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The structure of SiF_4.

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A determination of the Si–F bond distance at 1·56±0·01 Å has been made from an X-ray diffraction study of single crystals of SiF_4 at −145° C. The structure of the solid derived by Natta (1930) on the basis of powder diffraction patterns is confirmed. These are 2 Si at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and 8 F at x, x, x, etc., in the eightfold positions of T_d^3–$I\bar{4}3m$. The parameter $x = 0{\cdot}165$ was determined by three-dimensional Fourier methods, with correction for termination of the series. The X-ray diffraction data are summarized in Table 1.

Table 1. *Observed and calculated structure factors* for* SiF_4

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*hkl*	$\lvert F_o\rvert$	$\lvert F_c\rvert$
110	35·6	34·0	211	26·2	26·0
200	4·8	4·6	222	18·2	17·4
220	19·2	20·2	321	13·4	14·4
310	1·8	1·6	411	10·4	11·0
400	< 1·8	0·4	332	< 2·6	0·6
330	23·0	23·0	422	8·2	8·2
420	10·8	10·6	431	7·0	7·8
510	7·8	7·4	521	6·0	6·2
440	6·0	6·0	433	< 2·6	0·2
530	< 2·6	0·8	442	4·4	4·4
600	9·2	8·8	611	6·0	4·2
620	< 2·6	0·4	622	4·4	3·0
710	3·4	2·4	631	< 2·6	0·2
550	2·6	2·2	444	5·2	2·4

* The temperature factor is $\exp(-4{\cdot}1 \sin^2\theta/\lambda^2)$. The value of $R = \Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert \div \Sigma\lvert F_o\rvert$ is 0·064 for observed reflections only, and 0·075 for all reflections.

Previous determinations of the Si–F bond distance have led to values of 1·59 Å (Natta, 1930), and 1·54 Å (Brockway & Wall, 1934; cf. Braune & Pinnow, 1937), which are probably less precise than our value. With the use of 0·71 Å as a radius for F (Andrychuk, 1951), and the corrected additivity relation (Schomaker & Stevenson, 1941), the 'normal' single-bond Si–F distance is 1·68 Å. Of the various explanations for the shortening of 0·12 Å in SiF_4, the one given by Pitzer (1948) seems most reasonable to us in view of the uniquely high electronegativity of F (cf. also Pauling, 1952). Even so, the effect here is remarkably large, comparable with that shown by the ions of the general type XO_4^{-n} (Donohue & Shand, 1947).

In addition we have attempted to evaluate the crystal energy by methods similar to those of Heller (1941) but with the use of a R^{-12} repulsive potential, where R is the interatomic distance between non-bonded atoms. For this purpose the values of ΣR^{-n} have been evaluated for the SiF_4 crystal, and since they may prove useful and represent fairly extensive calculations we have listed them in Table 2.

Table 2. *Values of* ΣR^{-n} *for interactions in the* SiF_4 *crystal*

(Values in $Å^{-n}$)

	$\Sigma R^{-6}\times10^6$	$\Sigma R^{-8}\times10^7$	$\Sigma R^{-10}\times10^8$	$\Sigma R^{-12}\times10^9$
F · · · F	45788	39655	39365	40870
Si · · · F	10051	4301	2004	962
Si · · · Si	1077	408	168	71

With the use of the crude model of a harmonic oscillator with a single frequency, we have calculated the crystal energy from the expression (cf. Heller, 1941)

$$E = \frac{N}{2}\sum_R\left[\mathfrak{R}(R) - \tfrac{3}{4}\alpha^2\varepsilon R^{-6} - \frac{15}{4}\frac{\alpha^3\varepsilon^2}{e^2f}R^{-8} - \frac{735}{32}\frac{\alpha^4\varepsilon^3}{e^4f^2}R^{-10} - \frac{2835}{16}\frac{\alpha^5\varepsilon^4}{e^6f^3}R^{-12} - \ldots\right],$$

where N is Avagadro's number, $\mathfrak{R}(R)$ is the repulsive energy, α is the bond polarizability here taken as one-quarter of the total polarizability (3·32 $Å^3$) of SiF_4 and centered at the F atoms, $\varepsilon = h\nu$ is the energy corresponding to the principal specific frequency ν and is approximately equal to the ionization potential (17·4 e.V.) and $f = 4\pi m\varepsilon^2\alpha/e^2h^2 = 2{\cdot}26$ is the oscillator strength (Margenau, 1939). The repulsive energy was estimated as C_r/R^{12}, with $C_r = 58{\cdot}1\times10^{-10}$ ergs $Å^{12}$, from the pair interactions between F atoms determined from interactions between gaseous F_2 molecules. The calculated attractive energy of −5·9 kcal./mole and the repulsive energy of ±1·7 kcal./mole thus lead to an estimated crystal energy of −4·2 kcal./mole. The observed value is −6·2 kcal./mole (Patnode & Papish, 1930).

This agreement is not regarded as particularly good, especially in view of the extreme assumption of placement of the polarizability of the molecule at the four F atoms. This assumption leads to a maximum attractive energy for this model. These results suggest that the constants in the F · · · F interatomic interaction potential are not known with sufficient accuracy in the range of distances which occur in solid SiF_4. Certainly the use of the F · · · F interaction obtained from gaseous F_2 in the form of a Lennard-Jones 6:12 potential has proved to be unsatisfactory. However, if a satisfactory potential-energy constant becomes available, the results in Table 2 will become useful.

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