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Structure Investigation by Neutron Diffraction of Deuterated Cobalt Fluosilicate Hexahydrate

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Abstract. Cobalt hexafluorosilicate–deuterium oxide (1/6), $CoSiF_6.6D_2O$, $M_r = 321$, trigonal, $R\overline{3}$, $a = 9{\cdot}369\ (10)$, $c = 9{\cdot}731\ (10)$ Å, $V = 740\ (2)$ Å^3, $Z = 3$, $D_x = 2{\cdot}16$ g cm^{-3}, $\lambda = 0{\cdot}8307\ (5)$ Å, $\mu = 0{\cdot}430$ cm^{-1} (evaluated), $F(000) = 46{\cdot}6$, room temperature, final R factor 0·070 for 506 observed reflections, $wR = 0{\cdot}034$. The structure determined by X-ray diffraction on a hydrogenated crystal is almost confirmed. The F atoms of the disordered SiF_6 octahedra have the same occupation probability (0·5/0·5). The configuration of the water molecule is perfectly determined: the distances D—O are 0·943 (2) and 0·947 (2) Å and the angle D—O—D is 109·1 (3)°. The lengths of the hydrogen bonds are 1·789 (3) and 1·968 (3), and 1·786 (4) and 1·835 (4) Å for D(1)···F and D(2)···F, respectively. When the temperature is lowered $CoSiF_6.6D_2O$ undergoes a structural phase transition with a large hysteresis between 268·1 (2) and 254·1 (2) K.

Introduction. The fluosilicates MSiF$_6$.6H$_2$O (M = divalent metal) are now well known to present structural disorder. The two complex ions $M(H_2O)_6^{2+}$ and SiF_6^{2-} have an octahedral structure and can be distributed between two orientations around the threefold axis. In the case of $MgSiF_6.6H_2O$ ($T \geq 300$ K) and $FeSiF_6.6H_2O$ (at room temperature), a structural model involving two types, with equal probability, of ordered domains (space group $P\overline{3}$) (Jehanno & Varret, 1975; Chevrier & Jehanno, 1979; Chevrier, Hardy & Jehanno, 1981) can explain the superstructure peaks which were inconsistent with the structure

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models described by Syoyama & Osaki (1972), and Hamilton (1962). In the cases of $CoSiF_6.6H_2O$, $NiSiF_6.6H_2O$ and $ZnSiF_6.6H_2O$, at room termperature, Ray, Zalkin & Templeton (1973) proposed a disordered structure (space group $R\bar{3}$) with two completely independent fluorine positions; their occupation was determined as 0·43/0·57 for the cobalt fluosilicate and 0·33/0·67 for the corresponding Ni and Zn salts.

These fluosilicates, with the exception of $NiSiF_6.6H_2O$ and $ZnSiF_6.6H_2O$, undergo a structural phase transition to a low-temperature modification, the structure of which is described as in the space group $P2_1/c$: the transition temperature is 300 K for $MgSiF_6.6H_2O$ (Syoyama & Osaki, 1972; Jehanno & Varret, 1975; Chevrier & Jehanno, 1979); 240 K for $FeSiF_6.6H_2O$ (Jehanno & Varret, 1975; Chevrier *et al.*, 1981) and 246 K (Majumdar & Dutta, 1965), 230 K (Das & Pal, 1987) for $CoSiF_6.6H_2O$. A slightly increased value was found for the deuterated compound $CoSiF_6.6D_2O$: 263 K (Ghosh, Chatterjee, Das, Dutta Roy & Pal, 1977).

We studied the high-temperature phase of deuterated $CoSiF_6.6D_2O$ by neutron diffraction in order to refine the crystal structure with special respect to hydrogen bonding. By temperature-dependent measurements of the intensity of selected Bragg reflections, we were able to follow the phase transition properly.

Experimental. The crystals were obtained by slow evaporation of a slightly acidic solution kept in a closed container in the presence of a small quantity of silica gel half saturated with D_2O. The deuterated solution itself was obtained by evaporation under vacuum, at room temperature, almost to dryness, of a hydrated solution of $CoSiF_6.6H_2O$. The residue was dissolved in pure D_2O and the process repeated twice. The only problem is due to the hydrolysis of $CoSiF_6.6(H,D)_2O$: the solution has to be filtrated at every step and the growth of good crystals requires an acidic solution. As we did not have any D_2SiF_6 at hand, we added H_2SiF_6, which lowered the D_2O content. With this method, we obtained an estimated deuteration rate of about 80%.

Reddish pink prism (4·5 × 4·5 × 5·5 mm); four-circle diffractometer P110, Orphee reactor, Cu(220) monochromator, $\lambda = 0{\cdot}8307\,(5)$ Å, 20 reflections centered for lattice parameters and orientation matrix ($34{\cdot}8 \leq 2\theta \leq 45{\cdot}4°$), space group $R\bar{3}$ of the high-temperature phase verified: 46 peaks with $-h+k+l \neq 3n$ studied (ω-scans: 45 steps, 15 s per step of width 0·15° at two temperatures: 258 K as the temperature lowered, 278·1 K as it increased), no forbidden reflections observed; data collection: temperature 295 K, $3 \leq 2\theta \leq 75°$, ω-scans and $75 \leq 2\theta \leq 90°$, ω–2θ step scans (45 steps, ~1·5 s per step) of scan widths according to the instrumental resolution ($47–158\tan\theta + 258\tan^2\theta$); standard reflections 003 and 122 stable over five days within 1% (no decay or crystal movement); data collection index range h: −16 to 0, k: −16 to 16, l: 0 to 17, 1395 reflections measured, 542 unique reflections ($R_{\text{int}} = 0{\cdot}027$) of which 411 with $F \geq 3\sigma(F)$ for $3 \leq 2\theta \leq 75°$ and 95 with $F^2 \geq 3\sigma(F^2)$ for $75 \leq 2\theta \leq 90°$ considered observed; no absorption correction; isotropic extinction correction by the method of Zachariasen (1967), $G = 0{\cdot}005536\,(6)$; anisotropic temperature factors; full-matrix least-squares refinement based on F's, weighting scheme $\omega = 1/[\sigma^2(F)]$; factors: $R = 0{\cdot}070$, $wR = 0{\cdot}034$, $S = 2{\cdot}037$ for 53 parameters, $(\Delta/\sigma)_{\max} < 0{\cdot}006$.

Integrated intensities and their standard deviations were determined from resolution-adapted profile measurements of the peaks with the *COLL5* program (Lehmann & Wilson, 1979): for $3 \leq 2\theta \leq 75°$, background was determined with an average of the first and the last six steps of each side, for $75 \leq 2\theta \leq 90°$ only a variable number of steps was selected for the evaluation of the background. A careful study of the peaks for $2\theta \leq 75°$ has allowed the usual limit to retain peaks [intensity: $F^2 \geq 3\sigma(F^2)$] to be lowered to the limit $F \geq 3\sigma(F)$. The computer program used in refinement: *XFLS* (Busing, Martin & Levy, 1977). Neutron scattering lengths: Co $0{\cdot}253 \times 10^{-12}$, Si $0{\cdot}4149 \times 10^{-12}$, F $0{\cdot}565 \times 10^{-12}$, O $0{\cdot}5805 \times 10^{-12}$, D $0{\cdot}6674 \times 10^{-12}$ cm.

For the temperature-dependent study, three peaks of the same direction in the reciprocal lattice (22.3), (2,5 2,5 .3) and (33.3) were followed between 245·8 and 293 K, using a closed-cycle refrigerator; ω-scans (45 steps, 10 s per step) of width 0·15°; time between each temperature change: 10 min.

Discussion. The space group $R\bar{3}$ in the high-temperature phase is confirmed; atomic positions and equivalent isotropic thermal parameters are shown in Table 1, bond distances and angles in Table 2.*

Neutron diffraction is very useful for the determination of atomic parameters of lighter atoms (*i.e.* hydrogen or deuterium atoms). Although the parameters of $CoSiF_6.6D_2O$ in the high-temperature phase are rather similar to those reported by Ray *et al.* (1973) from X-ray data, the present study allows precise determination firstly of the position of D atoms (and thus the conformation of the water molecules) and secondly of the position of the F atoms

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* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52249 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters and isotropic equivalent temperature factors, with estimated standard deviations in parentheses*

U_{eq} defined as: $\frac{1}{3}\{U(3,3) + \frac{4}{3}[U(1,1) + U(2,2) - U(1,2)]\}$.

	x	y	z	U_{eq}(Å^2)
Co	0	0	0	0·0175
Si	0	0	0·5	0·0161
F(1)	0·1553 (4)	0·1314 (5)	0·4009 (3)	0·0478
F(2)	0·1672 (4)	0·0650 (4)	0·3997 (3)	0·0343
O	0·1747 (2)	0·1861 (2)	0·1250 (1)	0·0339
D(1)	0·1785 (3)	0·1654 (2)	0·2194 (2)	0·0566
D(2)	0·2053 (2)	0·2981 (2)	0·1129 (2)	0·0480

Table 2. *Bond distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Co—O	2·084 (2)	O—Co—O	89·4 (1)
Si—F(1)	1·665 (3)	O—Co—O′	90·6 (1)
Si—F(2)	1·680 (3)	Co—O—D(1)	119·5 (2)
F(1)—F(2)	0·685 (5)	Co—O—D(2)	122·1 (2)
O—D(1)	0·943 (2)	F(1)—Si—F(1)	89·8 (3)
O—D(2)	0·947 (2)	F(1)—Si—F(1′)	90·2 (2)
O···F(1)//	2·722 (4)	F(2)—Si—F(2)	89·7 (2)
O···F(2)//	2·891 (4)	F(2)—Si—F(2′)	90·4 (2)
O···F(1)⊥	2·710 (5)	D(1)—O—D(2)	109·1 (3)
O···F(2)⊥	2·770 (5)	F(1)···O···F(1)	111·4 (2)
D(1)···F(1)//	1·789 (3)	F(2)···O···F(2)	124·1 (2)
D(1)···F(2)//	1·968 (3)	O—D(1)···F(1)	169·8 (20)
D(2)···F(1)⊥	1·786 (4)	O—D(2)···F(1)	164·5 (15)
D(2)···F(2)⊥	1·835 (4)	O—D(1)···F(2)	165·5 (15)
		O—D(2)···F(2)	168·7 (21)

and their occupation ratio F(1)/F(2). In this way, an accurate determination of the hydrogen bonding is possible.

Furthermore, the large difference in neutron scattering lengths of D ($0{\cdot}6674 \times 10^{-12}$ cm) and H ($-0{\cdot}3741 \times 10^{-12}$ cm), with opposite signs, has allowed the determination of the rate of deuteration of the crystal. The refinement yielded 82·4 (6)% of D, which corroborates the estimated value from the crystal preparation of the compound.

(i) As reported before, the Co atom is octahedrally coordinated with the water molecules: the deformation of the elongated shape of the octahedra is not important [(O—Co—O′) − (O—Co—O) ≤ 1·2°]. On the other hand, the conformation of the water molecule [O—D(1) 0·943 (2), O—D(2) 0·947 (2) Å and D(1)—O—D(2) 109·1 (3)°] is almost perfect; the plane of the molecule is almost parallel with the threefold axis [the deviation is only 5·5 (2)°].

(ii) We obtain, in the refinement, disorder for the F atoms between two sites which cannot be occupied simultaneously [F(1)—F(2) 0·685 (5) Å], with an equal occupancy unrelated by any symmetry element (Fig. 1). First we tried to refine the structure with two unequal occupancy factors [we used 0·43/0·57 as did Ray *et al.* (1973) in their study, then 0·33/0·66 and 0·66/0·33]. In all cases, the convergence was very difficult to obtain and we noted strong correlations between the rate factors and the y parameters of F(1) and F(2); for instance, after 10 cycles, these parameters were not stabilized [max. shift/e.s.d. ≥ 0·14, starting F(1)/F(2) = 0·43/0·57 and reaching 0·45/0·55; max. shift/e.s.d. ≥ 0·24, starting F(1)/F(2) = 0·33/0·67 and reaching 0·40/0·60; max. shift/e.s.d. ≥ 0·57, starting F(1)/F(2) = 0·67/0·33 and reaching 0·52/0·48]. In addition, for these three refinements, all the R factors and the goodness of fit's were of the same order. For all these reasons, we decided to fix F(1)/F(2) to an equal occupancy (0·5/0·5), which is the best chemical solution. The superposition of the two split positions F(1) and F(2) gives rise to a very flat minimum in the refinement of the neutron data, which is probably related to the neutron scattering lengths being all of the same order of magnitude; in the case of the X-ray analysis where the atomic numbers of O, F and H are rather small with respect to that of Co, the mathematical minimum in the refinement with regard to the F occupation distribution can be an artefact.

(iii) Both of the $\mathrm{SiF_6}$ octahedra built with the F(1) atoms or the F(2) atoms are elongated with almost the same deformation (difference not significant) which is not very important: [F(*i*)—Si—F(*i*)] − [F(*i*)—(S*i*)—F(*i*′)] ≤ 0·4° (*i* = 1) and 0·7° (*i* = 2). The Si—F bond lengths of our neutron diffraction study [Si—F(2) 1·680 (3) and Si—F(1) 1·665 (3) Å] are very similar to those obtained for $\mathrm{CoSiF_6.6H_2O}$ [1·674 (1) and 1·678 (2) Å; Ray *et al.*, 1973], for $\mathrm{MgSiF_6.6H_2O}$ [1·67 (2) Å; Chevrier, 1981] and for $\mathrm{FeSiF_6.6H_2O}$ [1·706 (9) Å; Hamilton, 1962; 1·69 (1) Å; Chevrier, 1981].

(iv) The two complex ions $\mathrm{SiF_6^{2-}}$ and $\mathrm{Co(D_2O)_6^{2+}}$ are bound together by hydrogen bonds: D(1)···F is approximately parallel and D(2)···F approximately perpendicular to the threefold axis (Fig. 2). With the more accurate H/D positions we find that most of the hydrogen-bond lengths are shorter than those given by Ray *et al.* (1973) (Table 2).

The dihedral angle between the two least-squares mean planes F(1)—D(1)—O—D(2)—F(1′) [maximum deviation from the plane: D(2), 0·126 (2) Å] and F(2)—D(1)—O—D(2)—F(2′) [maximum deviation from the plane: D(2), 0·059 (2) Å] is 14·0 (2)°;

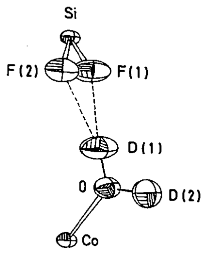

Fig. 1. Neighbouring atoms of oxygen: the two sites of fluorine are shown (drawing by *ORTEP*; Johnson, 1976).

the plane of the water molecule makes an angle of 8·8 (3) and 7·1 (6)°, respectively, with these two planes.

Contrary to the case of $FeSiF_6.6H_2O$, where Hamilton (1962) showed that the $Fe(H_2O)$ group is planar, the Co atom is found to be situated largely out of the D_2O plane (−0·986 Å). It is not impossible as Weir, Halstead & Staveley (1985) and Price (1987) report, that the nature and the size of the metal atom control the structure of the compound and so the rotation and the shape of the octahedral ions.

Transition temperature. Between the high-temperature phase ($R\bar{3}$) and the low-temperature one ($P2_1/c$), we have found, with slow temperature variations, a very large hysteresis for the transition: 254·1 (2) K with decreasing temperature, 268·1 (2) K with increasing temperature. Fig. 3 shows the very good agreement for the three measurements performed on the $R\bar{3}$ allowed (22.3 and 33.3) and forbidden (2,5 2,5 .3) reflections. With heat capacity measurements of $CoSiF_6.6H_2O$, Weir *et al.* (1985) display a transition temperature of 264·8 K, which is found within this hysteresis. The temperature domain (14 K) is comparable with those reported before [16 K (Das & Pal, 1987) and 13 K (Majumdar & Dutta, 1965) for $CoSiF_6.6H_2O$; 17 K (Ghosh *et al.*, 1977) for $CoSiF_6.6D_2O$]. Nevertheless, it occurs at a lower temperature than that given for the deuterated compound (263–278 K), although the rate of deuteration in our crystal was 82·4 (6)%. A comparison of this large thermal hysteresis with that of $FeSiF_6.6H_2O$ (space group $P\bar{3}$) shows a much reduced temperature domain of about 2·5 K, as reported by Volland, Hösl, Spiering, Dézsi, Kemény & Nagy (1978); thus besides the differences in the crystal structures of $FeSiF_6.6H_2O$ and the Co compound (*i.e.* space group $P\bar{3}$ rather than $R\bar{3}$), there is also a significant change in the temperature domain of the hysteresis at the phase transition.

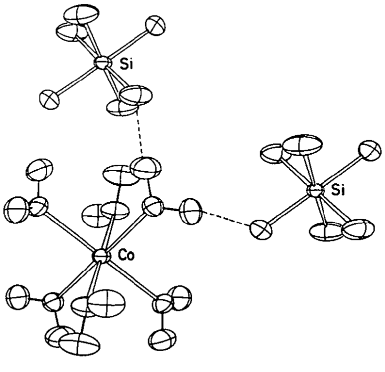

Fig. 2. *ORTEP* drawing (Johnson, 1976) showing the surroundings of $Co(D_2O)_6^{2+}$. We see the two types (parallel and perpendicular to the threefold axis) of hydrogen bonds.

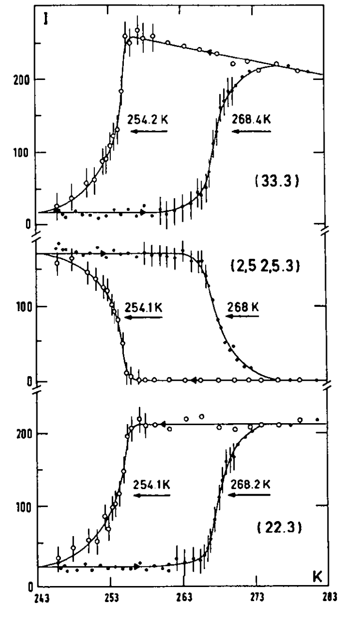

Fig. 3. Intensity of (22.3), (2,5 2,5 .3) and (33.3) peaks in the high-temperature phase of $CoSiF_6.6D_2O$ as a function of the temperature.

On the other hand, we have not found as for $MnSiF_6.6H_2O$ (Jehanno & Varret, 1975) the coexistence of the two phases; studies on $MnSiF_6.6D_2O$ are in progress in order to determine precisely the transition of this compound.

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