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SPACE GROUP SYMMETRY OF $K_2Cr_2O_7$

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ABSTRACT

The method of intensity statistics of X-ray reflections has been employed to resolve the controversy about the space group of the triclinic room temperature form of $K_2Cr_2O_7$. Intensity distribution curves definitely indicate the presence of centre of symmetry showing that the crystal belongs to the space group $P\bar{1}$.

INTRODUCTION

There is a considerable amount of controversy in the literature as to which space group, the room temperature form (α variety, triclinic) of potassium dichromate belongs : whether it belongs to the holohedral pinacoidal (centro-symmetric) Class $P\bar{1}$ or to the hemihedral pedial (non-centro-symmetric) Class P1. Groth (*1910*), quoting the *morphological measurements* of Scabus, states that the substance crystallises in the centro-symmetric class with the following axial parameters $a : b : c : : 0.5575 : 1 : 0.5511$; $\alpha = 82^\circ$, $\beta = 90^\circ 51'$ and $\gamma = 83^\circ 47'$. On the other hand Shubnikov (1931) from extended studies on the growth of crystals and etch figures finds that as specimens with two forms which are mirror images of one another, are obtained from the same solution, the substance must definitely belong to the asymmetric pedial class. From experiments on the development of crystal faces, Scoep (1932) supports Shubnikov's assignment. However not only have these experimental results been questioned by Stedehoulder and Tepstra (1930), who studied the growth on different crystal planes, but the fact that the

crystals do not show any piezo- or pyroelectricity (Elings and Tepstra, 1931; Greenwood, 1935) is taken by them as strong evidence that $K_2Cr_2O_7$ belongs to the centrosymmetric class. In a recent paper Podisco (1954) has again revived the controversy wherein he contends that the growth and etch figure experiments definitely indicate a lack of the centre of symmetry. He also points out that the failure to detect piezo- or pyroelectricity is by no means a positive proof of the existence of centre of symmetry.

In view of what has been stated above, an attempt has been made in the present note to see whether the method of intensity statistics, advocated by Wilson (1949) and which has worked satisfactorily in many cases (Wilson, 1950), would help in resolving the controversy. According to intensity statistics, the presence of centre of symmetry is indicated.

PREVIOUS X-RAY WORK

Grossner and Mussgnug (1930) have measured the unit cell dimensions and they give $a = 7.50$ Å ; $b = 7.38$ Å ; $c = 13.40$ Å ; $\alpha = 82^\circ$; $\beta = 96^\circ 13'$ and $\gamma = 90^\circ 51'$. The crystal belongs to the triclinic class with 4 molecules in the unit cell. There is a discrepancy between these results and morphological data of Scabus. Klement (1958) has suggested that the angle α has been erroneously given by these authors as 82° and that it should actually be the supplement 98°. Klement gives the unit cell parameters to be $a = 7.41$ Å ; $b = 7.49$ Å ; $c = 13.40$ Å ; $\alpha = 96.2^\circ$; $\beta = 98^\circ$; $\gamma = 90.8^\circ$. This nomenclature was especially chosen by him to be in accord with the fact that the crystal transforms to a monoclinic form at about 270°C. It may however be remarked that if as Shubnikov claims, two enantiomorphous forms exist, then it is quite probable that the values given by Grossner and Mussgnug on the one hand and Klement on the other are for two distinct enantiomorphous forms. In such a case there would be no real inconsistency.

PRESENT WORK

Sufficiently large crystals were obtained by slow cooling of warm saturated solution of $K_2Cr_2O_7$ (A.R.). From morphological measurements on a Unicam two circle goniometer, the three axes given by Scabus were easily identified. From the same crystal, three sections were cut and ground to cylindrical shape (of about 0.1 mm. diameter) with the axes of the cylinders coinciding with the three crystallographic axes. Oscillation and Weissenberg photographs using Cu $K\alpha$ radiation were taken. Fairly accurate measurements of high order reflections from the zero layer Weissenberg photographs taken about the three axes gave the following values of the axial parameters agreeing with those of Klement and they do not conform to those given by Grossner and Mussgnug and quoted by Wyckoff (1931). The values obtained are $a = 7.34$ Å ; $b = 7.49$ Å ;

$c = 13.39$ Å ; $\alpha = 96°20'$; $\beta = 97°56'$; $\gamma = 90°30'$. Intensity pictures of Weissenberg photographs using multifilm technique were obtained. Intensities of the different reflections were measured accurately by visual comparison with a standard intensity scale having similar spots covering the range of intensities recorded. The first film in the stack was not used for measurement as there was an appreciable amount of fluorescent radiation.

Absorption correction was applied using Bradley's data for cylindrical specimens. The Lorentz and polarisation correction was applied using the values given by Buerger (1941). For convenience, the intensities were put on an absolute scale using Wilson's method. Unfortunately, out of nearly 250 okl, 250 hol and 150 hko possible reflections, only about 125, 125 and 65 reflections in each of the respective zones were of observable intensity. The remaining unobservable reflections were assigned nearly half the minimum observable intensity on the first film used for measurement. Absorption and other geometric corrections were duly applied for these reflections also. To detect the presence of centre of symmetry, first the ratio of square of mean structure amplitude to the mean intensity $\langle |F| \rangle^2 / \langle I \rangle$ was calculated for the reflections in each of the three zones, care being taken to give each reflection its appropriate multiplicity. The value obtained is very much lower than the theoretical value 0.637 for a centro-symmetric crystal, the theoretical value for the non-centro-symmetric crystal being 0.785. The actual magnitude of the ratio depends on the minimum intensity assigned to the experimentally unobservable reflections (Rogers, Stanley and Wilson, 1955). It was found that the ratio considering only the observed reflections (assuming the unobserved reflections to be non-existent) is still nearer the theoretical value, for centro-symmetric than that for a non-centro-symmetric crystal (*a* axis 0.66, *b* axis 0.71 and *c* axis 0.72). Calculations were next made assigning nearly $\frac{1}{2}$, $\frac{1}{8}$, and $\frac{1}{4}$ the minimum observable intensity on the first film to the unobserved reflections and the value of the ratio was found to decrease regularly from 0.48 to about 0.45, 0.51 to 0.45 and 0.43 to 0.39 respectively in the case of *a*, *b* and *c* axes. The value of the Wilson's ratio for the reflections for all the three zones together is 0.49.

The second modification of Wilson's method of obtaining the distribution curves of intensities as suggested by Howells, Philips and Rogers (1950) was next used. Reflections and intensities were tabulated in the increasing order of $\sin\theta$ giving each its appropriate multiplicity. The list is divided into nearly equal groups each containing sufficiently large number of reflections for a small range of $\sin\theta$. For each group, the mean intensity $\langle I \rangle$ was calculated. For $Z = 10, 20 \ldots . 100\%$ of the mean intensity the corresponding values of N(Z), the fraction of reflections whose intensities are equal to or less than Z were determined. Finally for each value of Z, the mean of N(Z) for all the $\sin\theta$ groups was compared graphically with the theoretical values. In each case a curve close to the theoretical curve for centro-symmetric distribution was obtained. Fig. I gives the curves for the three zones, when approximately half

the minimum intensity observable on the first film was assigned to the experimentally unobservable reflections. Here again both the values and hence the shape of the curve vary slightly with the minimum intensity assigned to the unobservable reflections. The distribution curve for all the reflections in the

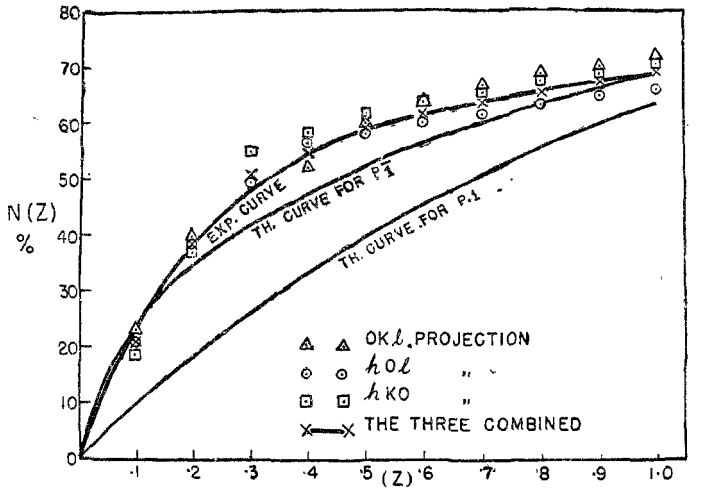

FIG. I

Distribution of intensities for $K_2Cr_2O_7$ compared to theoretical curves for P1, P$\bar{1}$

three zones taken together is also given. This again follows the theoretical curve for centro-symmetric distribution. Lest there be any error in the thickness measurements, different absorption corrections were also applied. The distribution remained centro-symmetric irrespective of the absorption factor used. Further the anomalies which are caused by heavy atoms in special positions [Sim (1958) Hargreaves (1956)] could not affect the present case as neither chromium nor potassium atoms can occupy special positions. Thus statistical survey of intensities of the X-ray reflections for the three zones individually and taken together, shows beyond any doubt that the crystal must belong to the holohedral symmetric (pinacoidal) class having the space group P$\bar{1}$.

However, it may be mentioned that in view of the fact, that the method of intensity statistics has given misleading results in a few cases (Robertson, *et.al.*, 1958, 1956), the above result must be accepted with some reserve. The

issue can be definitely settled only when the accurate atomic parameters are known. Determination of the crystal structure is in progress.

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