

higher apparent absorption coefficient than when off the Bragg angle (James, 1948, vol. 2, chap. 6). Some preliminary experiments in this Laboratory fail to confirm the existence of this effect.

A beam of copper $K\beta$ rays, rendered parallel and monochromatic by reflection from a cleavage plane of calcite, was diffracted by a second crystal. The second crystal was cut perpendicular to the reflecting plane so that when oriented in the reflecting position both the transmitted beam and reflected beam traversed the same amount of material.

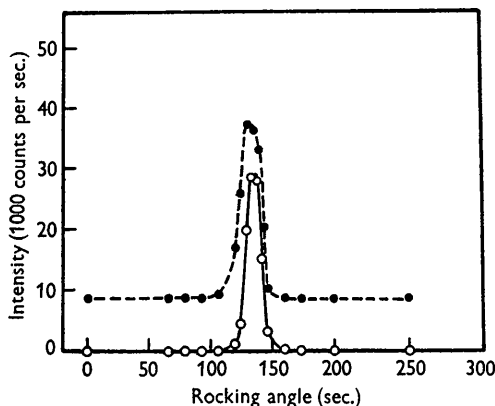


Fig. 1. Reflection from $(10\bar{1}1)$ plane in etched calcite crystal. Solid line: reflected beam; broken line: transmitted beam.

Two Geiger counters were set up; one to catch the transmitted beam and one to catch the reflected beam; and the crystal was rocked through the Bragg angle. Fig. 1 shows the intensities observed from the $(10\bar{1}1)$ plane in calcite.

These curves were obtained on a slice of calcite cut 3 mm. thick and reduced to 1 mm. by etching. The narrowness of the peak indicates that the crystal was fairly perfect. No extinction effect is observed; in fact there is an increase in the transmitted beam about equal to the intensity of the reflected beam. The slight relative shift of the beams is due to slight misalignment of the second crystal.

The homogeneity of the beams was checked by absorption in aluminum. The beam incident on the crystal contained 7% short-wavelength radiation, the reflected beam 2.3%. The beam transmitted within the reflection range consisted of about 20–50% short-wavelength radiation, and the beam transmitted off the Bragg angle

over 99%! If corrected for this short-wavelength radiation, the curves in Fig. 1 would nearly coincide.

Fig. 2 shows the same effect in another slice of calcite crystal which was ground down from 3 to 0.7 mm. The grinding rendered the crystal quite imperfect as judged by the peak width. The same increase in intensity of the transmitted beam was found except for a small minimum in the peak. This may be an indication of the presence of two close domains in the crystal.

The increase in the transmitted intensity is small in the case of mica. A crystal of hexamethylenetetramine gave

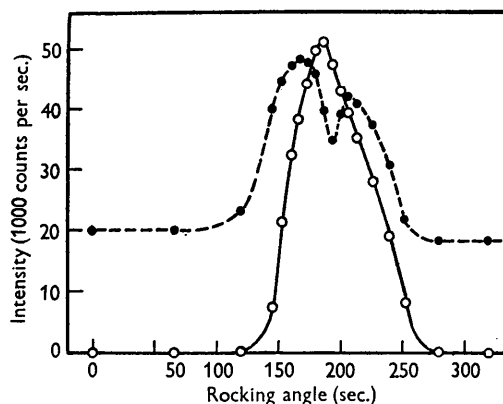


Fig. 2. Reflection from $(10\bar{1}1)$ plane in ground calcite crystal. Solid line: reflected beam; broken line: transmitted beam.

no increase. The transmitted intensity was constant within $\frac{1}{2}\%$ through the whole reflection range.

The best explanation of these data at this time is that when the Laue conditions are satisfied in a perfect crystal there is a resonance effect which decreases the effective absorption rather than increasing it as previously supposed. In a mosaic crystal this effect is not prominent. Dr F. W. Boggs of this Laboratory is considering an explanation involving wave propagation in a periodically conducting medium. The effect seems to be essentially that calculated by von Laue (1949) and investigated by Borrmann (1950) except that the curves do not have the same shape.

References

- BORRMANN, G. (1950). *Z. Phys.* **127**, 297.
 JAMES, R. W. (1948). *The Crystalline State*. London: Bell.
 LAUE, M. VON (1949). *Acta Cryst.* **2**, 106.

Acta Cryst. (1951). **4**, 181

The structure of potassium fluoride dihydrate. By T. H. ANDERSON and E. C. LINGAFELTER, *Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A.*

(Received 4 August 1950)

From the saturated aqueous solution, solid $KF \cdot 2H_2O$ forms needle-shaped crystals which are rapidly deliquescent. It was therefore necessary to carry out the diffraction studies in a dry atmosphere and to protect the crystals by a thin film of Formvar.

Observed structure factors were obtained by visual estimation of intensities from zero-, first- and second-level Weissenberg photographs around the c (needle) axis and a zero-level about $[110]$, using unfiltered copper radiation. These were used without correction for absorption or

temperature factors. The following summarizes the crystal data:

$$a_0 = 4.06, \quad b_0 = 5.15, \quad c_0 = 8.87 \text{ \AA.}$$

Laue symmetry, mmm .

Extinctions, $h0l$ absent for $l \neq 2n$.

A strongly positive test for pyroelectricity indicated the space group $Pmc2_1$. The calculated density was 1.677 g.cm.^{-3} , observed 1.658 g.cm.^{-3} , giving two molecules per unit cell. These results are not compatible with the monoclinic cell previously assigned on the basis of an optical study (Cook, 1914), nor with the handbook value of 2.454 g.cm.^{-3} for the density.

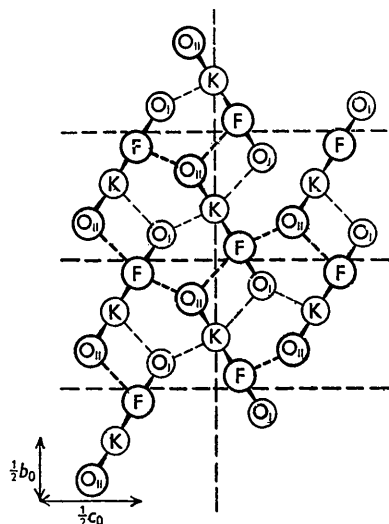


Fig. 1. Projection of $\text{KF} \cdot 2\text{H}_2\text{O}$ on (100) planes.

An easily interpretable Patterson projection on (001) gave approximate x and y co-ordinates, the x co-ordinates then being fixed at exactly 0 and $\frac{1}{2}$ by symmetry and packing considerations. These co-ordinates were:

| | x | y |
|--------------------------------|---------------|-----|
| K | $\frac{1}{2}$ | 0.4 |
| F | 0 | 0.1 |
| $\text{H}_2\text{O}_\text{I}$ | $\frac{1}{2}$ | 0.2 |
| $\text{H}_2\text{O}_\text{II}$ | 0 | 0.3 |

That the water molecules are in twofold rather than in fourfold positions is in keeping with the presence of the mirror planes only 2 Å. apart along the a axis, which can accommodate these units only in those planes.

The x and y co-ordinates permitted the calculation of the phase angles, 0 or π , for the $hk0$ planes, enabling further refinement by means of Fourier projections on

(001). These latter calculations were carried out at millicycle intervals using both unmodified values of F_{obs} and, later, values corrected for series termination, as suggested by Booth and Cochran (1948). It was not necessary to change any of the phase angles throughout the refinement procedure.

When packing considerations were applied to the displacements of the units in the x, y directions it became apparent that in the plane $(0, y, z)$ the fluoride ion and the water molecule, $\text{H}_2\text{O}_\text{II}$, differed in their z co-ordinates by one-fifth of a cell edge. Likewise, in $(\frac{1}{2}, y, z)$ the potassium ion and $\text{H}_2\text{O}_\text{I}$ differed by three-tenths. A Patterson projection parallel to the $[110]$ axis showed the fluoride and potassium ions to be $0.117c$ apart.

A one-dimensional projection using the $(00l)$ data was then made, giving the z parameters listed in Table 1. Although one cannot expect high accuracy for parameters determined from a projection using only the five available orders of $(00l)$, the parameters so determined gave a value of 0.18 for the reliability index for the 34 reflections in the $\{hhl\}$ zone. Consequently, since the projection parallel to $[110]$ does not have a center of symmetry, no further refinement was made. The reliability index,

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

had the value of 0.15 for 33 $hk0$ reflections and an overall value of 0.19 for 124 planes available from the four Weissenberg photographs. It may be pointed out that, since the scattering factor of the potassium ion is two to three times that of any of the others, the positions of the fluoride ion and water molecules are probably not as accurately fixed as that of the potassium ion.

Table 1. Final parameters

| | x | y | z |
|--------------------------------|---------------|-------|-------|
| K | $\frac{1}{2}$ | 0.391 | 0 |
| F | 0 | 0.091 | 0.117 |
| $\text{H}_2\text{O}_\text{I}$ | $\frac{1}{2}$ | 0.189 | 0.705 |
| $\text{H}_2\text{O}_\text{II}$ | 0 | 0.307 | 0.405 |

The crystal is made up of distorted octahedra about both the potassium and fluoride ions. About the water molecules are distorted tetrahedra of two cations and two anions, as is usually found in hydrates.

The two water molecules appear to form two different length hydrogen bonds with the fluoride ion. The $\text{H}_2\text{O}_\text{I}$ -F distance is 2.61 Å., whereas the $\text{H}_2\text{O}_\text{II}$ -F distance is 2.79 Å., as compared with the accepted radius sum of 2.76 Å. for the oxide and fluoride ions.

References

- COCHRAN, W. (1948). *Acta Cryst.* **1**, 138.
 COOK, C. W. (1914). *Amer. J. Sci.* **38**, 142.

Acta Cryst. (1951). **4**, 182

Preliminary study of the structure of citrinin. By STEPHEN G. CLARKE and A. J. KING, *Department of Chemistry, Syracuse University, Syracuse, N.Y., U.S.A.*

(Received 24 July 1950 and in revised form 24 August 1950)

Citrinin is produced as a crystalline metabolic product of the mold *Penicillium citrinum*, and has been of interest experimentally from the standpoint of its antibiotic pro-

perties. As a consequence of chemical studies of its degradation products, Gore, Panse & Venkataraman (1946) and Cartwright, Robertson & Whalley (1949 *a, b, c*) have