

CRYSTAL STRUCTURE DETERMINATION FROM ROUGH INTENSITY RELATIONS

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ABSTRACT

A method is described by means of which the most probable atomic locations in a crystal can be found through consideration of a few strong reflections. In the example cited, four potential arrays are determined. Through proper consideration of missing reflections, a unique solution is found whose parameters agree to within .02 of those determined by conventional methods. The method should also be useful for interpreting Patterson diagrams.

INTRODUCTION

In crystal structure determinations one is faced with the problem of proposing a reasonable structure and proving by computation of structure amplitudes and electron density maps that it is consistent with experimentally observed diffraction amplitudes. Often, one has the opportunity of choosing the trial structure on a logical basis, such as suspected isomorphism with another material, knowledge of the structure and packing of molecules or radicals, suspicion that the structure is derivative from a known one, and the like. Too often, however, one must begin the tedious computations with no idea, as to what the arrangement might be. In such instances, any device which may give a hint as to the most probable atomic locations, particularly if it can be accomplished rapidly and easily, is a useful and valuable addition to the techniques available to investigators, even though the results will not always be as definite as in the example to be cited. It is with that philosophy in mind that the following method for the preliminary steps of structure determination is presented. The discussion applies only to crystals with symmetry elements which project as centers of symmetry.

The method described here is based on an idea used so commonly by structure investigators as to have become almost second nature. If a given pinacoid "reflection," 300 for instance, is very strong—especially, though not necessarily—if succeeding orders of this reflection decrease in intensity in an orderly manner, one feels reasonably certain that there are accumulations of scattering matter at $x=0$, $1/3$, $2/3$. This information forms a starting point in the construction of a trial structure.

The above described concept need not be confined to reflections of

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simple indices. Robertson and White,¹ for example, have shown that one can obtain information concerning two parameters, in projection, by constructing lines representing the positions of maxima and minima of several strong reflections. Intersections of these are the most probable atomic positions. Donnay² described a similar technique. What has apparently been overlooked is that weak reflections, particularly those of zero intensity can give additional information. It is the purpose of this communication to demonstrate the usefulness of missing reflections in eliminating ambiguous atomic arrangements obtained from strong reflections only, by outlining a complete structure determination. For completeness, the entire theory will be developed.

THEORY

A reciprocal point, $hk0$, may be considered as having associated with it a cosine wave with a periodicity h in the a direction and k in the b direction. The distribution of electron density throughout the projected unit cell is determined by compounding the waves associated with all reciprocal lattice points. The amplitude of any individual wave is given in $F_{(hk0)}$. A large amplitude suggests either that there are heavy, controlling atoms separated by a distance which has a component normal to the wave front equal, or nearly so, to the wave length of the wave corresponding to $hk0$, or that there are groups of smaller atoms whose centers of gravity are separated by the same amount. In either case, there are accumulations of scattering matter whose centers of gravity are separated by approximately the wave length of the wave associated with $hk0$. In the centrosymmetrical case, the centers of gravity must necessarily lie on the center of symmetry or the center must bisect the distance between them. This means that the wave has either a maximum or a minimum at the symmetry center.

The wave associated with $hk0$ can be represented by lines indicating the positions of the maxima. Since the origin may be either a maximum or a minimum, the positions of the minima must also be indicated. These are shown in Fig. 1 for 210, where the solid lines are maxima and the dotted, minima. If F_{210} is large, the probability is high that there are pairs of accumulations of scattering matter separated by an integral number of wave lengths and lying near either set of lines. Assume a second reciprocal lattice point, 130 , whose amplitude is also large. The maxima and minima of its wave are shown in Fig. 2 superimposed on those of 210. Since the probability is high that there are accumulations of scatter-

¹ Robertson, J. M., and White, J. G., *Jour. Chem. Soc.*, **607** (1945).

² Donnay, J. D. H., Joint Meeting Crystallographic Society of America and American Society for X-Ray and Electron Diffraction, New Haven Conn., March 31-April 3, 1948.

ing matter along the lines representing both 210 and $\bar{1}30$, it is obvious that the probability is highest at the intersections of the two sets of lines. Clearly, the addition of the traces of the maxima and minima of the waves of additional strong points, particularly of low index, will further define the most probable atomic locations. However, there will, in general, be more than one possible array. A study of missing reciprocal lattice points frequently reduces the number.

The absence of a reciprocal lattice point implies destructive interference of the diffracted radiation arriving at that point. This means that there are centers of gravity of scattering matter separated by distances having components equal to an integral number of half wave lengths in

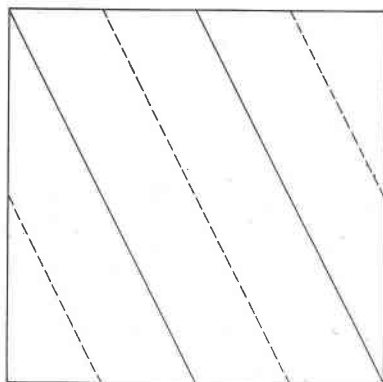


FIG. 1. Traces of the maxima and minima of the wave associated with 210 .

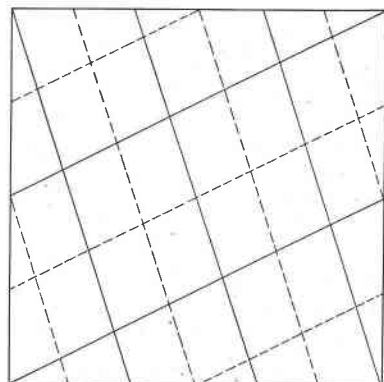


FIG. 2. Traces of the maxima and minima of the waves associated with 210 and $\bar{1}30$.

the direction normal to the wave front associated with the reciprocal lattice point. An even number of half wave lengths is possible only if the atoms lie along lines of zero amplitude. In other positions, each atom must have a centrosymmetrical equivalent separated from it by an odd number of half wave lengths in order for destructive interference to result. Atoms separated by an odd number of half wave lengths may lie along lines of zero, maximum or minimum amplitude since the conditions for destructive interference will always obtain. It is to be noted that, for each atom along a maximum, there will be a compensating one along a minimum.

EXAMPLE OF DETERMINATION OF ATOMIC POSITIONS

As an example of the use of the above described method, the most probable locations of the heavy atoms in lead chromate will be deter-

mined. The structure of lead chromate has been investigated by Brody³ who found the following parameters for lead and chromium:

	x	y	z
Pb	0.220	0.150	0.400
Cr	.215	.150	.896

The four strongest reciprocal lattice points in the $h0l$ series are 200, $\bar{1}03$, $\bar{2}02$, and 204. Figure 3 shows the traces of the maxima and minima of the cosine waves associated with these points. Probable atomic locations are indicated by circles; these are the regions where maxima or minima of all four waves either intersect or cooperate strongly.

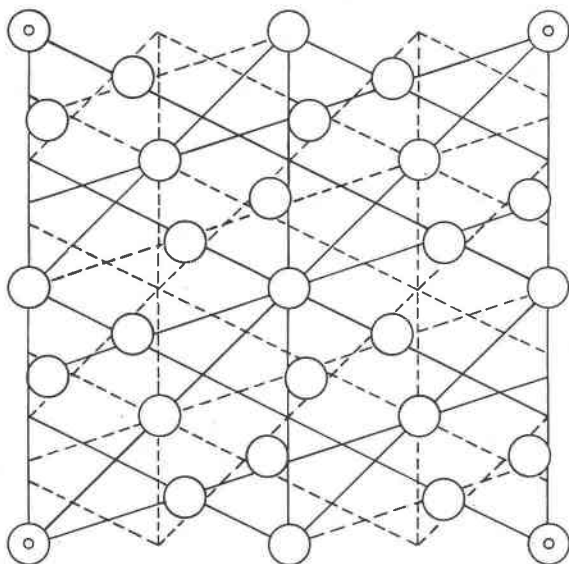


FIG. 3. Traces of the maxima and minima of the waves associated with 200, $\bar{2}02$, $\bar{1}03$, 204. Circles represent probable locations of the heavy atoms in PbCrO_4 .

It would appear from Fig. 3 that there is a large number of possible atomic arrangements. However, symmetry requirements reduce the number to a few possibilities. Lead chromate has the symmetry of the space group $P2_1n$. The $h0l$ projection is centrosymmetrical and the parameters of the general position are $x, z; \bar{x}, \bar{z}; 1/2+x, 1/2+z; 1/2-x, 1/2-z$. Since there are four formula weights of PbCrO_4 per unit cell, each real peak must generate three others by symmetry operations. (It is assumed that there are no coincidences of superimposed atoms in the projected cell.

³ Brody, S. B., *Jour. Chem. Phys.*, **10**, 650 (1942).

This is true in the present example, but in general it must not be assumed.) Applying these symmetry conditions, it is found that there are eight independent groups of the locations shown in Fig. 3. Four of these contain only two atoms per cell and may be discarded under the conditions noted above. The remaining four are shown in Fig. 4 (*A* through *D*).

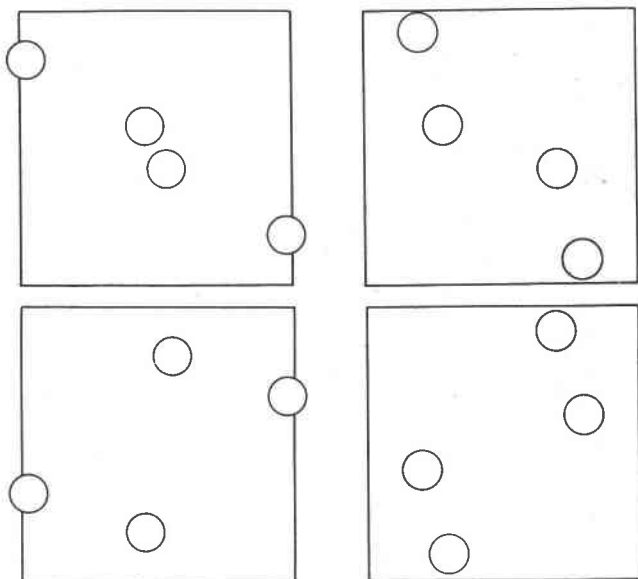


FIG. 4*A-D*. Possible arrays of atomic positions in PbCrO_4 .

Each array in Fig. 4 represents an atomic distribution for which the amplitudes of the reciprocal lattice points, 200 , $\bar{1}03$, $\bar{2}02$, and 204 will be large. Since there are two species of heavy atoms present, the correct atomic distribution will be represented by a combination of two of the arrays. In order to select the proper combination, we may now consider weak and missing reciprocal lattice points.

The proper combination of the maps of Fig. 4 will have all of the atoms lying along the lines of zero amplitude for a missing reciprocal lattice point or there will be as many along the maxima as along the minima. (The assumption is here made that the two atomic species have the same scattering power. Obviously they do not, but the approximation is useful.) By considering several missing reflections, it should be possible to reduce the various combinations of the maps to a number that can be handled easily.

In the case of lead chromate, the missing points of the $h0l$ series include

the following: $\bar{5}01$, 202, 406, and 105. Traces of the maxima and minima of the waves associated with these points are shown in Fig. 5. Only half of the cell is illustrated. Also in Fig. 5 are the most probable atomic locations determined previously. They are labelled according to which of maps of Fig. 4 they correspond. Thus *A* 1 and *A* 2 are the symmetrically related peaks in the left half of Fig. 4*A*.

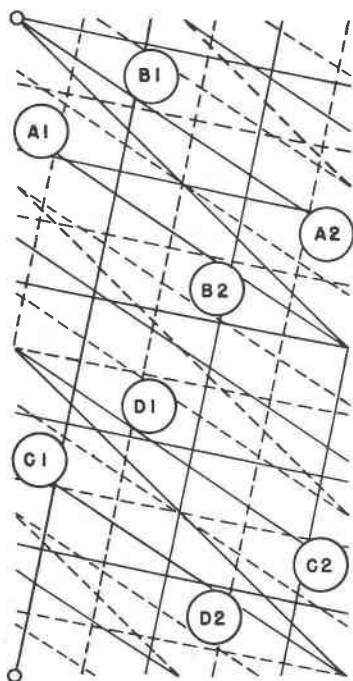


FIG. 5. Traces of the maxima and minima of the waves associated with $\bar{5}01$, 202, 105, and 406, showing the relation of amplitudes to probable atomic positions. (One-half the unit cell.)

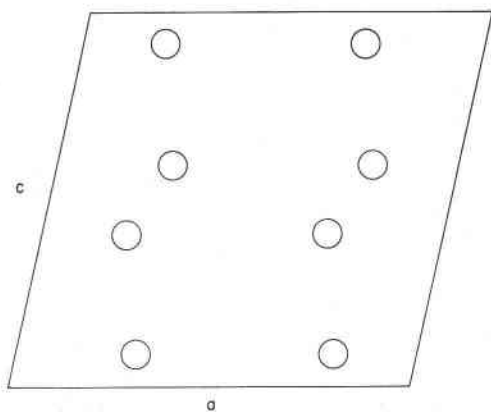


FIG. 6. Most probable structure of PbCrO_4 .

Figure 5 may be analyzed by tabulating for each wave what locations lie near maxima, minima, and zero. A possible combination is one for which all atoms lie near zero or for which there are as many near maxima as near minima. All others can be discarded as unlikely. Analysis of Fig. 5 is given in Table 1.

Consider first the wave associated with $\bar{5}01$. It is apparent from Table 1 that combinations which satisfy the conditions can be formed in the following manner:

TABLE 1. RELATION BETWEEN ATOMIC POSITIONS AND AMPLITUDES OF WAVES OF MISSING RECIPROCAL LATTICE POINTS

<i>Point</i>	<i>Maximum</i>	<i>Minimum</i>	<i>Zero</i>
501	B 1	A 1	None
	B 2	A 2	
	C 1	D 1	
	C 2	D 2	
202	None	None	All
105	A 1	C 1	B 1
	A 2	C 2	B 2
			D 1
			D 2
406	A 1	None	B 1
	A 2		B 2
	C 1		D 1
	C 2		D 2

The maps of Fig. 4 may be combined, in pairs, in the following ways:

A+B	B+C	C+D
A+C	B+D	
A+D		

B 1, B 2 and either A 1, A 2 or D 1, D 2 and C 1, C 2 and either A 1, A 2 or D 1, D 2. Combinations B 1, B 2 plus C 1, C 2 and A 1, A 2 plus D 1, D 2 can be eliminated, since all scattering matter would be concentrated along either maxima or minima. For 202, all combinations are possible because all positions lie near lines of zero amplitude. The other two waves can be analyzed similarly, and the results are given in Table 2. Since only the combination B+D satisfies the conditions for all four waves, it may be concluded that the most probable arrangement of the heavy atoms in lead chromate is that represented by the positions B and D. This combined array is shown in Fig. 6.

TABLE 2. MAP COMBINATIONS WHICH SATISFY CONDITIONS FOR MISSING RECIPROCAL LATTICE POINTS

<i>Point</i>	<i>Combination</i>					
	A+B	A+C	A+D	B+C	B+D	C+D
501	X	X			X	X
202	X	X	X	X	X	X
105		X			X	
406					X	

It is, of course, impossible to read accurate parameters from Fig. 6. However, crude values, representing the centers of the circles, can be refined by structure amplitude computations. Such rough parameters are listed in Table 3 along with the actual values found by Brody.

TABLE 3. COMPARISON OF ROUGH PARAMETERS FROM FIGURE 5 WITH VALUES REPORTED BY BRODY

Location	Parameters				Species
	Figure 6		Brody		
	<i>x</i>	<i>z</i>	<i>x</i>	<i>z</i>	
B 1	.20	.91	.215	.896	Cr
B 2	.29	.58	.285	.604	Cr
B 3	.80	.09	.785	.104	Cr
B 4	.71	.42	.715	.396	Cr
D 1	.21	.42	.22	.40	Pb
D 2	.30	.09	.28	.10	Pb
D 3	.79	.58	.78	.60	Pb
D 4	.70	.91	.72	.90	Pb

ANALYSIS OF PATTERSON VECTORS

In the preceding example, potential atomic positions were found to fall into four patterns which, when properly combined in pairs, give a composite pattern consistent with the structure determined by conventional methods. In general, analysis of the various maps will not be so simple. The well known Patterson vector diagram will be of aid in choosing the most likely map, since the vectors of the arrangement chosen must appear on the Patterson diagram. Inconsistent maps and combinations can thus be eliminated.

One may go even farther and, in many cases, actually construct a map of potential atomic positions corresponding to a particular Patterson vector. In the Patterson diagram, the direction and magnitude of an interatomic distance vector is known but, in general, the locations of the ends of the vector are unknown. Following the reasoning developed above, one can say that it is highly probable that the atoms which form the ends of the vector lie on or near maxima (or minima) of those waves of large amplitude whose wave lengths are approximately equal to the component of the vector in the direction normal to the wave front.

To determine potential sites for the atoms which produce the vector, one selects the strong reciprocal lattice points for whose waves the vector has the correct component. Maxima and minima of the waves may be plotted as before, and maps of possible atomic arrangements obtained. A simple and rapid method of accomplishing the selection is to prepare

in advance, on tracing cloth, charts with lines representing maxima and minima of all of the reciprocal lattice waves of the type $hk0$, similar to the transparencies prepared by Huggins⁴ for Fourier synthesis. The vector may then be drawn from the origin of the unit cell and the tracings placed in register one at a time. Those for which the end of the vector lies near a maximum or a minimum are the ones desired for construction of the maps. Tracings of this type are useful also when the type of map described earlier is constructed. The appropriate ones may be laid one over the other in register on a viewing box, and the potential atom locations marked off on a separate tracing. The same charts can, of course, be used in analysis of the missing reciprocal lattice points.

NOTE ON THE DETERMINATION OF PHASES

In cases such as the example described in this report where a logical structure can be deduced and where one may feel reasonably certain that the elements of the structure so determined control the phases of the various reflections, information concerning phases of additional reflections can also be deduced. Thus, in the case of lead chromate, it is apparent that all of the heavy atoms lie near maxima of 400, minima of 004, 103, and 402. The sign of 400 should, therefore, be positive and those of the latter three negative. Any analysis of this type must be viewed with considerable caution, however, particularly for the weaker reflections.

CONCLUSIONS

A method has been described by means of which probable atomic positions in crystals can be obtained rapidly and easily. The information thus obtained should prove useful in the selection of a logical structure for computation of structure amplitudes. In some cases, as in the example presented, the actual structure can be obtained uniquely. In general, this will not be so and many possibilities will exist. The use of Patterson vectors will help the selection. Results will probably be poor when there are many atoms of nearly the same scattering power and when there is no great variation of intensities. Accuracy cannot, of course, be obtained by use of the method, nor can low scattering atoms be located. It is believed that the method may be useful, under proper conditions, in guiding the preliminary steps of structure determinations.

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⁴ Huggins, M. L., *Jour. Am. Chem. Soc.*, **63**, 66 (1941).