LETTERS TO THE EDITORS

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Determination of the Absolute Configuration of α-Quartz

FOR the determination of the configuration, including handedness (that is, the absolute configuration), of non-centrosymmetrical crystals, use must be made of anomalous scattering[1]. In one set of applications the intensity difference between hkl and $\overline{hkl}$ reflexions is employed only in a qualitative way for a few reflexions, the structure except for handedness being known[2]. In others, methods have been devised for a fully direct Fourier synthesis, utilizing the anomalous effect of all reflexions in a qualitative[3] or quantitative[4] way. It was realized that applications of anomalous diffraction were not limited to crystals containing atoms with absorption edges very close to the frequency of the X-rays used[3].

The present investigation, the determination of the absolute configuration of α-quartz, is of the former type. It has been undertaken to reveal the absolute configuration of this historical crystal ; and in addition, to investigate whether the accuracy of intensity measurements could be improved to such a degree that anomalous diffraction could be utilized with these very light atoms, and consequently with X-ray frequencies very far from the absorption edge.

In the case of quartz, the determination of the absolute configuration means establishing whether the space group of a given crystal is $P3_12$ or $P3_22$. This can be decided by the comparison of calculated and measured intensities for a small number of reflexions. Intensities were calculated using the co-ordinates of Brill *et al.*[5] adapted to the space group $P3_12$. The measured intensities were obtained from a part of an α-quartz crystal turned off cylindrically, irradiated with chromium-$K\alpha$ X-rays (development of the faces, Fig. 1, as well as rotatory power proved the quartz crystal to be lævorotatory). The intensity of a given reflexion appeared to vary considerably with the part of the crystal irradiated, due to the degree of ideality of the natural quartz crystal varying from spot to spot. So averaging was required of repeated intensity measurements of the same reflexion from different parts of the crystal.
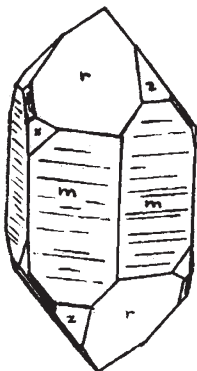
The pairs of reflexions $hkil$ and $\overline{hkil}$ measured can be divided into three groups. First, the pairs of reflexions with $l = 1$ and $k = \overline{h}$, which are structurally different (Table 1). Their intensities enable us to determine the directions of the crystallographic axes in the cylindrically shaped crystal sample. The large discrepancy between measured and calculated ΔI (per cent) for $1\,\overline{1}\,0$ is not surprising, for it is a strong reflexion likely to be affected by extinction.

Fig. 1

Table 1. REFLEXIONS $h\ \overline{h}\ 0\ 1$

| hki | Measured | | | | Calc. |
	I_{hkil}	$I_{\overline{hkil}}$	ΔI^*	ΔI (per cent)*	ΔI (per cent)
1 $\overline{1}$ 0 and cyclic	80·0	131·0	$\overline{51\cdot0}$	$\overline{48}$	$\overline{83}$
2 $\overline{2}$ 0 and cyclic	22·8	11·5	11·3	66	59
3 $\overline{3}$ 0 and cyclic	0·0	116·0	$\overline{116\cdot0}$	$\overline{200}$	$\overline{198}$

* In this table and in Tables 2 and 3 $\Delta I = I_{hkil} - I_{\overline{hkil}}$ and

$$\Delta I \text{ (per cent)} = 100 \times \frac{\Delta I}{\frac{1}{2}(I_{hkil} + I_{\overline{hkil}})}$$

In the second group, the reflexions with $l = 0$ and $k = \overline{h}$ (Table 2), the reflexions $hkil$ and $\overline{hkil}$ are equivalent. Their agreement is a test of the reliability of the intensities.

Table 2. REFLEXIONS $h\ \overline{h}\ 0\ 0$

| hki | Measured | | | |
	I_{hkil}	$I_{\overline{hkil}}$	ΔI	ΔI (per cent)
1 $\overline{1}$ 0 and cyclic	53·6	53·8	$\overline{0\cdot2}$	$\overline{0\cdot4}$
2 $\overline{2}$ 0 and cyclic	51·4	51·9	$\overline{0\cdot5}$	$\overline{1\cdot0}$
3 $\overline{3}$ 0 and cyclic	18·4	18·2	0·2	1·0

The third group consists of pairs with $l = 0$ or 1 and $i = k$ (Table 3). In these pairs, where $\overline{hkil}$ is equivalent to the anti-reflexion of $hkil$, the intensity difference is caused by anomalous scattering and therefore determines the handedness of the configuration.

Table 3. REFLEXIONS $h\ k\ k\ l$

| hki | l | Measured | | | | Calc. |
		I_{hkil}	$I_{\overline{hkil}}$	ΔI	ΔI (per cent)	ΔI (per cent)
2 $\overline{1}$ $\overline{1}$ and cyclic	0	51·1	59·8	$\overline{8\cdot7}$	$\overline{16}$	$\overline{16\cdot0}$
2 $\overline{1}$ $\overline{1}$ and cyclic	1	12·4	19·1	$\overline{6\cdot7}$	$\overline{42}$	$\overline{43\cdot0}$
4 $\overline{2}$ $\overline{2}$ and cyclic	1	51·8	47·8	4·0	7	6·4

From the discussion on the intensities the choice of space group is seen to be the right one. The lævorotatory α-quartz therefore belongs to the space group $P3_12$, in agreement to the prediction of Wooster[6]. The structure has right-handed spirals, which the light seems to follow in its rotation[6]. (The term lævorotatory refers to the observer to whom the light is travelling.) A further theoretical study of the rotatory power of quartz is intended.

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