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## A neutron diffraction study of topaz: evidence for a lower symmetry

THE structure of topaz,  $\text{Al}_2\text{SiO}_4(\text{OH},\text{F})_2$ , has been assigned to the orthorhombic space group,  $Pbnm$  (Alston and West, 1928; Pauling, 1928; Ladell, 1965), and the gross physical properties (cleavage, habit, thermal expansion) have been explained in terms of this symmetry (Ribbe and Gibbs, 1971). However, recent observations and interpretation of anomalous optical effects by Akizuki *et al.* (1979) have suggested a triclinic symmetry.

Akizuki *et al.* (1979) have suggested that the lower symmetry is due to the non-random substitution of hydroxide ( $\text{OH}^-$ ) for fluorine ( $\text{F}^-$ ) in the structure. They believe this to be a crystal growth phenomenon; the eight  $\text{F}^-$  sites having different chemical environments at the growth surface and hence a different affinity for  $\text{OH}^-$ . These sites, equivalent under orthorhombic symmetry, then become non-equivalent as  $\text{OH}^-$  substitutes for  $\text{F}^-$  and the symmetry is lowered to triclinic.

Earlier investigations have employed the single crystal X-ray method. In this technique the scattering power of a particular element is dependent on both its atomic number and the scattering angle. The low atomic number of hydrogen and hence its very weak scattering of X-rays, together with the low proportion of hydroxide in topaz, make its position difficult to ascertain. Relatively high scattering by hydrogen occurs in the case of neutron diffraction where there is only minor dependence on atomic number and no dependence on the scattering angle.

A suitably large single crystal of topaz from the O'Brien's Creek area, North Queensland, was mounted on the Australian Institute of Nuclear Science and Engineering's neutron diffractometer 2TanA, at the Australian Atomic Energy Commission reactor, HIFAR. The specimen studied showed sectorial texture similar to that described by Akizuki *et al.* (1979). No attempt was made to measure the optical properties of these sectors. One hemisphere ( $l \geq 0$ ) of data was collected in the range  $5^\circ \leq 2\theta \leq 120^\circ$  using the  $\omega$ - $2\theta$  step-scan technique. During the course of this data collection it became obvious that certain reflections, forbidden by the space group  $Pbnm$ , were in fact present. Correction for the half-wavelength component in the neutron beam failed to account for the presence of reflections of the type  $hol$ ,  $h+l = 2n+1$  and  $okl$ ,  $k = 2n+1$ . It was concluded that

topaz has a symmetry lower than the accepted orthorhombic symmetry. A subsequent X-ray investigation has also shown the presence of the forbidden reflections. Naturally these are not as obvious as in the neutron case.

As a preliminary step in resolving the structure of topaz, it is important to establish the position of the hydrogen atom in the 'basic' orthorhombic space group. The distribution of hydroxide over the eight available sites may then be determined by conventional modelling and least-squares procedures.

Accordingly those reflections not conforming to  $Pbnm$  symmetry were excluded from the data set and orthorhombically equivalent data averaged. Using the starting parameters of Ladell (1965), full matrix least squares refinement was carried out. The calculated structure factors so obtained for the average structure, excluding H atoms, along with the observed data, were used to compute a difference Fourier density map (fig. 1).

A model for topaz, which included the hydrogen atom position obtained from the difference Fourier map, was refined and the overall fit between observed and calculated data improved significantly. The position for the hydrogen atom found in this study ( $x = 0.006$ ,  $y = 0.753$ ,  $z = 0.160$ ) does not agree with that reported by Isette and Penco (1967). However, it is in good agreement with a recent study by Zemann (pers. comm.) in which no deviation from orthorhombic symmetry was observed.

The refined occupancy for hydrogen indicates that 9.0(5)%  $\text{F}^-$  is replaced by  $\text{OH}^-$ . Using the determinative tables of Rosenberg (1967) and the cell dimensions for topaz from our study ( $a = 0.46520(6)\text{nm}$ ,  $b = 0.88028(12)$ ,  $c = 0.83904(8)$ ) the extent of this substitution is predicted to be 9.5%.

From fig. 1, the shortest distance between two hydrogen atoms is 0.15nm. This is too short and only one of the sites can be occupied, thus giving a symmetry lower than  $Pbnm$  by breaking the mirror symmetry (fig. 1). It also precludes consideration of possible monoclinic symmetries such as  $Pm$ . Early models of the structure in the triclinic space group  $P1$  indicate that this deduction is correct, but consideration of hydrogen atoms only does not account completely for the effects

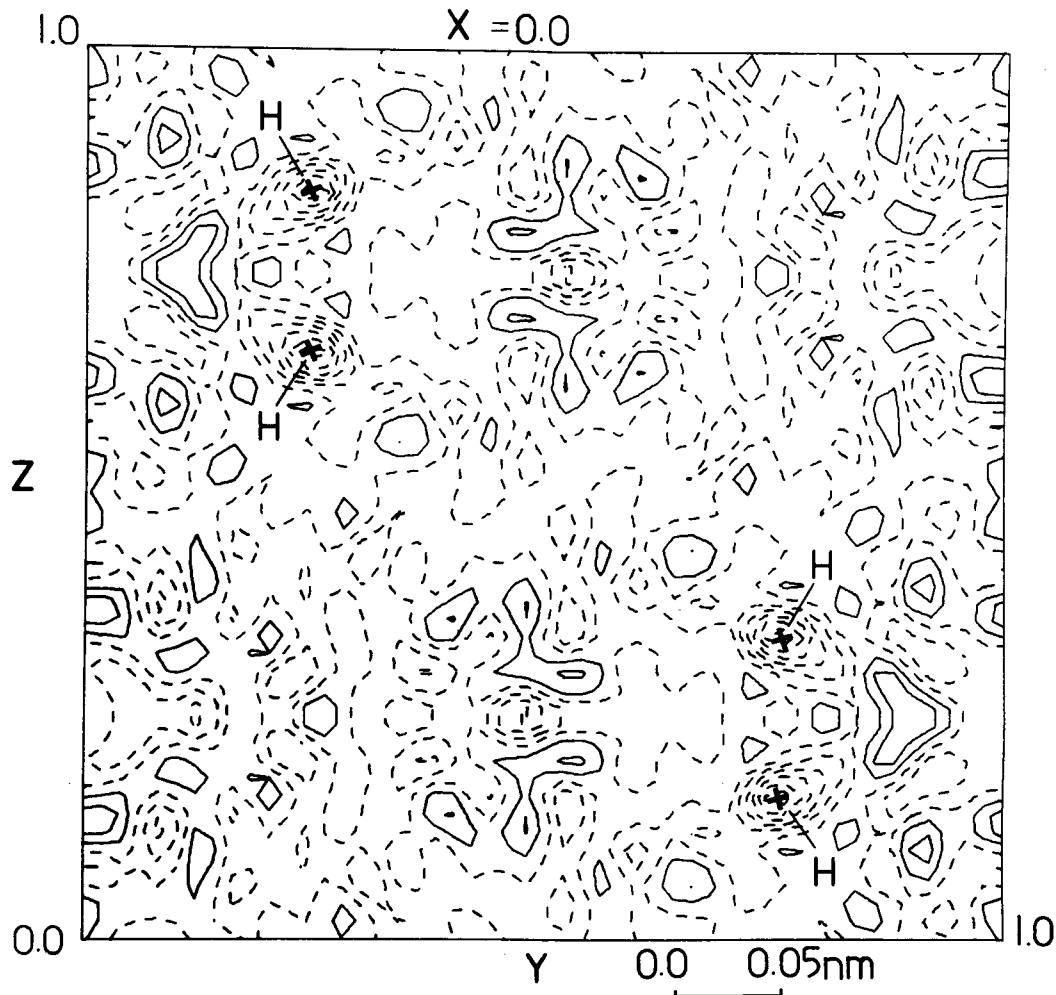


FIG. 1. OYZ section of the difference Fourier map showing four of the eight symmetry-related *H*-sites in topaz. Dashed lines represent contours of negative density, solid lines represent positive density. Each *H*-site indicated represents 0.1 of a hydrogen atom in the average structure.

observed. It appears that the presence of the hydroxyl groups also generates small triclinic distortions in the base structure itself.

Subsequent refinement in *P1* indicates a preferred site for hydrogen at ( $x = 0.50$ ,  $y = 0.25$ ,  $z = 0.17$ ).

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#### REFERENCES

- Alston (N. A.) and West (J.), 1928. *Zeits. Krist.* **69**, 149-67.
- Akizuki (M.), Hampar (M. S.), and Zussman (J.), 1979. *Mineral. Mag.* **43**, 237-41.
- Isetti (G.) and Penco (A. M.), 1967. per. *Min. (Roma)*, **36**, 995-1010.
- Ladell (J.), 1965. *Norelco Rep.* **12**, 34-9.
- Pauling (L.), 1928. *Proc. Nat. Acad. Sci. USA*, **14**, 603-6.
- Ribbe (P. H.) and Gibbs (G. V.), 1971. *Am. Mineral.* **56**, 24-30.
- Rosenberg (P. E.), 1967. *Ibid.* **52**, 1890-5.

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