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The Structures of Fluorides. XI. Cubic Harmonic Analysis of the Neutron Diffraction Pattern of the Body-Centred Cubic Phase of MoF₆ at 266 K

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Molybdenum hexafluoride, MoF₆, has a body-centred cubic plastically crystalline phase between 263.4 K and 290.6 K, with $a = 6.221(5)$ Å at 266 K and $Z = 2$. As the MoF₆ groups are in rapid rotational disorder, the powder neutron diffraction pattern collected at 266 K could not be analysed with conventional ordered models. The method of Cubic Harmonics, where cubic symmetry only is assumed and no molecular model presupposed, was found to work well with these data. Cubic Harmonic terms up to the fourth power were found to be sufficient, and a least-squares profile refinement gave a Mo–F distance of 1.802(14) Å, an $R = [\sum w(I_o - I_c)^2 / \sum w I_o^2]^{1/2}$ of 0.103 over the 205 background-corrected intensities I_o in the pattern, and a value of $\chi^2 = \sum w(I_o - I_c)^2 / (NO - NV)$ of 0.52. A model having a uniform fluorine distribution over the spherical surface with radius equal to the Mo–F distance was unsatisfactory with $R = 0.219$ and $\chi^2 = 2.32$. The fourth-order Cubic Harmonic model corresponded to a diffuse distribution of fluorine nuclear scattering density over the sphere, but with maxima on the fourfold axes.

Introduction

Molybdenum hexafluoride, MoF₆, is a liquid at room temperature. Between the melting point (290.6 K) and 263.4 K, MoF₆ is body-centred cubic, and below 263.4 K it has an orthorhombic structure of the UF₆ type (Hoard & Stroupe, 1958). The hexafluorides of the second and third row transition metals all have a cubic form near room temperature and an orthorhombic form at low temperatures (Siegel & Northrop, 1966). Cubic MoF₆, M.W. 209.93, has $a = 6.221(5)$ Å at 266 K, $Z = 2$, $U = 240.8$ Å³ and $D_x = 2.895$ g cm⁻³.

Fluorine-19 magnetic-resonance measurements (Rigny & Virlet, 1969) showed that cubic MoF₆ is a plastically crystalline phase with the octahedral MoF₆ molecules undergoing rapid rotational and slow translational motions.

So far, no structural studies have been made on the cubic MF₆ phases; this is probably due to the experimental difficulties involved. The compounds are highly moisture-sensitive and corrosive and must be handled in quartz or Kel-F, while the crystals sublime and recrystallize owing to their high vapour pressure. Siegel & Northrop (1966) were unable to isolate single crystals for X-ray structure determination in the course of their powder studies.

These difficulties can largely be overcome by using the method of powder neutron diffraction and a massive sample in a Kel-F tube. Compared with X-ray diffraction there is added advantage in that the neutron scattering factors for metal and halogen are nearly equal and absorption and extinction effects are eliminated.

Seymour & Pryor (1970) used Cubic Harmonic functions (von der Lage & Bethe, 1947) to describe the disordered hydrogen distribution in NH₄I. This method has the advantage that few adjustable parameters are necessary, and the only assumption about the structure is that it has cubic symmetry. It works best when the distribution is not too sharply peaked. Cubic Harmonics were therefore applied to the present problem, and this study is thus the second published example of the use of the method in a structural problem.

The NH₄I application was a single-crystal neutron study; in the present case, it was necessary to work with a powder pattern. Profile analysis (Rietveld, 1969) was used, since this enables more information to be extracted from the pattern than conventional integrated-intensity refinement.

Experimental

The MoF₆ sample was prepared by direct fluorination of molybdenum metal powder in a flow system (O'Donnell, 1956). To purify the sample, it was distilled over NaF before use. The sample was then distilled into a 17 mm diameter Kel-F tube. This tube was attached to the inner jacket of the cryostat described previously (Levy, Taylor & Wilson, 1975). To ensure random orientation of the crystallites, the melted sample was snap-frozen with liquid nitrogen and then allowed to warm to the temperature selected for the investigation. This temperature, (266 K, 2.6 deg above the transition point) was maintained with a CaCl₂ solution/dry ice slush bath (Bryan & Byrne, 1970). At 266 K, the calculated vapour pressure of MoF₆ was 14.7 kPa. To minimize sintering and development of preferred orientation

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tation effects, a diffraction pattern was obtained as rapidly as possible.

The neutron diffraction pattern of cubic MoF₆ was collected on the AAEC research reactor, HIFAR. The pattern (Fig. 1) was collected to $2\theta = 51.3^\circ$ with a neutron wavelength of 1.083 Å, using the elastic diffraction technique (Caglioti, 1970). A decline in diffracted intensity with increasing 2θ indicated a high degree of thermal disorder. Least-squares analysis of the peak positions gave a value of $a = 6.221(5)$ Å for the cubic cell edge.

Analysis and results

Conventional refinements with an ordered model with molybdenum at 0 0 0 + b.c. and fluorine atoms along the cell edges failed to give sensible results.

The Kubic Harmonic method was then applied. The molybdenum atoms were fixed at 000 + b.c. and the fluorine density distribution, with appropriate normalization, was defined as

$$t_F(\mathbf{r}) = \frac{6}{4\pi c^2} \sum a_m K_m \delta(r - c).$$

The K_m are the centric Kubic Harmonics (see Seymour & Pryor, 1970), a_m are amplitude coefficients, $\delta(r - c)$ is the Kronecker δ function, and c is the Mo-F distance.

Physically, the term K_0 implies a spherically symmetrical fluorine density over the surface of a sphere, radius c , centred at the molybdenum atom. The higher terms are perturbations of this density, obeying cubic symmetry. For example, K_2 introduces a tendency for the Mo-F bonds to align along $\langle 100 \rangle$, K_3 shows a tendency for the bonds to align along $\langle 111 \rangle$, and so on. However, effects of lower-order terms are also included in higher order terms.

The 205 experimental observations consisted of background-corrected scan intensities I within range of an hkl reflexion. For the MoF₆ cubic phase case, the calculated intensity at a point in the pattern was

$$I_c = \sum_{hkl} S \cdot W_{hkl} \cdot \exp(-2B \sin^2 \theta / \lambda^2) \{b_{Mo} + b_F T_F(hkl)\}^2$$

where S is the scale factor, W_{hkl} is a Gaussian weighting term depending on the deviation of the 2θ value of the data point from the theoretical 2θ of the hkl reflexion (Rietveld, 1969), B an overall isotropic Debye-Waller factor for the MoF₆ group, and b_{Mo} and b_F are the neutron scattering lengths for Mo and F (Neutron Diffraction Commission, 1972). \sum_{hkl} denotes superposition of reflexions with the same values of $h^2 + k^2 + l^2$. $T_F(hkl)$ was the Fourier transform of $t_F(\mathbf{r})$, given by the formula

$$T_F(hkl) = 6 \sum a_m A_m J_{2m}.$$

The functions A_m were given by Sanger (1968) and J_{2m} was the Bessel function of order $2m$. The problem was linearized for least-squares refinement by a Taylor expansion.

Full-matrix least-squares refinements were carried out for as many cycles as were needed for convergence with the Kubic Harmonic terms (a) K_0 (spherically symmetric F distribution), (b) K_0, K_2 and (c) K_0, K_2, K_3 . The Mo-F distance, c , and the B factor were also refined. In case (a) it was found necessary to hold B constant owing to interaction with the scale factor. A value of $B = 10 \text{ \AA}^2$ was selected, which was later found in agreement with refinement (b). The results of the refinements* are given in Table 1, which also gives R values $R = [\sum w(I_o - I_c)^2 / \sum w I_o^2]^{1/2}$ and the quantity $\chi^2 =$

* The observed and calculated intensities for refinement (b) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30791 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

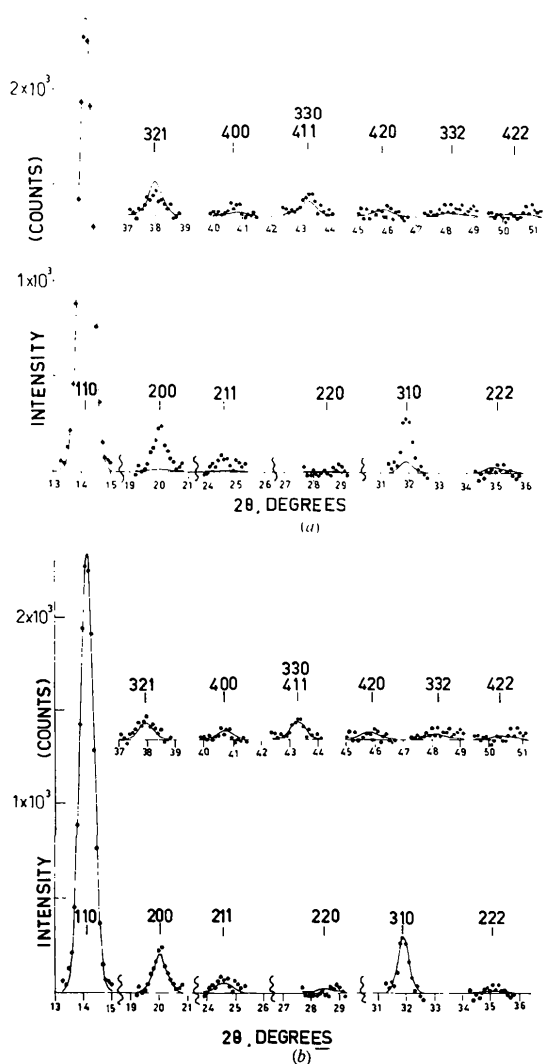


Fig. 1. Observed and calculated profiles for the neutron diffraction pattern of cubic MoF₆ at 266 K, for (a) the spherically symmetrical model (K_0), and (b) the Kubic Harmonic model with K_0 and K_2 .

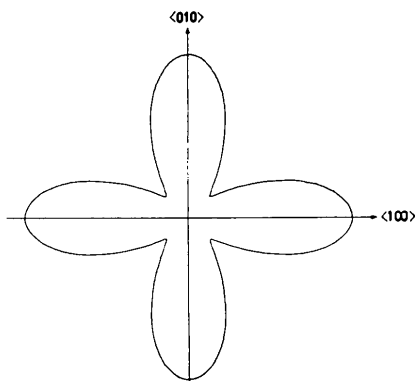


Fig. 2. Angular dependence of fluorine density distribution on the surface of a sphere of radius 1.802 Å, calculated with $a_0=1$ and $a_2=4.65$ (see *Discussion* for further explanation).

$\sum w(I_o - I_c)^2 / (NO - NV)$, NO being the number of observations (205) and NV the number of variables.

Table 1. *Results of Cubic Harmonic refinements for cubic MoF₆*

	Cubic harmonic terms		
	(a) K_0	(b) K_0, K_2	(c) K_0, K_2, K_3
S	24.6 (17)	23.0 (12)	23.0 (12)
a_2	—	4.65 (16)	4.63 (18)
a_3	—	—	6 (24)
c (Å)	1.84 (2)	1.802 (14)	1.803 (14)
B (Å ²)	10.0	9.1 (5)	9.1 (5)
R	0.219	0.103	0.103
χ^2	2.32	0.52	0.52
Number of cycles needed	10	7	12

Discussion

The results in Table 2 show that the refinement with K_0 only, corresponding to a spherically symmetric fluorine density, was the least satisfactory model, with $R=0.219$ and $\chi^2=2.32$. A highly significant improvement was made by introducing K_2 , upon which R reduced to 0.103 and χ^2 to 0.52. As χ^2 was less than 1, the observational errors, determined from counting statistics with adjustment for background errors, were probably overestimated. A smaller number of cycles was needed for convergence with K_0 and K_2 . The R -factor ratio tests of Hamilton (1965) showed that the spherically symmetrical model should be rejected in favour of the Cubic Harmonic model with K_0 and K_2 . No improvement was obtained on adding terms beyond K_2 ; $a_3=6 \pm 24$ was not significantly different from zero, and the other parameters were not significantly different from those obtained in refinement (b).

Fig. 1(a) shows the observed and calculated profiles for the spherically symmetrical model with K_0 only. Although the 110 reflexion is fitted well there

are significant differences between I_o and I_c for 200, 211, 310, 321, 400 and 330, 411. Fig. 1(b) shows the observed and calculated profiles for the fourth-power Cubic Harmonic model with K_0 and K_2 . Here, a good fit between the observed and calculated profiles is obtained for all lines.

The Cubic Harmonic model gave sensible values for the overall B factor and the Mo-F distance c (Table 1). The B factor of 9.1 (5) Å² is consistent with a high degree of thermal vibration, while the Mo-F distance of 1.802 (14) Å is in very good agreement with the results of a powder neutron diffraction study of the orthorhombic phase of MoF₆ at 193 K, where the profile-fitting technique gave Mo-F distances between 1.77 (2) and 1.84 (3) Å (Levy, Taylor & Wilson, 1975).

Up to the fourth order, the distribution function is proportional to $1 + a_2\{(x^4 + y^4 + z^4)/c^4 - 3/5\}$, where x , y and z are Cartesian coordinates ranging over the spherical surface. As an illustration, let $z=0$ and x and y range over a circular arc. Fig. 2 shows the angular dependence of the distribution function with $a_0=1$ and $a_2=4.65$. The value of the function at any point on the curve is equal to the distance from the origin to the point. Thus, the Cubic Harmonic model corresponds to a fluorine distribution, smeared out over the surfaces of a sphere, but with maxima along the fourfold axes.

Cubic Harmonics have worked well in the present case since the fluorine distribution is not sharply peaked, the effect is macroscopic, and there were very few least-squares variables.

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