of molecules much better resolved than the other. It is believed that the use of the template is unreliable because of the possibility that, in a cell that is divided into 60 dimensions each way, the atomic peaks may not be located at the centers of the squares. A direct use of equation (2) would be more reliable and should be used by those who have calculating machines of sufficient capacity. It is also suspected that these methods might require more accurate data than the more conventional methods.

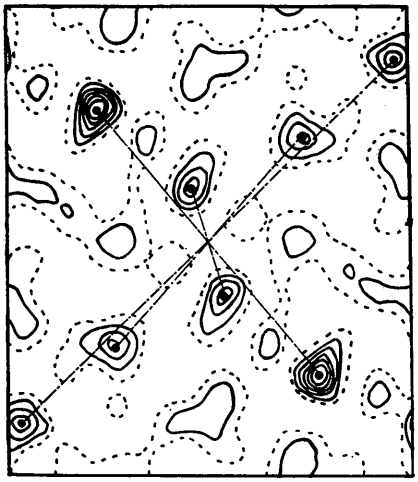

Fig. 5. A mixed projection by the method of sums showing the bromine maxima in hexamethylene-diamine dihydrobromide, using the data of Binnie & Robertson (1949*a*).

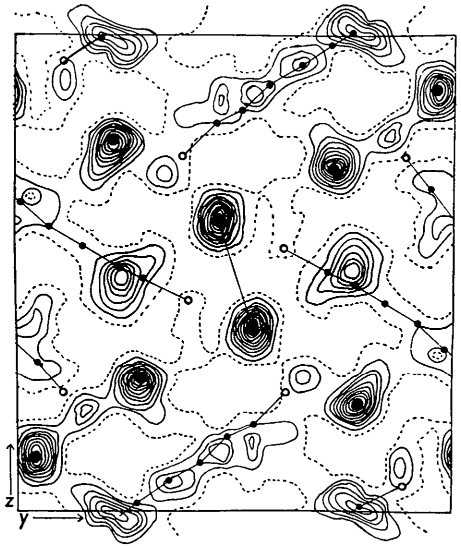

Fig. 6. A mixed projection by the method of products showing some detail regarding the carbon atoms in the same compound as is shown in Fig. 5.

The treatment of hexamethylenediamine dihydrochloride (Binnie & Robertson, 1949 *b*)

In order to test the possibility that these methods are very sensitive to the accuracy of the original X-ray data, it was decided to compare the results obtained from hexamethylenediamine dihydrobromide with those obtained from dihydrochloride of the same compound. This comparison was expected to be fruitful because it may be observed that the final contour maps of Binnie & Robertson on the two compounds do not appear to be equally refined. Since the carbon maxima in the bromine compound (see Binnie & Robertson, 1949*a*, Fig. 3) are not as round and well defined as they are in the later work on the chlorine compound (see Binnie & Robertson, 1949*b*, Fig. 2), it was suspected that the data from the chloride might be more sensitive to the carbon positions, and therefore a mixed projection (using products) might show some improvement. Fig. 7 shows the results, which, in comparison with Fig. 6, are definitely more instructive in locating the carbon atoms. Fig. 7 is, however, not satisfactory, possibly because of overlapping of Patterson maxima in the translation.

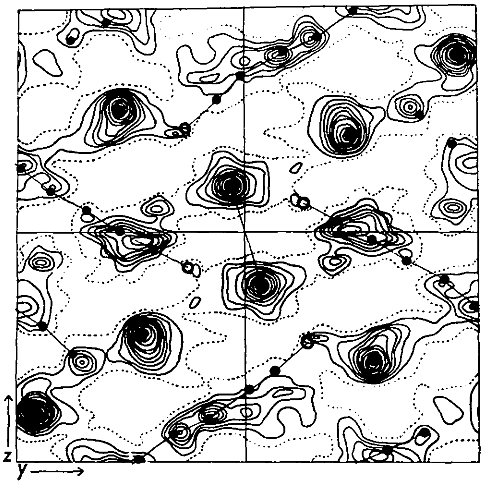

Fig. 7. A mixed projection by the method of products applied to hexamethylene-diamine dihydrochloride using the data of Binnie & Robertson (1949*b*). Better resolution of the carbon atoms was expected in this projection than in Fig. 6, because the data for the chloride appears in the original papers to be superior to those for the bromide.

The treatment of K_2CuCl_3 (Brink & MacGillavry, 1949)

Whereas the compounds which are treated in the forepart of this paper were chosen to find out the usefulness of our methods under favorable conditions, this last illustration is purposely chosen to demonstrate simultaneously several factors which limit the usefulness of the methods. The factors which this structure exhibit are: (*a*) There are 24 atoms in the unit cell. (*b*) The atoms are not the same and some of them have relatively larger radii. (*c*) The Patterson projection is very diffuse. (*d*) There exists a repeating distance of one-half which creates double structures (McLachlan, 1951) in the mixed projection.

Fig. 8 is a theoretical vector map of K_2CuCl_3 to justify the very diffuse Patterson projection which is obtained for this compound. The diagonal line in this figure is drawn from the origin to the only peak that is resolved in the Patterson projection, and, therefore, is the only translation distance that can be justifiably chosen for a mixed projection. Fig. 9 is the contour map of the mixed projection. Since the chosen translation distance (see Fig. 8) has an *x* component of one half, the images of each molecule are doubled, having one molecule with the configuration that Brink & MacGillavry found and a second molecule related to it by a horizontal mirror. The Brink–MacGillacry molecule is shown as black dots connected by solid lines and its image by open circles connected by broken lines. These two sets of molecules are predicted by theory but, in addition, there are maxima which must be ascribed to near coincidences. To demonstrate the overlapping due to near coincidences of Patterson maxima in the mixed projection of this structure, Fig. 10 has superposed on it two theoretical vector maps translated in the manner used in mixed projections. The peaks in one of these vector maps are shown by solid circles and the other by broken circles. A study of this figure reveals clearly the reasons for the occurrence of the unwanted maxima in the mixed projection (Fig. 9).

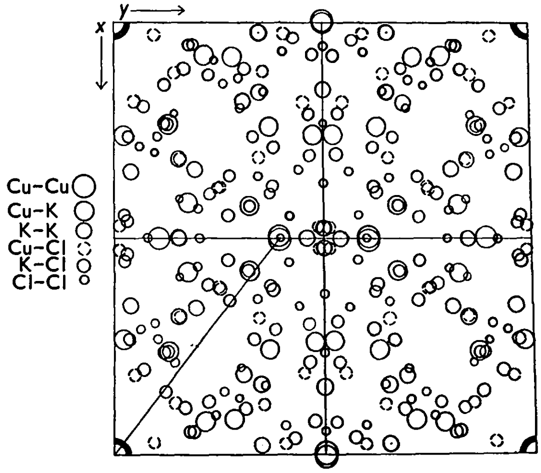

Fig. 8. A theoretical Patterson projection of K_2CuCl_3 from the final structure deduced by Brink & MacGillavry (1949).

It should be noted that although this method is called 'mixed projections' (thus implying a projection in two dimensions) after the method of their discovery (McLachlan, 1950), it is applicable to three-dimensional structures. These illustrations are two dimensional only because of the limitations of the computing equipment that is available.

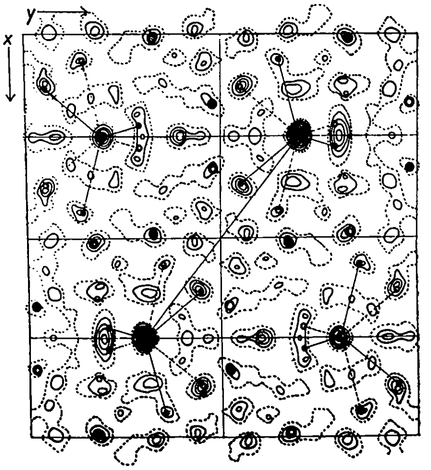

Fig. 9. A mixed projection by the method of products of K_2CuCl_3 showing the mirroring of the molecules. One set of molecules is connected by solid lines and the other by broken lines. Note the undesired maxima.

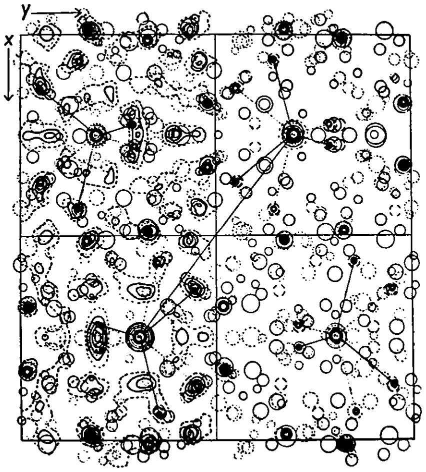

Fig. 10. This figure is so arranged that the 'theoretical' mixed projection can be compared with the computed mixed projection of Fig. 9. One set of theoretical Patterson peaks (see Fig. 8) is indicated by solid circles and the shifted set by broken circles. When two of these circles are too near one another an accidental coincidence may occur.

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