

Axial X-ray Scanning of Acicular Crystals. Two Experimental Methods

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Two X-ray methods are given for studying crystals grown mainly in one direction. The first is based on Laue photographs; the second on the diffractometer. Twist of the crystals, small misorientations and axial screw dislocations can be detected.

In KCl whiskers grown in water solutions, the Burgers vectors of screw dislocations have been measured by the Dragsdorf & Webb (1958) method by Bedarida & Della Giusta (1968).

The aim of the present work is to extend this type of X-ray study to acicular crystals in general. First the Dragsdorf & Webb method was modified to enable Laue photographs to be taken on different portions of the same crystal.

A Weissenberg camera (diameter 57.3 mm) was used, the upper levels being cut out, to avoid the overlapping of spots. After each exposure the film and the crystal were moved in the same direction, the distance moved being equal to the diameter of the collimator. Great care was taken to ensure that no rotation of the axis of the goniometric head occurred. KCl acicular crystals were used. The patterns of the various Laue photographs obtained are summarized in Fig. 1, and were as follows:

Fig. 1(a): spots obtained from an acicular crystal with no screw dislocation along the growth axis.

Fig. 1(b): this pattern was obtained only once. The crystal was in two parts, with no axial screw dislocation, the second part making an angle α with the

first (the fourfold axis of growth being the rotation axis).

Fig. 1(c): this was the case studied by Dragsdorf & Webb in Al_2O_3 whiskers and by two of the present authors in KCl whiskers. The screw dislocation remained constant along the whole whisker.

Fig. 1(d): this case occurred quite often. It is the result of a combination of cases 1(a) and 1(c). From a definite point on the first exposure, a twist developed which continued unchanged into the second and third exposures.

Fig. 1(e): the twist varied continuously along the crystal. This also occurred quite frequently.

The method just described is not satisfactory when $\Delta 2\theta$ and β are to be measured with accuracy, particularly when they have small values. A second method was therefore studied. A General Electric Company XRD3 diffractometer was equipped with a device for micromovement along the φ axis (χ circle kept at zero) on the single crystal orienter. After centring a reflexion, the crystals were scanned vertically.

A monochromatic beam collimated with a horizontal slit 0.1 mm. wide, as near as possible to the φ axis, was used. The twist was now given by the corrections

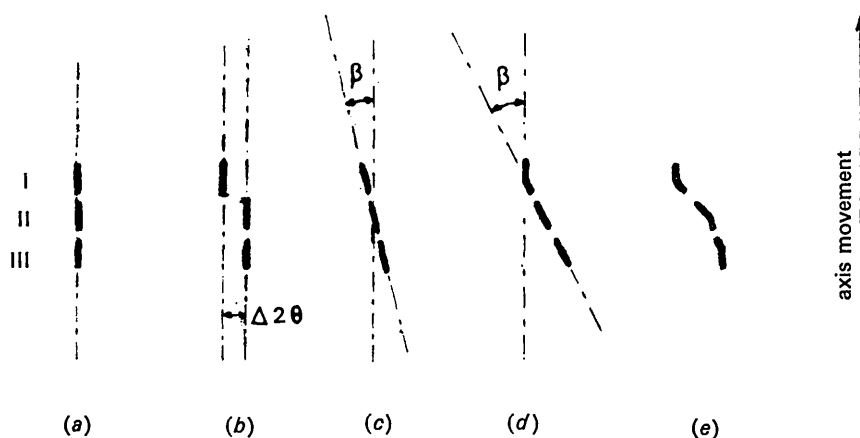
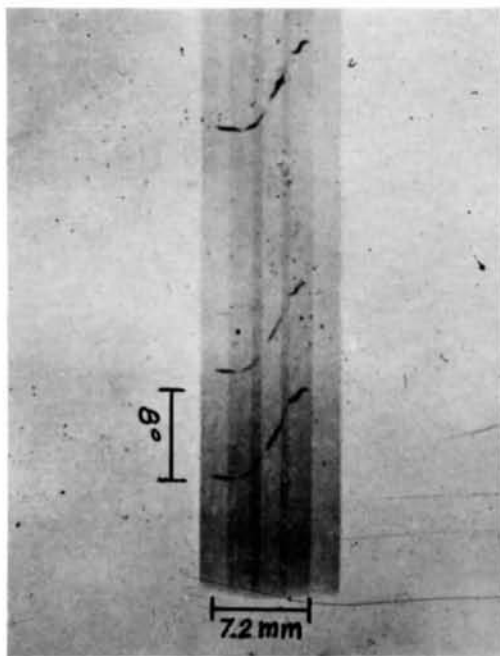
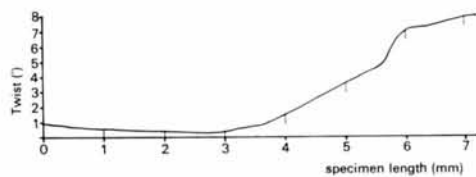


Fig. 1. Typical spot arrangements obtained with three exposures. β = spot tilt, 2θ = diffraction angle. (a) Crystal with no screw dislocation. (b) Crystal in two blocks with slight misorientation. (c) Screw dislocation constant along crystal. (d), (a) and (c) combined. (e) Twist varies along crystal.



(a)



(b)

Fig. 2. (a) Pattern obtained from a strongly twisted specimen. Only the left central part of the Laue photograph is reproduced. Five exposures. The central three are partially superposed ($2\times$). (b) The same as (a), recorded on the diffractometer. Twist in degrees is plotted against the specimen length in mm.

to the φ value required to keep the reflexion at a maximum. The plot of the φ variations against the crystal length corresponded quite well with the photographic record obtained with the multiple exposure technique previously described, and gave the twist in degrees per mm, regardless of the geometry of the system.

The precision obtained was ten times that of the photographic method, since by centring the crystal with great care, the error involved was always less than ± 0.01 degree. Fig. 2(a) and (b) compare the results obtained by the two above methods from a strongly twisted specimen.

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The Electron Density in the Hydrogen Atom of the Bifluoride Ion: a Comparison of Theory and Experiment

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A simple calculation shows that the experimentally determined electron density in the bifluoride ion is not incompatible with a theoretical model having a charge of $+\frac{1}{2}$ on the hydrogen atom, as was previously believed.

In a previous communication (McDonald, 1960), the author presented the results of an experimental determination of the electron density in the bifluoride ion which, at the time, were thought to be at variance with the theoretical charge distribution of $+0.56$ on H and -0.78 on F (Hamano, 1957). It is now realized that the disagreement between theory and experiment was, in fact, largely illusory. Further calculations show that the experimental and theoretical electron densities agree quite well up to a distance of about 0.5 \AA from the centre of the hydrogen atom, if allowance is made for the effects of thermal vibrations in the crystal, and if a reasonable value is assumed for the temperature factor. Beyond this limit, we are not justified in making any comparison, because of the relatively large experimental error and for other reasons mentioned below.

The results of Hamano's LCAO-SCF-MO treatment of HF_2^- were taken as the starting point of the calculations. Using standard (Slater-type) atomic wave functions, the total electron density in the ion was calculated, and from this a 'difference density' was derived by subtracting non-bonded atomic distributions from the F positions, allowance being made for the excess charge of $\frac{1}{2}e$ on each of the F atoms. The difference density so calculated was found to have roughly spherical symmetry within a radius of 0.5 \AA from the centre of the H atom. A line section of the radially averaged three-dimensional distribution is shown in Fig. 1 [curve (a)]. The departure from

These methods are now being applied on a large number of acicular KCl crystals. The results will be published soon.

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References

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spherical symmetry did not amount to more than $\pm 0.03 e.\text{\AA}^{-3}$ within the stated range, which is considerably less than the probable error of the experimental measurements (standard deviation $0.1 e.\text{\AA}^{-3}$). The distribution of curve (a) is probably a true representation of the electron density near the H atom, but no physical significance can be attached to it further out. The difference density goes negative near the F atoms, and its value is sensitive to the choice of basic wave functions. The density near the H atom, on the other hand, is largely independent of the precise method of derivation.

Curve (a) has two interesting features. Firstly, the peak density is only $1.27 e.\text{\AA}^{-3}$ compared with a value of $2.16 e.\text{\AA}^{-3}$ for an unbonded H atom at rest. The H atom appears to have lost about half an electron, in agreement with Hamano's estimate of the charge distribution. This effect is undoubtedly due to the large polarity of the F-H bond. Secondly, the shape of the charge cloud is found to be precisely the same as that in a free atom, again within the limits of accuracy to which we are working. We can make use of this fact to simplify the subsequent analysis.

The effects of thermal vibrations in the crystal lattice may be allowed for by convoluting the difference density with an appropriate function of a temperature parameter β , which is related to the mean square displacement of an atom from its equilibrium position by the expression $\beta = 2\pi^2 \langle u^2 \rangle$, and is numerically equal to