THE USE OF ANOMALOUS SCATTERING FOR THE DETERMINATION OF CRYSTAL STRUCTURES—$KMnO_4$

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1. Introduction

It is well known that when the frequency of the incident radiation is very close to that of the absorption edge of an atom, it scatters anomalously. The anomalous scattering makes itself felt in two ways; firstly by a decrease in the real part of the scattering factor, and secondly by an introduction of a phase-lag during the scattering process. The former effect manifests itself irrespective of whether the frequency of the incident radiation (ν) is smaller or larger than that of the absorption edge (ν_a), whereas the latter effect exists only when $\nu > \nu_a$ (James, 1948). This phase change during anomalous scattering is mainly responsible for the failure of the Friedel's law in non-centrosymmetric structures and has been used in a most elegant manner for the determination of the absolute configuration of non-centrosymmetric crystals (Bijvoet, 1954). Significant advance has recently been made in this method for the direct evaluation of the phases of the structure amplitudes by Ramachandran and Raman (1956) and by Okaya, Saito and Pepinsky (1955).

In this paper we shall concern ourselves only with the first effect, *i.e.*, the decrease in the real part of the scattering factor of an anomalously scattering atom. It is quite obvious that this effect can be used to great advantage in the direct determination of structures of crystals. For example, the relative intensity data obtained for a crystal with X-rays having wavelengths very far from the absorption edge of the atoms, would necessarily be different from those obtained with the incident radiation having a wavelength close to an absorption edge of one of the atoms. This difference, although very small, is very well within the limits of experimental determination and has been measured to a fair degree of accuracy by different authors (James, 1948).

The use of two appropriate wavelengths with one crystal would in effect, be equivalent to the substitution of one of the atoms of the crystal by an atom of slightly different scattering power. Consequently, all the methods and techniques that are applicable to the isomorphous replacement method can

be used. There have been a few attempts to make use of the anomalous scattering for structure determination. Particular mention may be made of the work of Bradley and Rodgers (1934) in the determination of the structure of Heusler alloys and that of Jones and Sykes (1937) in establishing the super-lattice structure of copper-zinc alloys. Although this technique has long been thought of by many (*see* for example *The Crystalline State*, Vol. III, p. 227) it has never been used for solving a structure or for the determination of the signs of the structure factors. It is the purpose of this paper to show that the anomalous scattering method is practicable and can be used with success at least in the case of relatively simple structures.

The substance used in this investigation is $KMnO_4$. The choice of the substance was governed by many factors. The primary one was that the Mn atom gave the maximum decrease in the real part of the scattering factor for the radiations most readily available in this laboratory (copper, cobalt and iron). Further at the commencement of this investigation it was thought that as the structure of this crystal had been solved (Mooney, 1931) the practicability or otherwise of this technique could be decided quite easily. Unfortunately, a careful study of the literature (Wyckoff, 1935) revealed that the published atomic parameters for $KMnO_4$ were by no means accurate, thus necessitating a complete redetermination of the structure.

Potassium permanganate belongs to the orthorhombic space group *Pnma* with cell dimensions $a = 9{\cdot}09$ Å, $b = 7{\cdot}41$ Å, $c = 5{\cdot}72$ Å, with four molecules per unit cell.

2. EXPERIMENTAL PROCEDURE

From the remarks made above, the procedure to be followed for obtaining the data for structure computations would be the following:—(i) to choose the appropriate radiations for the particular crystal under study, (ii) using these to obtain satisfactory Weissenberg photographs and to measure the intensities of all the recorded reflexions, (iii) to make the proper corrections for geometrical and physical factors and finally (iv) to reduce the data obtained with the two radiations to the same relative scale.

The success of the investigation would largely depend on the preciseness with which each of these operations can be carried out. For example, any inaccuracy in the reading of the intensity or in the application of the absorption correction may completely mask the comparatively small differences in the relative intensities caused by the anomalous scattering of one of the atoms.

It would obviously be most advantageous to use two radiations for which the anomalous scattering atom (Mn in the present case) exhibits the maximum

difference in scattering power. The scattering factor f of an atom is given by

$$f = f_\theta + \Delta f' + i\,\Delta f'' \qquad (1)$$

TABLE I (*a*)

$\Delta f'$ and $\Delta f''$ for manganese for CuKα, CoKα and FeKα f_0 for Mn is 25. The K-absorption edge of Mn.....1·895 Å

Radiation	λ_i	λ_i/λ_k	$-\Delta f'$	$\Delta f''$
CuKα ..	1·541 Å	0·813	0·789	2·63
CoKα ..	1·789	0·944	2·62	3·34
FeKα ..	1·936	1·021	4·21	0·00

TABLE I (*b*)

Values of $|f|$ for Mn, K and O for different values of $\sin\theta/\lambda$

$10^{-8}\times \frac{\sin\theta}{\lambda}$ / $\lvert f\rvert$	0·0	0·1	0·2	0·3	0·4	0·5	0·6
f^{Mn}_{Cu}	24·4	21·5	17·6	14·4	12·2	10·6	9·3
f^{Mn}_{Fe}	20·2	17·9	15·9	10·7	8·5	6·9	5·5
f^{Mn}_{Co}	22·7	19·8	14·0	12·7	10·6	9·1	7·8
f^{K}	18·0	16·5	13·3	10·8	8·9	7·8	7·1
f^{O}	8·0	7·1	5·3	3·9	2·9	2·2	1·8

where f_θ is the scattering factor for waves short in comparison with the wavelength of the absorption edge of the scattering element and $\Delta f'$ and $\Delta f''$ are the real and the imaginary parts of the corrections to be applied to the scattering factor on account of the dispersion effects. The values of these scattering constants for manganese for CuK_α, CoK_α and FeK_α calculated on the basis of Honl's theory are given in Table I *a*. The absence of the phase-lag for FeK_α (*i.e.*, $\Delta f'' = 0$) must be noted. Further, since f_θ is a decreasing function of $\sin\theta/\lambda$ and $\Delta f'$ and $\Delta f''$ are for most practical purposes independent of the angle of scattering, the effect of anomalous scattering is most evident for large

values of θ. The scattering factor $|f|$ for Mn for the three wavelengths for different values of $\sin\theta/\lambda$ are given in Table I *b*. The scattering factors for potassium and oxygen have also been entered in this table. It has been assumed that as the three radiations used are quite away from the absorption edge of these atoms, their scattering factors are independent of the incident frequency. It must be mentioned that although data using the K_α radiations of Cu, Co and Fe were recorded, most of the computations were made using those for CuK_α and FeK_α.

Using a cylindrical specimen having diameter less than 0·08 mm., multiple film zero-layer Weissenberg photographs about the *b*-axis (*hol*) were taken with copper K_α, cobalt K_α and Iron K_α radiations. Although there was a considerable amount of fluorescence, particularly for the first two radiations, the first film in the stack served as an efficient filter. The intensity was, therefore, measured from the second film onwards. Care was taken to adjust the times of exposure to compensate for the considerable differences in the absorption coefficients of the crystal and of the film for the three radiations.

The intensities were estimated visually, the comparison being made with a standard scale independently by the three investigators. The film factor for each of the three radiations was also determined accurately and it was found to follow the λ^{-3} law fairly well. The relative intensities were corrected for Lorentz and polarisation factors and also for absorption, using Bradley's table for cylindrical specimens.

The (*hko*) data were obtained only for CuK_α and the (*hol*) and (*hko*) data for $KClO_4$ were also recorded for the same radiation.

The next important problem is to put the data obtained with the different radiations on the same relative scale. This becomes significant particularly when " difference techniques " are adopted. For example, when a difference Patterson projection is made, if the relative scaling is not perfect, the map would be superposed on a faint Patterson which, by the introduction of more peaks, would very much complicate the interpretation.

A modification of the Wilson's method similar to the one suggested by Harker (1956) was used. The equation

$$C\frac{\langle I_{Cu}\rangle}{\langle I_{Fe}\rangle} = \frac{\sum_{r=1}^{N}\langle {}_{Cu}f_r^2\rangle}{\sum_{r=1}^{N}\langle {}_{Fe}f_r^2\rangle} \qquad (2)$$

was employed in the estimation of the scale factor C. Here $\langle I_{Cu}\rangle$ and $\langle I_{Fe}\rangle$ are the average intensities over particular ranges of $\sin^2\theta/\lambda^2$ and $\langle f_r\rangle$ the corresponding values of the scattering factors of all the representative atoms.

This method proves eminently successful as the *relative scale factor* between copper and iron data obtained by this method was correct to within 2% of the final value found at the completion of the investigation, although the *absolute scale factor* had to be altered by a considerable extent during the structure determination.

3. The Anomalous Difference Patterson

When the X-ray diffraction data for a pair of isomorphous crystals are available, perhaps the simplest method of utilising this data for a direct solution of the structure is the " Difference Patterson " technique. This method first suggested by Buerger (1942) has been thoroughly investigated by Kartha and Ramachandran (1955). The method consists of making a Patterson with $(|F_{M_1}|^2 - |F_{M_2}|^2)$ as coefficient, where M_1 and M_2 refer to the two isomorphous crystals. The peaks in such a diagram represent the interactions between the replaceable atoms themselves and also those between the replaceable atoms and the rest of the atoms in the structure, while the interactions between the non-replaceable atoms get cancelled out. This considerably reduces the number of peaks present, thus facilitating the interpretation. The symmetries introduced into this Difference Patterson due to the very nature of the Patterson function together with the symmetry of the replaceable atoms themselves have been most exhaustively treated in the paper by Kartha and Ramachandran cited above and will therefore not be dealt with here. Suffice it to say that in the most general case it is essential to know the positions of the replaceable atoms if the complete structure is to be obtained from the Difference Patterson diagram. Once the co-ordinates of the replaceable atoms are known, the correct structure can be obtained using Buerger's minimum function method (Buerger, 1951).

It is quite evident that the above methods can be directly applied when accurate intensity data are available for the same crystal with two wavelengths which are scattered anomalously by one set of atoms in the crystal; for in this case an exact isomorphism can be realized. With the (*hol*) data obtained for $KMnO_4$ with CuK_α, and FeK_α, a Difference Patterson map was computed with $(|F_{Cu}|^2 - |F_{Fe}|^2)$ as coefficient. Since the total number of reflexions observed with CuK_α for this zone was 90 and that obtained with FeK_α was only 60, the Difference Patterson could only be made using these 60 reflexions and the diagram obtained is given in Fig. 1. To see whether this map has any significance at all a Difference Patterson given in Fig. 2 was made using $(|F_{Cu}^{KMnO_4}|^2 - |F_{Cu}^{KClO_4}|^2)$ as coefficient. The striking similarity between the Anomalous Difference Patterson (A.D.P.) and the Isomorphous Difference Patterson (I.D.P.) was most gratifying and it indicated without any doubt

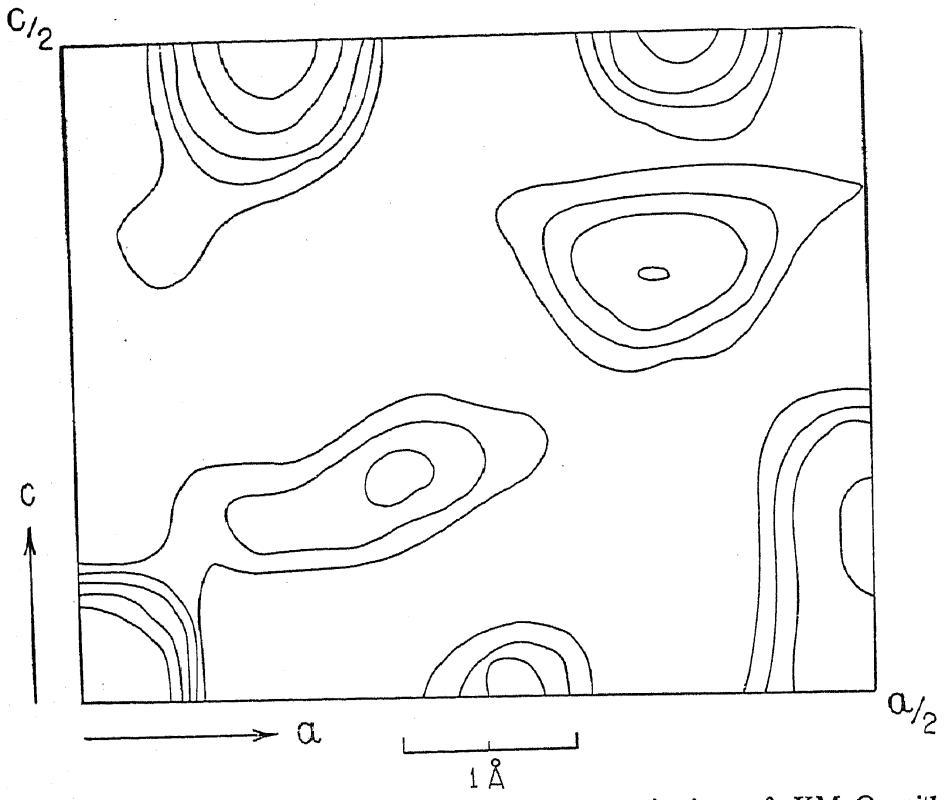

FIG. 1. The *b*-axis Anomalous Difference Patterson projection of $KMnO_4$ with $(|F_{Cu}|^2 - |F_{Fe}|^2)$ as coefficient.

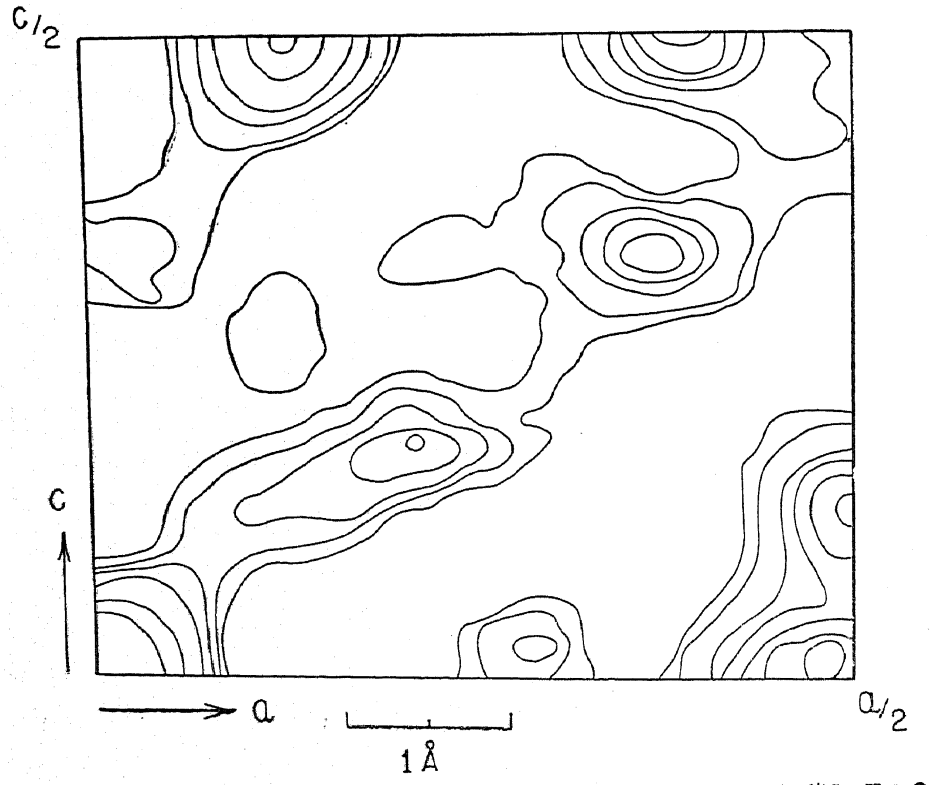

FIG. 2. The *b*-axis Isomorphous Difference Patterson projection with $(|F_{Cu}^{KMnO_4}|^2 - F_{Cu}^{KClO_4}|^2)$ as coefficient.

that the anomalous technique can be used with success, at least for this particular structure. It may be remarked that it was rather difficult to distinguish between the Mn-Mn peak and the Mn-2 (0) peak in the simple Patterson projection. But this ambiguity was completely removed in the A.D.P. map because of the considerable enhancement of the peak due to the Mn-Mn interaction.

Knowing the Mn-Mn peaks the complete structure can be recovered, as has been remarked earlier, by the use of Buerger's minimum function method. This is done by drawing contours corresponding to the lower of the two values in two superposed A.D.P. diagrams, one translated with respect to the other in such a manner that the origin of one was on one of the identifiable atoms of the other. Figure 3 represents the minimum function diagram obtained after two translations. The different atoms of the $KMnO_4$ structure can be easily identified. These atomic co-ordinates could well be the starting point for the refinement of the parameters by the Fourier synthesis method. But before proceeding to refine the atomic parameters we shall investigate whether the position of the anomalously scattering atom can be determined by a direct method and, if so, whether the signs of the structure factors can also be evaluated.

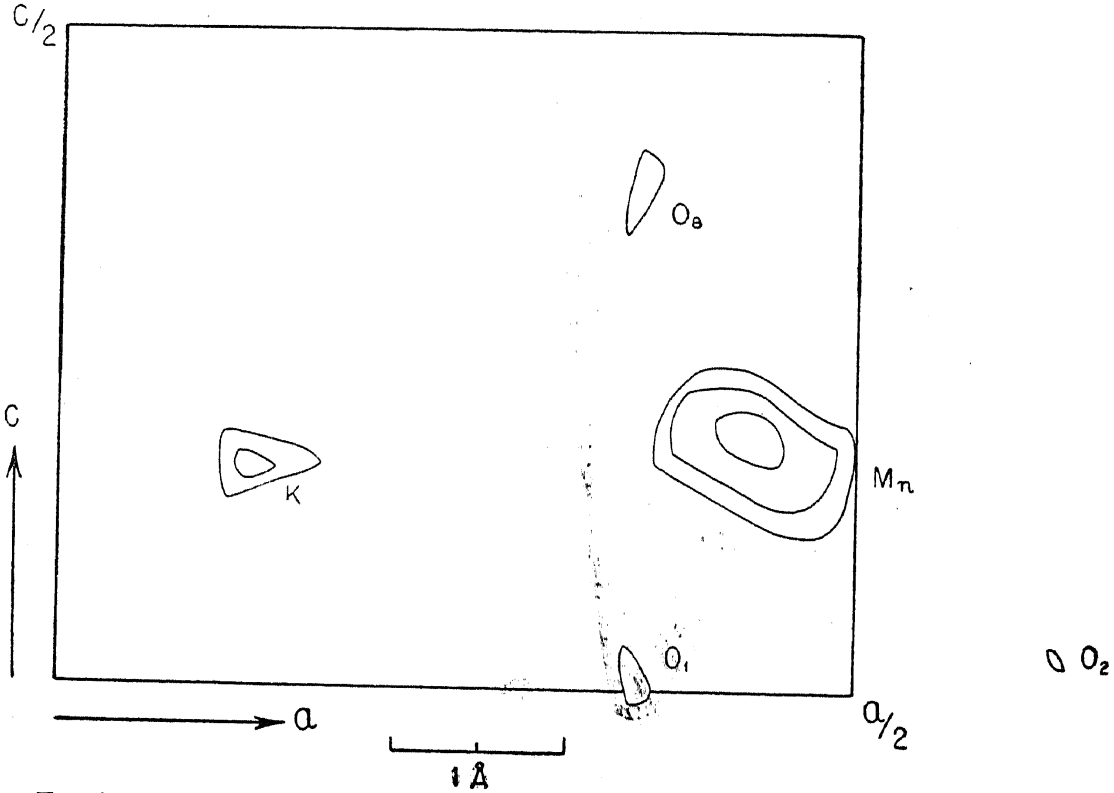

FIG. 3. Structure of $KMnO_4$ derived from the A.D.P. by Buerger's minimum function method.

4. Position of the Anomalously Scattering Atom

The Harker section of the A.D.P. diagram can be used to fix the position of the excited atom because this map will contain only the excited atom interactions, apart from accidental non-Harker peaks [Buerger (1942); Kartha and Ramachandran (1955)]. Instead, the positions of the anomalous scatterers can be determined directly by making a Patterson projection with $(|F_{Cu}| - |F_{Fe}|)^2$ as coefficient.* The corresponding function for isomorphous replacement was first used by Frueh (1953) for a different purpose and has been called by him the "Patterson function of the difference structure". In the equation for centrosymmetric crystals

$$(F_{Cu} - F_{Fe}) = \sum_j (f_j^{Cu} - f_j^{Fe}) \cos 2\pi (hx_j + ky_j + lz_j)$$

the right-hand-side exists only for the anomalously scattering atoms. Hence the Patterson using $(F_{Cu} - F_{Fe})^2$ corresponds to the interaction due to the anomalously scattering atoms only. Since one does not know the signs of F_{Cu} and F_{Fe} there would be some difficulty. By the very nature of the function, $(|F_{Cu}| - |F_{Fe}|)^2 = (F_{Cu} - F_{Fe})^2$ when F_{Cu} and F_{Fe} are of the same sign. If, however, the two are of different signs the value of the coefficient used will be different. For most practical purposes in the present case, $f_{Cu} - f_{Fe} \simeq 4$ and so the number of reflexions wherein there would be such a change in sign would be very small indeed. Even here such a reflexion is not completely omitted from the calculation but a slightly different weight for the reflexion is used. This should hardly affect the position of the peaks. Figure 4 gives the projection made with $(|F_{Cu}| - |F_{Fe}|)^2$ as coefficient. The position of the anomalously scattering atom can be directly obtained from the map. The other faint peaks corresponding to other interactions (*cf.* Anomalous Difference Patterson in Fig. 1) appear because of one or more of the following reasons: (*a*) errors in the measurement of the intensities, (*b*) errors due to differences in extinctions of the intense reflexions for the different radiations and (*c*) error in the scale factor. In spite of these errors the positions of the Mn-Mn interactions are quite unmistakable.

5. Determination of the Signs of the Structure Factors

Once the position of the anomalously scattering atom is determined, it must be possible to obtain the signs of the structure amplitudes by the method suggested by Booth (1948) for isomorphous crystals. If j represents the anomalously scattering atoms and p the other atoms in the structure and if F_{Cu}

* The authors are most grateful to Dr. Gopinath Kartha for drawing their attention to this extremely useful function.

and F_{Fe} are the structure factors for CuK_α and FeK_α then for a centrosymmetric crystal,

$$\pm F_{Cu} = \sum_j f_j^{Cu} \cos 2\pi (hx_j + ky_j + lz_j) + \sum_p f_p^{Cu} \cos 2\pi (hx_p + ky_p + lz_p) \tag{3}$$

$$\pm F_{Fe} = \sum_j f_j^{Fe} \cos 2\pi (hx_j + ky_j + lz_j) + \sum_p f_p^{Fe} \cos 2\pi (hx_p + ky_p + lz_p) \tag{4}$$

Since $f_p^{Cu} = f_p^{Fe}$ and $f_j^{Cu} \neq f_j^{Fe}$

$$(\pm F_{Cu}) - (\pm F_{Fe}) = \sum_j (f_j^{Cu} - f_j^{Fe}) \cos 2\pi (hx_j + ky_j + lz_j) \tag{5}$$

For the (*hol*) reflexions of the space group *Pnma* equation (5) reduces to

$$(\pm F_{Cu}) - (\pm F_{Fe}) = 4 \sum_j (f_j^{Cu} - f_j^{Fe}) \cos 2\pi hx_j \cos 2\pi lz_j \tag{6}$$

$$\text{for } h + l = 2n \text{ and}$$

$$(\pm F_{Cu}) - (\pm F_{Fe}) = -4 \sum_j (f_j^{Cu} - f_j^{Fe}) \sin 2\pi hx_j \sin 2\pi lz_j \tag{7}$$

$$\text{for } h + l = 2n + 1$$

Since the positions of the anomalously scattering atoms are known (*see* previous section) the trigonometric part of equation can be computed. Further as f_j^{Cu} and f_j^{Fe} are known the signs of F_{Cu} or F_{Fe} can be fixed by inspection. In the present case $f^{Cu} - f^{Fe} \simeq 4$ and using equations (6) and (7), it was possible to determine the signs of as many as 50% of the reflexions recorded with CuK_α (*i.e.*, 75% of the reflexions recorded with FeK_α). The structure factors whose signs could be unambiguously determined have been indicated in Table IV. From this the determination of the structure and the refinement of the parameters is almost a routine procedure.

6. Refinement of the Parameters

Only the barest details of the determination of the structure will be given in this section. For any further details one may refer to the forthcoming papers on the structure of NH_4ClO_4 and $KClO_4$ by two of the present writers (K. V. and N. V. M.). Since $KMnO_4$ belongs to the space group *Pnma*, the K, Mn and two oxygen atoms lie on the symmetry planes. It is, therefore, necessary to determine only the x and z co-ordinates for these atoms while all the three co-ordinates have to be found for the two remaining oxygens which lie on either side of the symmetry plane.

The x and z co-ordinates are determined from the b-axis data. The first (*hol*) Fourier projection was made with 42 structure factors whose signs were determined by the method indicated in the previous section.

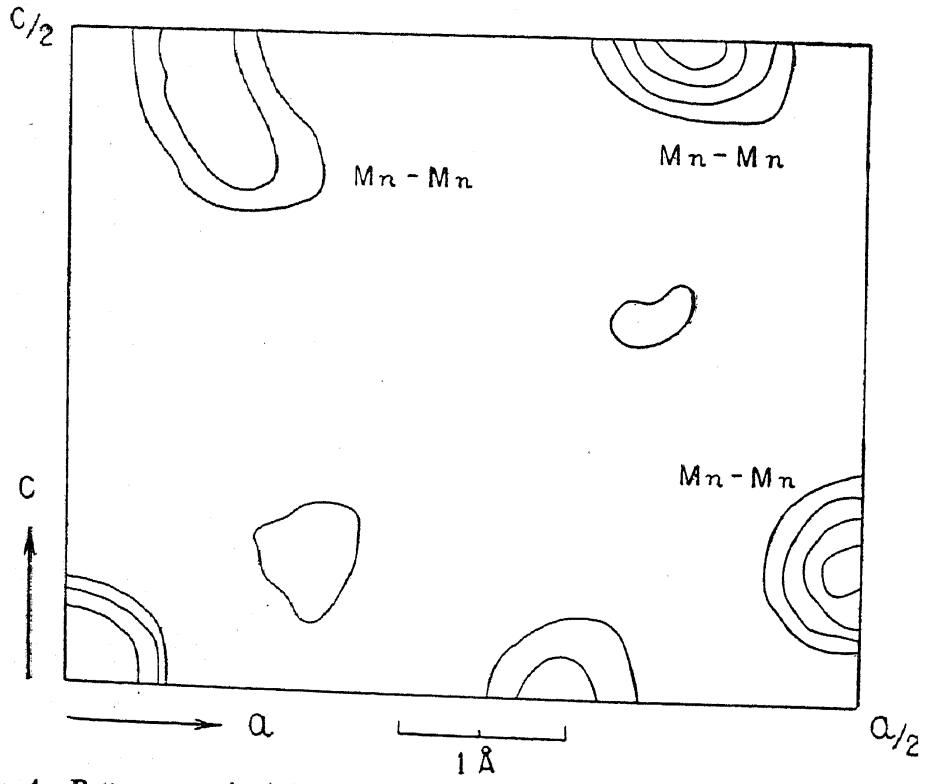

FIG. 4. Patterson projection made with $(|F_{Cu}| - |F_{Fe}|)^2$ as coefficient to obtain the position of the anomalously scattering atom.

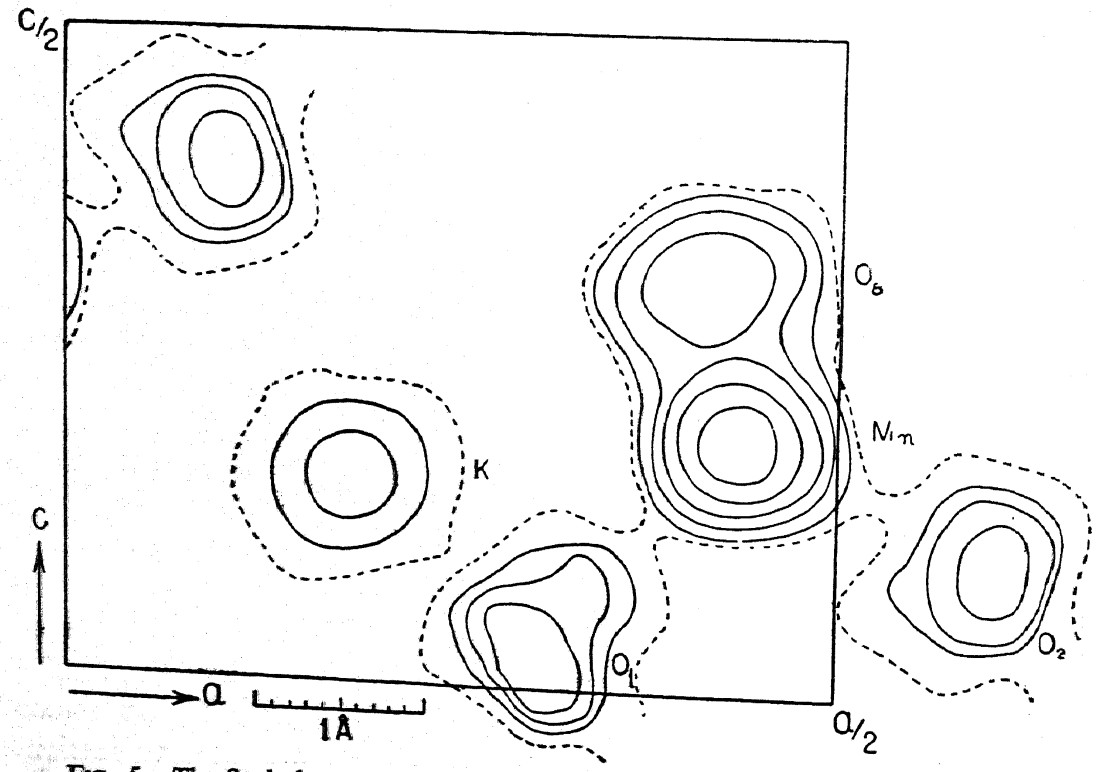

FIG. 5. The final electron density projection of $KMnO_4$ on the (010) plane.

Subsequent refinement of x and z parameters was carried out by the iterative process of Fourier and difference syntheses. At each stage the scale and temperature factors were estimated. A correction was applied for the few reflexions which were obviously affected by extinction effects. The final (*hol*) projection is given in Fig. 5. The R-factor for this projection was 0·145 (omitting a few unobservable reflexions).

The only other parameter that remains to be determined is the y parameter of the oxygen atoms off the symmetry plane. An approximate order of this co-ordinate was first estimated by assuming the MnO_4 group to be nearly a regular tetrahedron. The refinement of this parameter was carried out by the method of least squares, a method most suitable in this case as there were only 30 reflexions in this projection. The R-factor for this zone was 0·153 (removing the three most intense reflexions 020, 040 and 210 which suffer extinction effects). Table II gives the final parameters of the different atoms together with those reported by Mooney referred to the centre of

TABLE II

The final atomic parameters in fractional co-ordinates

Atom	Present work			Previous work		
	x	y	z	x	y	z
Potassium ..	0·183	0·750	0·158	0·185	0·750	0·160
Manganese ..	0·438	0·250	0·192	0·445	0·250	0·170
Oxygen 1 ..	0·321	0·250	0·038	0·365	0·250	−0·010
Oxygen 2 ..	0·594	0·250	0·106	0·625	0·250	0·110
Oxygen 3 ..	0·417	0·037	0·317	0·435	0·030	0·300
Oxygen 4 ..	0·417	0·463	0·317	0·435	0·470	0·300

symmetry as the origin. Significant differences particularly in the positions of the oxygens atoms (O_1 and O_2) can be noticed. Table III gives the different atomic distances in the MnO_4 group. It is rather difficult to determine the order of the errors present in the values given in Table III because of the presence of two heavy atoms in the asymmetric unit. It is estimated that the Mn–O distance will be correct to within 5%. The R-factor for the structure

TABLE III

Interatomic distances in $KMnO_4$ structure

Atoms	Present work	Previous work
Mn—O_1 ..	1·56 Å	1·69 Å
Mn—O_2 ..	1·56	1·52
Mn—O_3 ..	1·54	1·58
Mn—O_4 ..	1·54	1·58
O_1—O_2 ..	2·53	2·54
O_2—O_3 ..	2·55	2·62
O_1—O_3 ..	2·55	2·70
O_3—O_4 ..	2·44	2·53

with the K and Mn contributions removed is about 30%. The observed structure factors and those calculated using the final atomic positions for (*hol*) reflexions for the three radiations are given in Table IV and Table V gives the corresponding quantities for (*hko*) reflexions. Table VI gives the discrepancy factors.

7. CONCLUDING REMARKS

It is clear that if the structure is accurately known, one could reverse the process and compute the experimental scattering curve for the anomalously scattering atom for the different incident radiations. This would involve assuming a knowledge of the scattering factor curves for the non-anomalously scattering atoms. Even in the present investigation there are some indications that for Iron radiation $\Delta f'$ for Mn is not quite independent of the angle of the scattering. More accurate experimentation is necessary before one could assert this.

It is not necessary to deal here specifically with the properties of the Anomalous Difference Patterson for it behaves practically as the Isomorphous Difference Patterson does. Probably the only significant difference between the two will be the considerably greater amount of diffraction or termination errors that would exist in the former. This arises because $(f_{Cu} - f_{Fe})$ is practically constant and not a decreasing function of θ as it is in isomorphous case.

TABLE IV

Observed and calculated values of the structure factor for the (hol) reflexions of $KMnO_4$ for CuK_α, FeK_α and CoK_α

h o	F_0^{Cu}	F_c^{Cu}	F_0^{Fe}	F_c^{Fe}	F_0^{Co}	F_c^{Co}	*h o l*	F_0^{Cu}	F_c^{Cu}	F_0^{Fe}	F_c^{Fe}	F_0^{Co}	F_c^{Co}
1	2	3	4	5	6	7	8	9	10	11	12	13	14
0 0 2†	80·4	−88·9	70·6	−77·6	75·2	−83·3	9 0 1	VVW	<1	..	..	..	..
0 0 4†	23·9	−27·3	26·1	−29·5	24·9	−28·5	9 0 3	4·0	5·5	..	..	..	..
0 0 6†	61·0	51·7	47·8	45·2	50·4	48·5	9 0 5	15·7	15·7	..	..	..	..
0 0 8	26·7	−27·6	..	..	..	..							
							2 0 1†	47·9	45·3	36·5	38·7	40·5	43·3
2 0 0†	44·0	40·4	28·3	28·5	32·4	33·6	2 0 3†	44·8	−41·5	35·9	−36·7	37·9	−39·0
4 0 0	40·6	−40·3	37·8	−40·0	41·5	−40·2	2 0 5	16·1	13·3	15·8	16·1	11·7	15·0
6 0 0†	24·3	−25·3	12·7	−16·0	18·4	−20·7	2 0 7	18·2	23·6	20·5	19·0	18·3	21·3
8 0 0	49·9	−63·7	46·7	−54·3	51·8	−59·6	2 0 9	15·5	15·4	..	..	..	..
10 0 0	VVW	∼0	..	..	..	..							
							4 0 1†	102·0	108·6	84·5	94·9	92·3	101·4
2 0 2†	58·6	−48·4	45·8	−40·5	46·7	−44·2	4 0 3†	49·2	−38·8	37·0	−31·4	40·5	−35·1
2 0 4†	14·1	11·4	6·8	10·5	9·3	11·0	4 0 5†	48·2	−45·1	32·4	−36·1	42·2	−43·1
2 0 6†	VVW	1·8	3·3	− 2·2	8·4	<1	4 0 7	30·2	35·1	..	..	..	..
2 0 8	13·5	15·7	..	..	..	..	4 0 9	VVW	3·8	..	..	..	..
4 0 2	8·2	6·8	5·7	6·6	7·3	6·6	6 0 1†	21·4	16·8	VVW	1·4	VVW	5·7
4 0 4	11·4	8·7	12·3	9·6	12·6	9·6	6 0 3	9·6	10·6	VVW	− 1·4	VVW	− 2·0
4 0 6	VVW	4·3	..	..	..	..	6 0 5	VVW	7·8	VVW	− 1·0	VVW	<1
4 0 8	VVW	2·0	..	..	..	..	6 0 7	6·0	6·6	..	..	..	..
6 0 2†	25·8	27·8	18·8	22·0	21·7	25·2	8 0 1	7·4	9·0	14·3	− 8·6	7·9	− 8·6
6 0 4†	12·1	4·8	4·2	− 3·0	5·7	− 3·6	8 0 3	4·8	7·3	10·6	7·7	5·7	7·7
6 0 6	VVW	∼0	..	..	..	..	8 0 5	5·2	7·4	..	..	..	..
6 0 8	6·7	13·0	..	..	..	..	8 0 7	2·8	5·2	..	..	..	..

† Reflexions whose signs could be determined by the method given in Section 5.

TABLE IV—(*Contd.*)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
8 0 2†	25·4	29·0	19·7	21·2	22·2	25·1	10 0 1	VVW	− 8·1	..	..	..	..
8 0 4†	VVW	6·0	2·5	6·0	VVW	5·4	10 0 3	6·3	8·7	..	..	..	..
8 0 6	24·8	23·8	..	..	..	..							
							1 0 2†	50·3	−44·9	35·2	−40·8	43·9	−42·5
10 0 2	6·4	6·5	..	..	..	..	1 0 4†	25·2	25·1	17·6	18·5	21·8	21·2
10 0 4	7·2	7·2	..	..	..	..	1 0 6†	3·9	− 8·9	VVW	− 5·4	4·5	− 7·3
							1 0 8	12·0	−15·3	..	..	18·4	−14·9
1 0 1†	32·9	−25·5	27·3	−20·2	28·4	−22·8							
1 0 3†	5·9	1·5	15·7	−12·7	10·7	− 7·0	3 0 2†	25·0	19·5	25·8	29·2	26·1	24·5
1 0 5†	16·4	−13·0	VVW	− 1·7	9·8	− 7·5	3 0 4†	28·8	19·6	3·5	7·0	15·8	13·0
1 0 7†	15·1	18·0	6·3	10·9	11·0	13·5	3 0 6†	19·1	−21·1	8·4	−13·9	13·7	−18·3
1 0 9	3·0	1·0	..	..	..	..	3 0 8	4·9	8·3	..	..	..	..
3 0 1†	13·8	−12·2	3·3	− 9·8	6·3	−10·7	5 0 2	VVW	~ 0	VVW	− 1·8	VVW	2·5
3 0 3†	70·3	64·5	53·7	59·9	59·8	62·0	5 0 4†	24·4	20·4	4·2	8·4	15·6	13·7
3 0 5†	23·2	−18·6	17·3	−14·6	19·3	−16·9	5 0 6†	16·5	−16·4	..	..	..	..
3 0 7†	5·6	− 8·2	11·8	−10·6	6·2	− 9·9							
3 0 9	10·0	8·1	..	..	..	..	7 0 2†	40·4	−45·4	31·7	−42·3	35·3	−43·9
							7 0 4†	24·7	24·5	21·8	18·8	24·7	19·7
5 0 1†	15·9	14·5	9·9	12·6	11·5	13·2	7 0 6	VVW	− 5·9	..	..	..	..
5 0 3†	40·9	−34·0	33·6	−29·7	36·3	−31·8							
5 0 5	VVW	~0	..	..	VVW	− 1·6	9 0 2	8·8	9·4	10·0	6·0	9·4	6·9
5 0 7	6·0	6·9	..	..	8·5	9·3	9 0 4	8·5	7·6	..	..	..	..
							9 0 6	VVW	1·6	..	..	..	..
7 0 1†	9·6	6·7	..	..	3·5	4·7							
7 0 3†	11·9	−11·5	..	..	4·7	− 8·0	11 0 2	7·8	7·3	..	..	..	..
7 0 5†	12·5	11·2	..	..	10·0	6·1							
7 0 7	9·6	− 8·8	..	..	..	..							

† Reflexions whose signs could be determined by the method given in Section 5.

TABLE V

Observed and calculated structure factors, for the (hko) reflexions of $KMnO_4$ for CuK_α radiation

h k o	F_0	F_c	*h k o*	F_0	F_c
2 0 0	41·5	34·7	8 2 0	28·9	38·4
4 0 0	43·5	— 38·4	8 4 0	18·8	31·0
6 0 0	24·9	— 23·7			
8 0 0	53·8	— 56·1	2 1 0	89·3	100·3
10 0 0	VVW	~0	2 3 0	36·4	— 41·8
			2 5 0	21·1	38·3
0 2 0	112·3	—124·9			
0 4 0	82·0	94·5	4 1 0	11·2	— 5·8
0 6 0	30·2	— 37·8	4 3 0	10·3	18·1
			4 5 0	7·7	5·1
2 2 0	14·3	8·5			
2 4 0	16·0	9·8	6 1 0	55·5	52·6
2 6 0	VVW	— 1·9	6 3 0	30·8	— 37·4
			6 5 0	13·1	21·7
4 2 0	4·0	5·4			
4 4 0	10·0	— 12·8	8 1 0	7·4	10·4
4 6 0	2·0	3·7	8 3 0	9·5	— 13·8
6 2 0	11·0	— 12·6	10 1 0	23·6	— 24·3
6 4 0	9·6	— 7·2	10 3 0	18·8	15·4

TABLE VI

Discrepancy factor for $KMnO_4$ for (hol) reflexions

	CuKα	FeKα	CoKα
$\Sigma \lvert F_0 \rvert$ ..	1623·5	1016·7	1180·7
Taking all reflexions			
$\Sigma \lvert \lvert F_0 \rvert - \lvert F_c \rvert \rvert$ ..	275·9	167·0	174·0
R ..	0·170	0·164	0·147
Omitting unobservable reflexions			
$\Sigma \lvert \lvert F_0 \rvert - \lvert F_c \rvert \rvert$ ..	234·6	159·7	156·8
R ..	0·145	0·157	0·133

There is no doubt that theoretically at least the method of anomalous dispersion is capable of varied application. The method of using a wavelength longer than that of the absorption edge can be used for the determina-

tion of both centrosymmetric and non-centrosymmetric structures (not, however, the absolute configuration). When, on the other hand, a wavelength smaller than that of the absorption edge is used, the structure of both centro and non-centrosymmetric crystals can again be determined but with one significant difference, that the structure obtained in the non-centrosymmetric case would be the absolute configuration.

The determination of the signs of the structure factors of centrosymmetric crystals by the anomalous dispersion method seems to be very promising. But it is rather difficult to evaluate at this stage the power of this method. Whether this method would remain just a novelty or whether it would be capable of yielding practical results of significance is yet to be seen. One thing, however, is certain: that if any advance in this direction is to be made one has to abandon the photographic technique in favour of the very much more accurate Geiger or scintillation counter method of measuring intensities.

SUMMARY

The decrease in the scattering factor when the incident radiation is close to the absorption edge of an atom has been utilized for determining the structure of the centrosymmetric crystal $KMnO_4$. Multiple film zero-layer Weissenberg photographs were taken with CuK_α, CoK_α and FeK_α radiations, all of which are quite close to the K-absorption edge of the Mn atom. After reducing these data to the same relative scale, an Anomalous Difference Patterson (A.D.P.) map was computed with $(|F_{Cu}|^2 - |F_{Fe}|^2)$ as coefficient and it was found to have striking resemblance to the Isomorphous Difference Patterson map made with $(|F_{Cu}{}^{KMnO_4}|^2 - |F_{Cu}{}^{KClO_4}|^2)$ as coefficient. The structure was recovered from the A.D.P. diagram by means of the Buerger Vector shift method. An interesting offshoot of this technique is that the position of the excited atom could be directly determined by making a Patterson with $(|F_{Cu}| - |F_{Fe}|)^2$ as coefficient. From the knowledge of the position of the anomalously scattering atom and also its scattering factors for the different radiations, it was possible to assign the signs of as many as 50% of the reflexions. Commencing with these the structure was determined and the atomic parameters were refined. The final R-factor for the (*hol*) and (*hko*) projections were respectively 0·145 and 0·153. The parameters found are appreciably different from those reported earlier.

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