X-ray determination of centrosymmetry in three felspars.[1]

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Introduction.

THE recently developed X-ray methods for determining the presence or absence of certain symmetry elements in a crystal have been applied, with reference to centrosymmetry, to orthoclase, sanidine, and albite. The methods depend upon the fact that the presence or absence of certain symmetry elements in a structure affects the probability distribution of the X-ray intensities. The methods were first investigated theoretically by Wilson (1949), and have since been extended and applied by Wilson and several of his colleagues. The potential importance of these new methods for problems of mineralogical interest justifies the brief descriptions of the three methods of testing for centrosymmetry given below; further details may be had from the original papers to which we refer. The theory assumes that a relatively large number of atoms occupy general positions in the unit cell, and that the intensity distribution is not dominated by a few of them; in practice the methods tolerate considerable departure from these conditions and may be applied to a wide variety of crystals.

Methods.

The presence of a symmetry-centre tends to create sharp intensity differences from reflection to reflection; the absence of one tends to create uniformity in the intensity distribution. The effect is sometimes apparent on inspection of single-crystal photographs, but it may always be investigated statistically by considering the accurately measured intensities of a large number of general reflections, *hkl*. Special reflections (*hk*0, 0*kl*, &c.) may not be sufficient for a satisfactory test for centrosymmetry in general, because a zone may be centrosymmetric when the crystal as a whole is not.

[1] The substance of this paper was presented briefly during discussion at a special meeting of the Mineralogical Society devoted to felspars, May 16, 1951.

1. $N(z)$ test (Howells, Phillips, and Rogers, 1950).—The reflections are divided into several groups containing approximately equal numbers of reflections. Each group consists of all reflections, including those accidentally absent, within a small range of $\sin\theta$ or $(\sin\theta/\lambda)^2$. For each group the average intensity $\langle I \rangle$ is calculated, and the percentage $N(z)$ of the total number of reflections is found for which the intensity is less than or equal to progressive fractions z of the average intensity. Finally, for each z the weighted mean of $N(z)$ over all $\sin\theta$ groups is compared graphically with the theoretical values. In the accompanying figure (fig. 1), theoretical values for the centrosymmetric case ($\bar{1}$) are shown as solid curves, for the non-centrosymmetric (1) as broken curves.

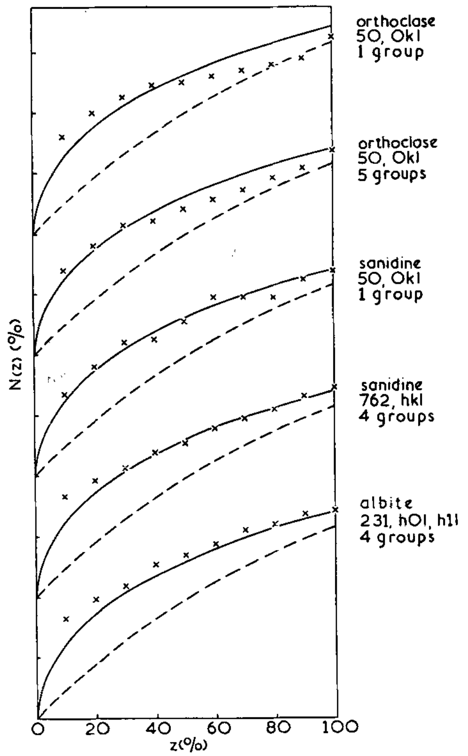

FIG. 1. $N(z)$ plots of the X-ray intensity distributions for orthoclase, sanidine, and albite. The crosses represent experimental values. The solid line curves give the theoretical values expected for centrosymmetric crystals ($\bar{1}$); the broken line curves give the theoretical values for non-centrosymmetric crystals (1). Individual curves have been displaced vertically 40% for clarity.

2. Wilson ratio test (Wilson, 1949; Howells, Phillips, and Rogers, 1950). — The reflections may be divided into several $\sin\theta$ groups as in the $N(z)$ test or they may be treated as one large group. The average structure amplitude $\langle|F|\rangle$ and the average intensity $\langle I \rangle$ are determined for each group, and then the ratio $\langle|F|\rangle^2/\langle I \rangle$ is calculated. The weighted mean over all $\sin\theta$ groups of this expression, known as the Wilson ratio ρ, has the theoretical values 0·637 for ($\bar{1}$) and 0·785 for (1).

3. Variance test (Wilson, 1951).—Again a distinguishing ratio is deter-

mined, in this case $\langle(\mathrm{I}-\langle\mathrm{I}\rangle)^2\rangle/\langle\mathrm{I}\rangle^2$, the mean square deviation of I from its average. This ratio has the theoretical values 2·00 for ($\bar{1}$) and 1·00 for (1).

Material and results.

Orthoclase.—We have applied all three methods to 50 *0kl* intensities published by Chao, Hargreaves, and Taylor (1940) for a typical orthoclase from Mogok in Upper Burma, specimen *C* of Edmondson Spencer's suite of potash-soda-felspars (Spencer, 1930, 1937). Cole, Sörum, and Kennard (1949) showed that these *0kl* intensities are somewhat inaccurate in that some reflections which are actually present were listed with zero intensity. We have therefore altered the published intensity data by adopting the calculated intensities for these few reflections.

The $N(z)$ plots are shown in the figure both for a single grouping of the reflections and for a division into five overlapping groups, this division simply having the effect of smoothing the plot. The plots are only in fair agreement with the theoretical curve for centrosymmetry. Howells, Phillips, and Rogers (1950) discuss the factors which may alter the shape of the plot. In particular, extinction frequently reduces the intensities of the strongest reflections, and the plot may agree with the theoretical curve at the low intensity end where extinction is not appreciable, but it may sag as the intensity increases. This may well explain the shape of the plots for orthoclase. Although our $N(z)$ plot is not convincing evidence for a centre of symmetry in orthoclase, the Wilson ratio of 0·626 (theoretical for ($\bar{1}$), 0·637) and the variance average of 2·12 (theoretical for ($\bar{1}$), 2·00) shown in table I leave little doubt that orthoclase is

TABLE I. Wilson ratios and variance averages of three felspars.

	Number of reflections.	Type of reflections.	Limits of $(\sin\theta/\lambda)^2$.	Number of groups.	Wilson Ratio $\langle\lvert F\rvert\rangle^2/\langle\mathrm{I}\rangle$.	Variance average $\langle(\mathrm{I}-\langle\mathrm{I}\rangle)^2\rangle/\langle\mathrm{I}\rangle^2$.
Orthoclase ..	50	*0kl*	0·025–0·400	1	0·626	2·12
Sanidine ..	50	*0kl*	0·025–0·400	1	0·664	2·54
Sanidine ..	762	*hkl*	0·025–0·400	4	0·561	—
Albite ..	231	*h0l, hll*	0·025–0·500	4	0·564	—
			Theoretical values	($\bar{1}$)	0·637	2·00
				(1)	0·785	1·00

centrosymmetric. A larger number of reflections such as we describe below for sanidine and albite would have been more favourable for statistical averaging and might have improved our $N(z)$ plot.

Sanidine.—The intensities we have used are 762 of those obtained for the high accuracy analysis of sanidine reported by Cole, Sörum, and

Kennard (1949); the intensities were taken from Cole (1949). This sanidine is the material from Upper Burma referred to above, but sanidinized by heating at 1070° C. for 300 hours (Spencer, 1937). For comparison with our results for orthoclase, we have analysed the same 50 $0kl$ reflections of sanidine in one group by all three methods. The $N(z)$ curve agrees fairly well with the theoretical curve for $(\bar{1})$, and the Wilson ratio and the variance average agree reasonably well with the theoretical values for centrosymmetry. There is an apparent discrepancy between the Wilson ratio and the variance average: the former, 0·664, departs from the centrosymmetric value towards the non-centrosymmetric value of 0·785, whereas the latter, 2·54, shows a departure in the opposite direction, i.e. away from the non-centrosymmetric value of 1·00. This is explained by the fact that all sources of error in the variance test tend to increase the experimental value, whereas various sources of error affect the Wilson ratio differently.

When all 762 reflections are used for sanidine the $N(z)$ plot agrees very closely with the theoretical curve for the centrosymmetric case. The Wilson ratio of 0·561 is appreciably lower than the theoretical value for $(\bar{1})$, 0·637. The reason for this deviation is not known.

Albite.—We have used a very pure typical low-temperature albite from a pegmatite located at Ramona, California. We are indebted to Dr. W. T. Schaller and Dr. C. S. Ross of the U.S. Geological Survey for the use of this specimen. The material is part of a suite of plagioclase felspars kindly supplied by Professor R. C. Emmons of the University of Wisconsin, who is presently to publish chemical, optical, and petrological descriptions of them. An X-ray investigation of several of these specimens carried out in this Laboratory has already been published (Cole, Sörum, and Taylor, 1951). This albite from California is at present being analysed in detail by three-dimensional Fourier methods by one of us (R. B. F.) in order to refine the earlier parameters published by Taylor, Darbyshire, and Strunz (1934). The results of our statistical analysis carried out on 231 reflections of the types $h0l$, $h1l$, prove conclusively that albite is centrosymmetric. The low value of the Wilson ratio, 0·564, is surprisingly close to our value of 0·561 for the 762 reflections of sanidine.

Discussion and conclusions.

This newly developed X-ray method of testing certain types of crystals for centrosymmetry (and, indeed, for other symmetry elements, see Wilson (1950) and Rogers (1950)), should prove a very important addition to the older morphological, etching, and piezo- and pyro-electric methods. If a crystal satisfies, or nearly satisfies, the conditions mentioned earlier, the presence or absence of specified symmetry elements (in particular, symmetry-centres) can probably be decided. Because the method requires only the minute fragment necessary for single-crystal photographs, or in favourable cases sufficient powder for a powder photograph, it is a particularly powerful tool for the structural mineralogist. The intensity data used for the test are those normally prepared for structure analysis, and so the test may be quickly applied as a routine part of any structure analysis in which the space-group is not uniquely determined by the ordinary methods.

In relation to the structures of the felspars, the method removes one of the previous uncertainties, that concerning the space-group, and our present work has shown that the assumption of the holohedral space-group $C2/m$ for orthoclase and sanidine by Chao, Hargreaves, and Taylor (1940) and later by Cole, Sörum, and Kennard (1949) was correct. It is doubtful whether the method will prove of direct assistance in clarifying the Si–Al order-disorder phenomena widely believed to be primarily responsible for the polymorphism of the alkali-felspars. This X-ray test for centrosymmetry depends upon the diffracting powers of the atoms and thus, for the purpose of the test, the Si and Al atoms will behave almost identically. If one or more of the felspars should have a structural arrangement in which the Si and Al atoms are segregated into positions compatible with only a hemihedral space-group, it is almost certain that the statistical method would show the crystal to be centrosymmetric if all the other atoms were arranged according to the corresponding holohedral space-group.

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Summary.—Three statistical tests, depending upon the probability distribution of X-ray intensities, have been applied to orthoclase, sanidine, and albite. It is concluded that these three felspars possess centres of symmetry, justifying the assumption of holohedral symmetry made in earlier structure analyses.

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