The Anomalous Behaviour of the Neutron Reflexions of Fluorite

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At room temperature the neutron intensities of the Bragg reflexions of CaF_2 cannot be interpreted satisfactorily by the ideal fluorite model, with calcium atoms at the 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$ positions of the cubic cell, fluorine atoms at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ ... etc. and with all atoms executing isotropic thermal motion. Closer agreement with the observed data is obtained by assuming that the fluorine atoms are displaced slightly towards the centres of the interstices, which surround each fluorine tetrahedrally. This displacement can be ascribed to the anharmonic vibration of the fluorine atoms about their ideal positions. A similar effect has been reported previously for UO_2 and ThO_2 at high temperatures.

In cubic calcium fluoride, with calcium atoms at 000 + face-centred positions and fluorine atoms at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ + face-centred positions, the calculated neutron structure factors can be expressed in the form:

$$F_c = 4b_{Ca} + 8b_F \ldots h+k+l = 4n$$
$$\left. = 4b_{Ca} \quad \ldots h+k+l = 4n \pm 1 \right\} \quad (1)$$
$$= 4b_{Ca} - 8b_F \ldots h+k+l = 4n+2$$

where the nuclear scattering amplitudes are $b_{Ca} = 0.49 \times 10^{-12}$ cm and $b_F = 0.55 \times 10^{-12}$ cm (Bacon, 1962). To account for the effect of thermal motion, b_{Ca} in (1) must be multiplied by the Debye–Waller factor $\exp(-B_{Ca} \sin^2 \theta/\lambda^2)$ and b_F by $\exp(-B_F \sin^2 \theta/\lambda^2)$. The calcium and fluorine atoms both occupy sites with cubic point symmetry ($m3m$ for calcium and $\bar{4}3m$ for fluorine), so that, provided the thermal motion can be treated in terms of harmonic interatomic forces, the temperature factors B_{Ca}, B_F are independent of direction in the crystal.

The purpose of this paper is to point out that neutron diffraction measurements on single crystals of CaF_2 indicate that equations (1), modified to include isotropic Debye–Waller factors, do not account satisfactorily for the magnitudes of the observed structure factors F_o, particularly at high temperatures.

Fig. 1 shows the dependence on temperature of F_o for the three reflexions 755, 771 and 933. As these reflexions have equal values of $h^2 + k^2 + l^2$, they occur at the same value of $\sin^2 \theta/\lambda^2$, and $F_c = b_{Ca} \exp(-B_{Ca} \sin^2 \theta/\lambda^2)$ is the same for all three reflexions at any given temperature. However, the magnitudes of the observed structure factors are in the order $F_{755} > F_{771} > F_{933}$: at 20 °C F_{755} is 12% greater than F_{933} and at 500 °C the proportion is 40%, representing nearly a twofold increase in intensity of 755 compared with 933. Curves closely similar to Fig. 1 have also been obtained with UO_2 and ThO_2 (Willis, 1963), both of which have the fluorite structure.
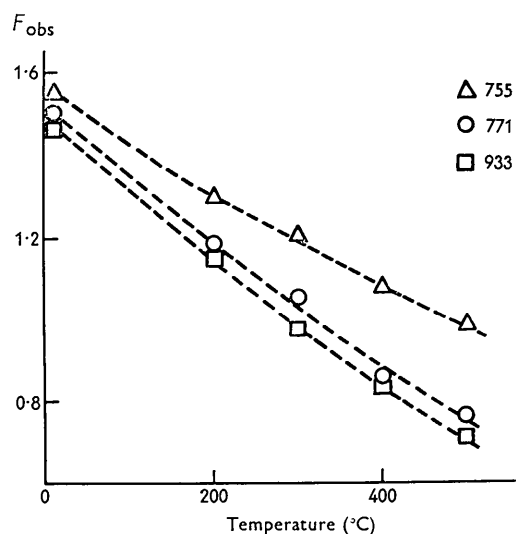

Fig. 1. Observed neutron structure factors for 755, 771 and 933 reflexions, as a function of temperature.

Closer agreement between F_o and F_c is obtained by allowing the fluorine atom at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ to move along the four tetrahedral directions joining the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ site with the adjacent holes or interstices at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, and $00\frac{1}{2}$. Table 1 lists F_o for several high-angle reflexions together with the calculated structure factors determined for the fluorite arrangement, F_c, and for the modified arrangement, F_c', with the fluorine atoms distributed at positions $\frac{1}{4} + \delta$, $\frac{1}{4} + \delta$, $\frac{1}{4} + \delta$ ... in the $Fm3m$ space group. The structure factors were calculated by a least-squares analysis (Busing, Martin & Levy, 1962) of the observed data, using three adjustable parameters (B_{Ca}, B_F and scale factor) for F_c and a fourth adjustable parameter (δ) for F_c'. The refined values of B_{Ca}, B_F and δ are listed in Table 2, where the figures in brackets represent estimated standard deviations. By introducing the extra parameter δ, the discrepancy index $R =$

$\Sigma ||F_o| - |F_c||/\Sigma |F_o|$ has fallen from 3·6% to 1·9%, a drop of nearly one-half. No further reduction in R was obtained by allowing displacement of the calcium atoms, and, indeed, difference Fourier syntheses, using coefficients $F_o - F_c$ with phases derived from F_c (ideal fluorite model), indicated that the displacement effect was restricted to the anion sub-lattice.

Table 1. *Neutron diffraction data for* CaF_2 *at 20 °C*

hkl	F_o	F_c	F_c'
733	1·626	1·535	1·580
644	1·652	1·642	1·651
555	1·440	1·496	1·417
662	1·571	1·571	1·578
911	1·329	1·458	1·454
933	1·341	1·384	1·337
771	1·402	1·384	1·357
755	1·500	1·384	1·492
10,0,0	1·368	1·376	1·363

F_c: Ideal fluorite model.
F_c': Fluorite model with displacement of fluorine atoms.

Table 2. *Least-squares refinement of* CaF_2 *data at 20 °C*

Model	B_{Ca} (Å²)	B_F (Å²)	δ	R
Ideal fluorite	0·39 (0·17)	0·53 (0·18)	0	0·036
Fluorite with displacement	0·39 (0·13)	0·32 (0·14)	0·009 (0·001)	0·019

Careful checks showed that the observed data in Table 1 were free from systematic errors due to extinction or multiple scattering. Moreover, if the displacement effect were associated with either of these errors, the effect would diminish with increasing temperature: the opposite is the case (Fig. 1). Most of the reflexions included in the least-squares analysis were those with odd indices, as (*a*) these reflexions are most sensitive to changes in δ and (*b*) the strong reflexions with even indices are not entirely extinction-free.

There are, at least, two alternative interpretations of the displacement effect: the fluorite structure is disordered, with some or all of the fluorine atoms displaced at random intervals towards the adjacent interstices at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$... (Willis, 1963), or each fluorine atom vibrates in an asymmetric manner across the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ position. The second case is illustrated by Fig. 2, showing the fluorine atom drawn out along the four

tetrahedral directions while retaining the $\bar{4}3m$ point symmetry. Such an asymmetrical vibration must arise from anharmonic contributions to the Debye–Waller factor: when these contributions are included the Debye–Waller factor for an atom is no longer isotropic in the components of the scattering vector, even though it occupies a site of cubic symmetry (Maradudin & Flinn, 1963). A clear distinction between the two interpretations cannot be made from an analysis of the Bragg reflexions alone, although the general occurrence of the effect in CaF_2, UO_2 and ThO_2, and its moderate dependence on temperature, favour the anharmonic interpretation.
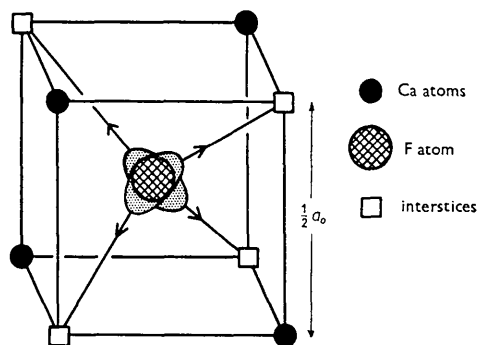
Fig. 2. Anharmonic vibration of the fluorine atom, leading to displacements along the four $\langle 111 \rangle$ directions shown.

The displacement effect was not observed by Weiss, Witte & Wölfel (1957), who carried out a careful X-ray investigation of CaF_2 single crystals at room temperature, using a counter diffractometer. This apparent discrepancy with the present results may be due to the greater precision of the neutron data, which require no correction for absorption.

References

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