Cu–O(4′) est plus longue (2,50 Å). La présence d'un sixième atome d'oxygène O(2″) situé à une distance Cu–O(2″) = 3,02 Å beaucoup trop grande du cuivre permet cependant de décrire cet environnement comme résultant de l'élongation d'un octaèdre oxygéné le long de l'axe quaternaire [ici le long de O(4′)–O(2″)] par effet Jahn–Teller, phénomène classique dans les composés du cuivre (II).

Conclusions

La structure cristalline de la phase $Cu_2V_2O_7\ \alpha$ est caractérisée par la présence de groupements anioniques $[V_2O_7]^{4-}$ nettement individualisés. Ces groupements, dont le caractère covalent joue un rôle prépondérant, constituent des feuillets parallèles au plan yOz et reliés par les atomes de cuivre. La configuration même de ces anions permet de rattacher la variété basse température du pyrovanadate de cuivre au groupe structural de la thorveitite; cependant, leur disposition relative est originale et donne un caractère inédit à cette structure.

L'environnement du cuivre(II), quoique moins classique, a été signalé cependant dans la variété α du pyrophosphate de cuivre $Cu_2P_2O_7$ par Robertson & Calvo (1967).

L'étude structurale actuellement en cours de la variété $Cu_2V_2O_7\ \beta$ haute température permettra vraisemblablement d'expliquer le processus cristallographique de la transition $\alpha \rightleftarrows \beta$.

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Crystal Structures of the Fluosilicate Hexahydrates of Cobalt, Nickel and Zinc*

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Of seven fluosilicate hexahydrates supposedly isomorphous with $NiSnCl_6.6H_2O$, only $CoSiF_6.6H_2O$, $NiSiF_6.6H_2O$ and $ZnSiF_6.6H_2O$ have the typical space group ($R\bar{3}$) and cell size (a = 9·366 (2), 9·313 (3), 9·363 (3); c = 9·730 (4), 9·623 (2), 9·690 (5) Å, respectively, for the hexagonal cell). These three crystal structures were refined with single-crystal X-ray diffraction data obtained by counter methods to conventional R values of 0·033, 0·022 and 0·018. The structures are essentially the same, and there is disorder of F between two positions unrelated by any symmetry element and with unequal occupancy. With either of the disordered sites, the $M(H_2O)_6^{2+}$ (M = Co, Ni or Zn) and SiF_6^{2-} octahedra are stacked alternately along the threefold axis in approximately CsCl-type packing. The hydrogen atoms take part in hydrogen bonds with O–F distances ranging from 2·68 to 2·88 Å. Other bond distances are Co–O = 2·081, Ni–O = 2·047, Zn–O = 2·078, Si–F (average) = 1·676 Å.

Fluosilicate hexahydrates of several bivalent metals have been considered to be isomorphous with a large number of salts with the general formula MG_6LR_6, where M is a bivalent metal, G may be water or ammonia, L is a quadrivalent element like Si, Sn, Ti or Zr, and R may be Cl, F or CN. These crystals have a rhombohedrally distorted CsCl-type packing and similar cell dimensions, except for possible doubling of axes (Hassel, 1927, 1931; Hassel & Richter-Salvesen, 1927).

Pauling (1930) determined a structure in space group $R\bar{3}$ for $NiSnCl_6.6H_2O$, and this result has been widely regarded as typical for the entire series. The oxygen and chlorine atoms are arranged in nearly regular octahedra with identical orientations and dimensions, and this structure must be regarded as approximate at best. In a neutron-diffraction study of $FeSiF_6.6H_2O$ Hamilton (1962) deduced the space group to be $R\bar{3}m$. Disorder was postulated to explain this enhancement of

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symmetry because it gave better agreement with the data than did the alternative of twinning of crystals of $R\bar{3}$ symmetry. The structure is a superposition of two components, each of symmetry $R\bar{3}$, related to each other by a mirror. The component structure resembles that determined by Pauling except for significant differences in the dimensions and orientations of the two kinds of octahedra.

A phase transition occurs near 230°K in $MnSiF_6.6H_2O$ (Tsujikawa & Couture, 1955) and near 250°K in $CoSiF_6.6H_2O$ (Ray, 1964; Majumdar & Datta, 1965). While studying these transitions we became interested in the room-temperature structures of this series of salts and learned that they are remarkably diverse in spite of the close isomorphism in the sense of similar axial ratios. We have examined crystals of fluosilicate hexahydrates of Mg, Mn, Co, Ni, Cu and Zn with the result that all are different from the Fe salt and only the Co, Ni and Zn salts have the typical cell dimensions and space group. The Cu salt also exhibits space group $R\bar{3}$ but with a cell four times as large. The Mn compound has a primitive hexagonal cell rather than a rhombohedral one, a fact also reported by Kodera, Torii & Osaki (1972). In our work at 23°C we observed crystals of the Mg salt to be of lower symmetry than trigonal, but twinned. Syoyami & Osaki (1972) discovered a transition at about 25° in this salt, with space group $R\bar{3}m$ above the transition. They determined the structure of the low-temperature form to be monoclinic, space group $P2_1/c$.

The present paper describes the structures of the Co, Ni and Zn salts; they differ significantly from the structure reported by Pauling (1930) for $NiSnCl_6.6H_2O$.

Experimental

The salts $CoSiF_6.6H_2O$, $NiSiF_6.6H_2O$ and $ZnSiF_6.6H_2O$ were prepared by dissolving respectively cobalt carbonate, nickel carbonate and metallic zinc in fluosilicic acid and slowly evaporating the filtered solutions. Crystals were selected from crops recrystallized from aqueous solution by slow evaporation.

The Co crystal selected for study was a hexagonal (almost triangular) prism of length 0·13 mm and maximum thickness 0·10 mm. The cell dimensions were derived from measurements of 2θ for $h00$, $hh0$ and $00l$ reflections with a manual General Electric goniostat, using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}70926$ Å for α_1). The α doublet was resolved in each case. Intensity data were collected with Zr-filtered Mo radiation and a card-controlled General Electric automatic diffractometer which was equipped with a scintillation counter and pulse-height discriminator. The θ–2θ scan technique was used with 2θ scanned at the rate of 1° $\min^{-1}$, starting 0·6° below the α_1 peak and ending 0·6° beyond the α_2 peak, for all reflections with l zero or positive and $2\theta < 70°$. Background was counted for 10 s each at 0·5° below the start and 0·5° beyond the end of each scan. Four reflections were checked at regular intervals, and no systematic variation was observed. The measurements included 2666 reflections of which 721 were independent; 60 of these had observed intensity less than the estimated standard deviation.

The Ni crystal was of rhombohedral shape with height ~0·2 mm and maximum thickness ~0·2 mm. It showed all six faces of the form $\{01\bar{1}2\}$, three faces of the form $\{10\bar{1}1\}$, and four of the form $\{11\bar{2}0\}$. A computer-controlled Picker four-circle diffractometer with a scintillation counter and pulse-height discriminator was used for the diffraction experiments with Cu $K\alpha$ radiation and an oriented-graphite monochromator. Cell dimensions were derived by least squares from measurements of 12 high-angle reflections ($\lambda = 1{\cdot}54051$ Å for α_1). Intensities were scanned as described above. The whole sphere of reciprocal space out to $2\theta = 162°$, except for certain blind regions, was explored. Above 128°, the χ circle was in the parallel position. Standard reflections were checked periodically, and no systematic variation was observed. 1873 reflections were measured, of which 298 were independent. Only 4 of these had intensity less than the standard deviation.

The Zn crystal was a regular hexagonal prism of height 0·10 mm and thickness 0·10 mm. Cell dimensions were derived by least squares from measurements of 24 high-angle reflections with the manual goniostat, the α-doublet being resolved in each case, and using Cu $K\alpha$ radiation. Intensities were measured with the Picker diffractometer as described above, except that monochromated Mo $K\alpha$ radiation was used. The whole sphere out to $2\theta = 70°$ was explored. No significant variation of standard reflections was observed. Intensities of 726 independent reflections, of which 92 were less than the standard deviation, were obtained from 4336 reflections.

Linear absorption coefficients of the Co and Zn salts are respectively 20·4 and 27·8 cm^{-1} for Mo $K\alpha$ radiation. An estimation of absorption correction factors for the first case indicated less than 2% difference between maximum and minimum values, and the other case is comparable. No corrections were made for these two crystals. For the Ni compound, $\mu = 50{\cdot}3$ cm^{-1} for Cu $K\alpha$ radiation, and a correction was made by numerical integration. The correction factors ranged from 1·40 to 2·19, and they significantly improved the agreement for cases in which the same reflection was measured in both the 'bisecting' and 'parallel' positions of the χ circle.

Intensities were corrected for background, converted to structure-factor magnitudes averaged for measurements of equivalent reflections, and assigned standard deviations which included contributions for counting statistics, excessive scatter, and systematic effects proportional to intensity as described by Fischer, Templeton & Zalkin (1970). The factor p for systematic effects was chosen as 0·05, 0·06 and 0·025 respectively for the Co, Ni and Zn salts.

A CDC-6600 computer was used for the calculations. Refinement by least squares was carried out with a full-matrix program which minimizes $R_2^2=\sum w(\Delta F)^2/\sum w|F_o|^2$, where $w=[\sigma(F)]^{-2}$. Temperature factors were of the form $\exp(-B\lambda^{-2}\sin^2\theta)$ if isotropic or $\exp(-\sum\sum B_{ij}b_ib_jh_ih_j/4)$ if anisotropic, where b_i is the magnitude of the ith reciprocal axis. Neutral-atom form factors of Cromer & Waber (1965) were used for atoms other than hydrogen, for which the values of Stewart, Davidson & Simpson (1965) were used. Anomalous dispersion corrections (Cromer, 1965) were, for Mo $K\alpha$, Co: $0{\cdot}37+i1{\cdot}06$, Zn: $0{\cdot}33+i1{\cdot}54$, Si: $0{\cdot}09+i0{\cdot}09$; for Cu $K\alpha$, Ni: $-3{\cdot}20+i0{\cdot}67$, Si: $0{\cdot}23+i0{\cdot}36$.

Crystal data

$CoSiF_6.6H_2O$: reddish-pink hexagonal prisms.
Hexagonal cell: $a=9{\cdot}366$ (2), $c=9{\cdot}730$ (4) Å, $Z=3$.
Rhombohedral cell: $a=6{\cdot}306$ (3) Å, $\alpha=95°55$ (4)′, $Z=1$.
Space group: $R\overline{3}$; $D_m=2{\cdot}07$, $D_x=2{\cdot}08$ g cm^{-3}.
$NiSiF_6.6H_2O$: apple-green rhombohedra.
Hexagonal cell: $a=9{\cdot}313$ (3), $c=9{\cdot}623$ (2) Å, $Z=3$.
Rhombohedral cell: $a=6{\cdot}261$ (2) Å, $\alpha=96°6$ (5)′, $Z=1$.
Space group: $R\overline{3}$; $D_m=2{\cdot}12$, $D_x=2{\cdot}13$ g cm^{-3}.
$ZnSiF_6.6H_2O$: colorless hexagonal prisms.
Hexagonal cell: $a=9{\cdot}363$ (3), $c=9{\cdot}690$ (5) Å, $Z=3$.
Rhombohedral cell: $a=6{\cdot}297$ (3) Å, $\alpha=96°3$ (6)′, $Z=1$.
Space group: $R\overline{3}$; $D_m=2{\cdot}12$, $D_x=2{\cdot}13$ g cm^{-3}.

Determination of the structure

The structure was determined in much the same way in each case, but we give more details for the Co salt. Atoms were assigned coordinates similar to those of one of the lower symmetry ($R\overline{3}$) components of $FeSiF_6.6H_2O$ (Hamilton, 1962). With isotropic temperature factors, least-squares refinement reduced the conventional $R=\sum|\Delta F|/\sum|F_o|$ to 0·16. With anisotropic temperature factors, R was reduced to 0·11, but B_{11} and B_{22} for F were unusually high. A Fourier synthesis of ΔF showed two prominent but unequal peaks, one on each side (in the same xy plane) of the assumed position of F. The only satisfactory explanation of this was the assumption of a disordered model. Fractional atoms, referred to as F(1) and F(2), were assigned to these two positions with occupation factors adding to unity. With equal occupancy, R was reduced to 0·07; with $F(1)/F(2)=\frac{1}{2}$, $R=0{\cdot}05$. Serious discrepancies remained between F_o and F_c for the 00l reflections. A ΔF map at this stage showed clearly the positions of the two hydrogen atoms. Introduction of these atoms with isotropic temperature factors removed the above discrepancies and reduced R to 0·033. Trial of various values of the occupation factors yielded the best fit with $F(1)/F(2)=0{\cdot}43/0{\cdot}57$: $R=0{\cdot}033$ [excluding data where $I<\sigma(I)$], $R=0{\cdot}038$ (all data), $R_2=0{\cdot}038$, estimated standard deviation of an observation of unit weight = 1·03. In the last cycle no parameter shifted more than 3% of its standard deviation.

In the case of $NiSiF_6.6H_2O$ we introduced an empirical extinction correction: $F_o'=F_o(1+1{\cdot}3\times10^{-7}I)$, where F_o' is the corrected structure factor. The correction factor was 1·43 for the strongest reflection, 110, and exceeded 1·13 for only three other reflections. With occupancy factors $F(1)/F(2)=0{\cdot}33/0{\cdot}67$, $R=0{\cdot}022$ (with or without the four zero-weighted data), $R_2=0{\cdot}040$, and the standard deviation of an observa-

Table 1. *Coordinates and thermal parameters, with estimated standard deviations in parentheses*

For atoms with site symmetry $\overline{3}$, $B_{11}=B_{22}=2B_{12}$; $B_{13}=B_{23}=0$.

	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
(*a*) $CoSiF_6.6H_2O$									
Co	0	0	0	2·00 (1)	2·00	1·45 (2)	1·00	0	0
Si	0	0	½	1·88 (2)	1·88	1·35 (3)	0·94	0	0
F(1)	0·1536 (4)	0·1356 (4)	0·4001 (3)	3·1 (1)	4·0 (1)	2·16 (8)	0·5 (1)	0·46 (8)	0·5 (1)
F(2)	0·1673 (3)	0·0679 (3)	0·3997 (2)	2·30 (7)	4·9 (1)	2·58 (7)	1·42 (8)	0·60 (5)	0·23 (9)
O	0·1745 (2)	0·1860 (2)	0·1247 (1)	3·84 (6)	3·52 (4)	2·26 (4)	0·94 (4)	−0·66 (4)	−0·28 (3)
H(1)	0·187 (4)	0·172 (4)	0·212 (3)	4·6 (6)					
H(2)	0·191 (3)	0·278 (4)	0·114 (2)	4·3 (6)					
(*b*) $NiSiF_6.6H_2O$									
Ni	0	0	0	1·79 (3)	1·79	1·34 (4)	0·895	0	0
Si	0	0	½	1·71 (3)	1·71	1·22 (5)	0·855	0	0
F(1)	0·1610 (8)	0·1258 (8)	0·3999 (7)	2·9 (2)	4·4 (3)	2·0 (2)	−0·6 (2)	0·6 (1)	0·1 (2)
F(2)	0·1681 (3)	0·0647 (3)	0·3981 (3)	2·20 (7)	3·8 (1)	2·46 (9)	1·22 (9)	0·49 (5)	−0·1 (1)
O	0·1772 (2)	0·1830 (1)	0·1218 (1)	3·02 (5)	2·17 (5)	2·20 (6)	0·88 (4)	−0·48 (4)	−0·15 (4)
H(1)	0·181 (3)	0·164 (3)	0·209 (3)	4·2 (5)					
H(2)	0·184 (3)	0·262 (3)	0·116 (2)	4·3 (6)					
(*c*) $ZnSiF_6.6H_2O$									
Zn	0	0	0	1·968 (9)	1·968	1·49 (1)	0·984	0	0
Si	0	0	½	1·68 (1)	1·68	1·23 (2)	0·84	0	0
F(1)	0·1555 (4)	0·1326 (4)	0·4001 (3)	2·8 (1)	3·8 (1)	2·08 (8)	0·2 (1)	0·52 (7)	0·53 (9)
F(2)	0·1676 (2)	0·0685 (2)	0·3992 (2)	2·25 (4)	4·56 (8)	2·36 (4)	1·33 (5)	0·59 (3)	0·14 (5)
O	0·1766 (1)	0·1853 (1)	0·1240 (1)	3·47 (4)	2·35 (3)	2·18 (3)	0·95 (3)	−0·62 (2)	−0·21 (2)
H(1)	0·184 (2)	0·169 (2)	0·202 (2)	4·0 (4)					
H(2)	0·192 (2)	0·274 (2)	0·117 (2)	4·3 (4)					

Table 2. *Observed and calculated structure factors*

Data where $I < \sigma(I)$ are marked with an asterisk.

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TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COBALT FLUOSILICATE HEXAHYDRATE

     FCA(0,0,0) =  2332

 L FOB FCA    5  20   9   H,K=  1,  8  H,K=  2,  5   1 372 366   15  32  19    4  81  79    6 106 108    1  17  22    6 109 105    4 145 146    2 112 113    5  47  44    2  58  49    7  29  24   H,K= 13,-10
H,K=  0,  0   8  75  75    2 180 180    0 304 298    4 342 329   H,K=  4, -1   7  29  27    9  61  61    4 188 192    9  42  49    7  18  16    5  50  53   H,K=  9,  5   5  14  16*  H,K= 11,  2   2  96  95
 3  75  77   H,K=  0, 11   5  16  11    3  79  77    7  33  37    2  33  28   H,K=  4, 10  H,K=  5,  6   7  59  57   12 100 100   10 138 136    8  93  90    1  24   6    8  84  83    0  80  81    5  22  18
 6  42  41    1  33  32    8  98  96    6 211 214   10 146 151    5 146 143    0  64  59    2 132 130   10 129 130   H,K=  7, -1  13  38  40   11  40  39    4  60  62   H,K= 10,  3   3  22  20   H,K= 13, -9
 9  48  46    4  59  61   11  64  64    9  13  17*  13  44  33    8 194 194    3  33  28    5  29  21   13  23  18    2 290 290   H,K=  8, -4  H,K=  9, -7  H,K=  9,  6   1  19  19   H,K= 11,  3   1  20  24
12  88  90    7  57  52   H,K=  1,  9  12 102 103   H,K=  3,  3  11  71  73   H,K=  5, -4   8 107 106   H,K=  6,  3   5  76  77    3 208 211    1  17  12    0  60  61    4  57  58    2  67  65    4  83  82
15  99  94   H,K=  0, 12   1  79  78   H,K=  2,  6   0 268 261   14 122 119    3 173 172   H,K=  5,  7   0 172 176    8 154 155    6  87  86    4 178 177   H,K= 10, -9  H,K= 10,  4  H,K= 12,-11   7  25  14
H,K=  0,  1   3  20  12    4 125 129    2 185 184    3 116 117   H,K=  4,  0   6 220 221    1  45  49    3  87  88   11   0   9*   9  19  18    7  26  32    1  50  45    0  69  66    2  87  90   H,K= 13, -8
 2 661 691    6  50  51    7  22  10    5 105 109    6 275 278    1 463 453    9 133 139    4  80  84    6  78  76   H,K=  7,  0  12  87  92   10  52  52    4 142 145    3  29  17    5  31  16    3  41  41
 5 320 309   H,K=  1,  0  10  67  73    8 124 126    9  19  15*   4 289 281   12 117 116    7  49  49    9  38  42    1  22  18   H,K=  8, -3  H,K=  9, -6   7  38  36   H,K= 11,-10  H,K= 12,-10   6  45  45
 8 416 422    1  59  66   H,K=  1, 10  11  40  45   12 107 107    7  26  23   H,K=  5, -3  H,K=  5,  8  12  90  87    4 179 183    2 307 311    3  79  76   10  56  55    3  28  19    1  31  35   H,K= 13, -7
11  56  53    4 191 167    0 117 116   H,K=  2,  7  H,K=  3,  4  10 113 114    2 355 354    0  77  78   H,K=  6,  4   7 106 102    5  85  87    6 188 189   H,K= 10, -8   6  64  65    4  72  75    2  87  85
14  69  68    7 260 257    3  17   7*   1 100 106    2 152 148   13  49  46    5  92  90    3  24  17    2 199 201   10 109 110    8 123 121    9  29  13    3  26  16    9  52  50    7  48  44    5  26  27
H,K=  0,  2  10 290 293    6  73  76    4 174 176    5 233 239   H,K=  4,  1   8 118 114    6  63  68    5   0   7*  13  21  17*  11  45  45   12  68  64    6 143 145   H,K= 11, -9  H,K= 12, -9  H,K= 13, -6
 1  20  24   13  40  31    9  32  33    7  44  38    8 132 129    0 436 433   11  26  33   H,K=  5,  9   8  97  99   H,K=  7,  1  H,K=  8, -2  H,K=  9, -5   9  26  24    2 139 140    3  14  16*   1  21  28
 4 461 455   H,K=  1,  1  H,K=  1, 11  10 109 107   11   0   7*   3 170 168   14 116 113    2  68  68   11  45  33    0 198 197    1  25  21    2 158 157   H,K= 10, -7   5  13   9*   6  48  51    4  73  74
 7 119 122    0 763 794    2  73  73   H,K=  2,  8  H,K=  3,  5   6 325 328   H,K=  5, -2   5  26  26   H,K=  6,  5   3  61  62    4 210 218    5  72  71    2  89  84    8  57  50   H,K= 12, -8   7  30  22
10 206 207    3 373 358    5  37  39    0  99 101    1  64  66    9  88  89    1  80  79   H,K=  6, -5   1  87  86    6 102 101    7  64  62    8 140 141    5  64  62   H,K= 11, -8   2 135 130   H,K= 13, -5
13  38  33    6 175 172   H,K=  1, 12   3  83  84    4 207 213   12  59  54    4 477 464    2 368 368    4  97 102    9  32  33   10 112 110   11  36  36    8  73  78    1  22  26    5  15  17*   3  32  33
H,K=  0,  3   9  52  54    1  23   7*   6 101 101    7  52  52   H,K=  4,  2   7  65  64    5  23  25    7  34  42   12  96  97   13  30  24   H,K=  9, -4  11  32  28    4 155 154    8  42  41    6  65  66
 3  68  67   12 136 134    4  54  51    9  46  44   10  99  98    2 201 194   10  90  95    8 225 229   10  65  65   H,K=  7,  2  H,K=  8, -1   1  70  71   H,K= 10, -6   7  40  32   H,K= 12, -7  H,K= 13, -4
 6 269 267   15  44  32   H,K=  2, -1  H,K=  2,  9  13  52  52    5  90  89   13  53  45   11  30  20   H,K=  6,  6   2 256 261    3   9   9*   4 143 144    1  53  53   10  43  47    1  47  47    2  99  93
 9 125 128   H,K=  1,  2   3  64  65    2 104 102   H,K=  3,  6   8 231 235   H,K=  5, -1  14  77  70    0 116 114    5  38  37    6 158 162    7  19  16    4 133 130   H,K= 11, -7   4 102 103    5  19  22
12 163 164    2 819 838    6 345 340    5  13  22*   0 164 167   11  14  18*   3 131 131   H,K=  6, -4   3   0   6*   8  74  75    9  20  15   10 116 115    7  27  32    3  15  17    7  19  23   H,K= 13, -3
15  21   6    5  14  13    9  11  11*   8  69  71    3  97  98   14  88  81    6 346 347    1 124 126    6  89  90   11  49  49   12  94  93   H,K=  9, -3  10  58  60    6 121 118   H,K= 12, -6   1  18  19
H,K=  0,  4   8 146 144   12 140 137   H,K=  2, 10   6 134 138   H,K=  4,  3   9  63  67    4 242 237    9  37  36   H,K=  7,  3  H,K=  8,  0   3  44  53   H,K= 10, -5   9  32  30    3  12  19*   4  71  72
 2 603 581   11 125 128   15  56  51    1   0   6*   9  29  19    1 104 107   12  86  84    7 116 116   H,K=  6,  7   1  83  85    2 194 195    6 140 139    3  33  34   H,K= 11, -6   6  93  91   H,K= 13, -2
 5  69  64   14  69  71   H,K=  2,  0   4  76  78   12  75  74    4 222 222   H,K=  5,  0  10 154 158    2  92  89    4 161 160    5  86  88    9  27  26    6 140 140    2  96  98    9  41  35    3  34  36
 8 133 134   H,K=  1,  3   2 336 327    7  44  37   H,K=  3,  7   7 109 113    2 186 178   13   9  10*   5  34  26    7  25  10    8  69  69   12  77  70    9  40  40    5  15   7*  H,K= 12, -5  H,K= 13, -1
11  35  40    1 363 338    5 262 256   H,K=  2, 11   2 159 155   10  98  98    5  30  39   H,K=  6, -3  H,K=  6,  8  10  98  98   11  19  22   H,K=  9, -2  H,K= 10, -4   8 106 103    2  95  95    2  68  65
14 107 100    4 610 604    8 282 281    0  72  70    5  26   7   13  51  48    8 299 307    3 165 168    1  12  16*  H,K=  7,  4  H,K=  8,  1   2 138 141    2 127 131   H,K= 11, -5   5  10   6*  H,K= 13,  0
H,K=  0,  5   7   0  11*  11  51  51    3  30  27    8 103 102   H,K=  4,  4  11  28  29    6 166 162    4  75  69    0 101 102    1  46  47    5  92  90    5   9  10*   1 103 106    8  86  84    1  14   4*
 1 232 225   10 181 182   14  87  88   H,K=  3, -2  11  31  38    0 240 237   14  74  72    9  56  52   H,K=  6,  9   3  45  45    4 191 193    8  79  78    8 124 127    4  78  78   H,K= 12, -4  H,K= 14,-11
 4 200 195   13   0   7*  H,K=  2,  1   2 300 296   H,K=  3,  8   3  49  53   H,K=  5,  1  12 131 133    0  48  51    6 100 100    7   6  11*  11   0  13*  11  17  20*   7  53  40    1  61  61    1  17  14*
 7 189 197   H,K=  1,  4   1 470 454    5 241 237    1  56  56    6 183 185    1 222 221   H,K=  6, -2  H,K=  7, -6   9  37  39   10  80  89   H,K=  9, -1  H,K= 10, -3  10  60  58    4  88  88   H,K= 14,-10
10 144 149    0 331 328    4 511 501    8 133 127    4 112 110    9  31  24    4  76  66    2 363 358    1  97  98   H,K=  7,  5  H,K=  8,  2   1  26  29    1  42  43   H,K= 11, -4   7  22  17*   3  39  29
13  16  21*   3  34  34    7 121 125   11  35  35    7  23  34*  12 105 106    7 118 121    5  68  70    4  83  82    2  84  85    0  87  87    4 203 205    4 149 146    3  28  15   H,K= 12, -3  H,K= 14, -9
H,K=  0,  6   6 210 206   10 206 211   14 131 134   10  51  50   H,K=  4,  5  10 128 131    8 163 163    7  83  88    5  33  23    3  93  89    7  59  61    7  55  51    6 115 113    3  49  50    2  80  78
 3  41  11    9 131 137   13  53  49   H,K=  3, -1  H,K=  3,  9   2 179 179   13  19  13   11  54  58   10 124 127    8  68  69    6 102 101   10  50  51   10  53  55    9  44  43    6  55  57    5  24  25
 6 169 169   12 113 111   H,K=  2,  2   1 166 166    0  86  86    5  78  80   H,K=  5,  2  14  69  63   13  23  29   H,K=  7,  6   9  25  32*  H,K=  9,  0  H,K= 10, -2  H,K= 11, -3  H,K= 12, -2  H,K= 14, -8
 9  62  65   H,K=  1,  5   0   0  20*   4 584 582    3  18  10    8 108 109    0 394 394   H,K=  6, -1  H,K=  7, -5   1   9  13*  H,K=  8,  3   0 100  99    3  13   8*   2 113 114    2 108 107    1  16   7*
12  64  65    2 295 285    3 476 463    7 105 106    6  99  95   11  21  24    3  38  35    1 216 216    3 102 106    4  84  87    2  90  90    3  30  29    6 144 143    5  11  16*   5  17  20*   4  70  63
H,K=  0,  7   5  70  71    6 240 231   10  79  77   H,K=  3, 10  H,K=  4,  6   6 176 175    4 151 150    6 142 141    7  27  23    5  17  17    6 136 136    9   9  18*   8  68  73    8  53  55   H,K= 14, -7
 2 176 175    8 199 205    9 113 118   13  79  79    2  50  55    1  93  93    9  27  28    7  74  73    9  18  28   H,K=  7,  7   8  87  87    9  17  18   H,K= 10, -1  H,K= 11, -2  H,K= 12, -1   3  30  27
 5  78  79   11  30   8   12 128 129   H,K=  3,  0   5  57  52    4 121 120   12  88  87   10 147 151   12  81  83    0  61  61   H,K=  8,  4  H,K=  9,  1   2  91  95    1  44  44    1  37  31   H,K= 14, -6
 8 181 185   14  72  72   15  27  20    0  81  88   H,K=  3, 11   7  45  43   H,K=  5,  3  13  14  11*  H,K=  7, -4   3  34  36    1  32  29*   2  99  98    5  34  38    4 109 110    4  51  54    2  50  53
11  23  23   H,K=  1,  6  H,K=  2,  3   3 371 345    1  14   7*  10  78  76    2 251 256   H,K=  6,  0   2 392 393   H,K=  8, -7   4  98  96    5  19  16    8  73  73    7  17  21    7  22  18*   5  41  35
H,K=  0,  8   1  90  91    2 447 438    6 483 486   H,K=  4, -3  H,K=  4,  7   5 137 138    0 490 496    5 106 107    3  99 104    7  38  20    8  89  93   H,K= 10,  0  H,K= 11, -1  H,K= 12,  0  H,K= 14, -5
 1  79  79    4 139 135    5  18  13    9  19  21    1  10  16*   0 138 138    8 111 110    3  20  14    8 151 147    6 191 193   H,K=  8,  5  H,K=  9,  2   1  69  67    3  22  32    0  92  91    1   0   9*
 4 170 174    7  40  50    8 151 156   12 112 113    4 625 619    3   0   9*  11  18  13*   6 172 176   11  47  45    9   8  10*   0  72  69    1  71  72    4  81  85    6  73  75    3  21  23    4  63  63
 7  20  21   10 133 133   11  86  86   15  14   9*   7 191 193    6 113 114   H,K=  5,  4   9  82  81   H,K=  7, -3  12  64  62    3  21  26    4  85  84    7  28  25    9  25  29    6  47  49   H,K= 14, -4
10  96  95   13  50  35   14  76  76   H,K=  3,  1  10  88  82    9  48  49    1  12  14*  12  62  61    1  87  80   H,K=  8, -6   6  83  81    7  11  11*  10  55  57   H,K= 11,  0  H,K= 12,  1   3  34  27
H,K=  0,  9  H,K=  1,  7  H,K=  2,  4   2 295 291   13  22  18   H,K=  4,  8   4 170 175   H,K=  6,  1   4 246 249    2 131 128   H,K=  8,  6  H,K=  9,  3  H,K= 10,  1   2  77  78    2  74  68   H,K= 14, -3
 3  72  72    0 171 173    1  20  15    5  63  64   H,K=  4, -2   2  77  79    7  55  51    2 300 301    7  12  19*   5 124 126    2  66  67    0  86  84    0 126 124    5  16   8   H,K= 13,-12   2  65  62
 6 112 110    3 181 182    4 296 293    8 250 250    3  59  55    5  27  27   10 103 106    5  70  68   10 190 191    8 162 165    5  49  39    3  35  33    3  36  29    8  85  86    1  29  13   H,K= 15, -7
 9  43  46    6 136 135    7 101 103   11 136 135    6 510 511    8  62  68   H,K=  5,  5   8 164 171   13  27  22   11   6  15*  H,K=  8,  7   6 108 108    6  96  98   H,K= 11,  1   4  44  43    1   0   6*
H,K=  0, 10   9   2  13*  10 121 122   14  73  69    9  22  23   H,K=  4,  9   0 186 187   11   9   7*  H,K=  7, -2  H,K=  8, -5   1  41  10   H,K=  9,  4   9  22  28    1  46  47   H,K= 13,-11
 2 137 137   12  75  74   13  26  32   H,K=  3,  2  12 156 155    1  23   5    3  18  10   H,K=  6,  2   3 149 153    1  41  41   H,K=  9, -8   2  44  44   H,K= 10,  2   4  43  40    3   7  11*
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TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR NICKEL FLUOSILICATE HEXAHYDRATE

     FCA(0,0,0) =  2296

 L FOB FCA   H,K=  0,  6   8  75  74    4 114 118   H,K=  2,  5   6 465 475    2 151 151    2 194 191    8 112 113   H,K=  5,  5   3  64  64    8 119 119   H,K=  8, -7   1  40  39    4 208 202   H,K= 10, -1
H,K=  0,  0   3  42  41   H,K=  1,  3  H,K=  2, -1   0 273 274    9  18  11*  H,K=  3,  8   5  92  93   H,K=  5, -2   0 188 185    6 164 157   H,K=  7, -3   3  67  67    4 190 187   H,K=  9,  0   2  75  77
 3  76  81    6 154 154    1 245 245    3  46  45    3  48  50   H,K=  3,  1   1  21  23    8 200 206    1  83  79    3  27  25   H,K=  6,  1   1  31  27    6 199 197   H,K=  8,  2   0  76  77   H,K= 10,  0
 6  17  17   H,K=  0,  7   4 628 636    6 312 319    6 203 199    2 294 304   H,K=  4, -3  H,K=  4,  3   4 388 387   H,K=  5,  6   2 290 289    4 227 224   H,K=  8, -6   0  62  63    3  10   7    1  50  50
 9  23  20    2 128 123    7  15  15    9  27  26   H,K=  2,  6   5  96  94    1  66  76    1 196 202    7  11  13    2 124 123    5  31  31    7  50  50    2 120 115    3  84  85    6 112 116   H,K= 11, -9
H,K=  0,  1   5  19  19   10 153 151   H,K=  2,  0   2 146 145    8 203 200    4 577 579    4 176 170   H,K=  5, -1  H,K=  6, -5  H,K=  6,  2  H,K=  7, -2   5 113 113   H,K=  8,  3  H,K=  9,  1   2 125 130
 2 692 661   H,K=  0,  8  H,K=  1,  4   2 282 285    5  57  59   H,K=  3,  2   7 172 177    7  95  97    3 129 127    2 349 348    1  24  25    3  95  95   H,K=  8, -5   2  67  71    2  89  91   H,K= 11, -8
 5 258 257    1  76  71    0 292 302    5 203 202   H,K=  2,  7   1 269 272   10  53  55   H,K=  4,  4   6 349 351    5  15  12    4 167 166    6 104  96    1  29  24   H,K=  9, -8  H,K=  9,  2   1   6   3
 8 392 398    4 169 167    3 129 129    8 266 264    1 106 106    4 336 335   H,K=  4, -2   0 244 241    9  45  45    8 208 209    7  25  27   H,K=  7, -1   4 122 120    2  74  71    1  54  55   H,K= 11, -7
11  68  69   H,K=  0,  9   6 161 159   H,K=  2,  1   4 180 177    7  50  50    3  44  37    3  39  41   H,K=  5,  0  H,K=  6, -4  H,K=  6,  3   2 272 269    7  17  16   H,K=  9, -7  H,K= 10, -9   3  15  15
H,K=  0,  2   3  43  43    9 128 126    1 415 405   H,K=  2,  8  H,K=  3,  3   6 510 520    6 169 171    2 134 137    1  56  59    0 175 172    5  15  15   H,K=  8, -4   1  54  52    1  15  15   H,K= 11, -6
 1  47  46    6 100 108   H,K=  1,  5   4 514 514    0  71  73    0 252 260    9  22  23   H,K=  4,  5   5 107 110    4 204 199    3  80  78   H,K=  7,  0   3 201 200    4 166 162    4 131 135    2  82  84
 4 427 435   H,K=  0, 10   2 277 270    7 146 151    3  73  75    3  66  68   H,K=  4, -1   2 151 145    8 290 294    7  74  70   H,K=  6,  4   1  12  11    6  50  40   H,K=  9, -6  H,K= 10, -8  H,K= 11, -5
 7 101 104    2 125 127    5   5   6*  10 179 178   H,K=  2,  9   6 229 231    2 151 147    5  66  68   H,K=  5,  1  H,K=  6, -3   2 174 174    4 185 184   H,K=  8, -3   3  51  48    3  25  25    1 101 105
10 180 178   H,K=  1,  0   8 185 191   H,K=  2,  2   2  98 102    9  24  24    5  90  87   H,K=  4,  6   1 186 190    3 183 190   H,K=  6,  5   7  85  84    2 311 306   H,K=  9, -5  H,K= 10, -7   4  51  53
H,K=  0,  3   1  38  49   H,K=  1,  6   0  37  30   H,K=  3, -2  H,K=  3,  4   8 213 214    1  72  70    4  47  43    6 143 135    1  77  78   H,K=  7,  1   5  73  72    2 182 170    2  71  71   H,K= 11, -4
 3  42  39    4 226 206    1 128 131    3 375 374    2 197 200    2 122 116   H,K=  4,  0   4 107 108    7  84  85    9   4   3*   4  76  80    0 181 166   H,K=  8, -2   5  56  54   H,K= 10, -6   3   4   3*
 6 238 242    7 195 193    4 116 112    6 176 178    5 210 215    5 230 234    1 481 482   H,K=  4,  7  H,K=  5,  2  H,K=  6, -2  H,K=  7, -6   3  39  38    1  51  53   H,K=  9, -4   1  32  35   H,K= 11, -3
 9  98  96   10 282 281    7   9   6    9  89  87    8 124 122    8 121 126    4 239 237    0 114 116    0 380 388    2 294 300    1  83  82    6  74  74    4 226 223    1  32  31    4 105 100    2  84  89
H,K=  0,  4  H,K=  1,  1  H,K=  1,  7  H,K=  2,  3  H,K=  3, -1  H,K=  3,  5   7  79  77    3  36  34    3  20  20    5  36  33    4  61  59   H,K=  7,  2   7  57  57    4 130 126   H,K= 10, -5  H,K= 11, -2
 2 591 586    0 742 764    0 136 127    2 491 495    1 128 139    1  87  86   10  85  89   H,K=  5, -4   6 142 142    8 154 157    7  51  51    2 251 251   H,K=  8, -1  H,K=  9, -3   3  11  10    1  17  15
 5  96  93    3 312 301    3 172 169    5  20  11    4 506 502    4 174 173   H,K=  4,  1   3 200 198   H,K=  5,  3  H,K=  6, -1  H,K=  7, -5   5  14  14    3  70  69    3  11   8   H,K= 10, -4
 8  86  88    6 129 134    6 143 142    8  92  93    7  55  54    7  18  20    0 393 403    6 169 188    2 215 214    1 231 236    3 103 108   H,K=  7,  3   6 155 153   H,K=  9, -2   2 112 109
H,K=  0,  5   9  27  25   H,K=  1,  8  H,K=  2,  4  10  46  49   H,K=  3,  6   3 150 149    9 109 104    5 157 155    4 123 125    6 100  96    1  69  71   H,K=  8,  0   2 122 116   H,K= 10, -3
 1 210 214   H,K=  1,  2   2 156 153    1  26  29   H,K=  3,  0   0 139 135    6 285 289   H,K=  5, -3  H,K=  5,  4   7  40  39   H,K=  7, -4  H,K=  7,  4   2 196 193    5  72  70    1   6   6
 4 182 178    2 864 872   H,K=  1,  9   4 269 266    0  37  45    3  95  94    9  67  64    2 268 273    1  39  36   H,K=  6,  0   2 396 402    0  88  91    5  46  47   H,K=  9, -1  H,K= 10, -2
 7 171 172    5  23  22    1  55  55    7  92  92    3 368 357   H,K=  3,  7  H,K=  4,  2   5  86  91    4 131 132    0 452 461    5 118 118    3  21  20   H,K=  8,  1   1  58  57    3  23  24
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TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ZINC FLUOSILICATE HEXAHYDRATE

     FCA(0,0,0) =  2376

 L FOB FCA    8  89  87   H,K=  1,  8   0 335 334    7  17  15*   5 169 167    3  31  32    8 118 119    0 210 212    8 168 168    3 241 242    4 204 202    1  62  60    3   9  21*  H,K= 12,-10  H,K= 13, -7
H,K=  0,  0  H,K=  0, 11   2 197 197    3 109 108   10 171 170    8 243 246   H,K=  5, -4  H,K=  5,  7   3 114 116   11  13  17*   6  91  88    7  41  47    4 160 162   H,K= 11,-10   1  35  41    2  95  93
 3  27  38*   1  41  41    5  17  17*   6 238 240   13  28  38   11  95  93    3 147 146    1  58  59    6  92  91   H,K=  7,  0   9  15  23*  10  50  58    7  50  47    3  16  15*   4  88  89    5  33  31
 6  81  81    4  62  65    8 108 109    9  17  12*  H,K=  3,  3  14 127 126    6 253 250    4 104 103    9  39  44    1  54  52   12 106 107   H,K=  9, -6  10  57  60    6  71  74    7  48  48    8  57  60
 9  69  68    7  59  60   11  81  76   12 111 110    0 313 311   H,K=  4,  0   9 157 157    7  59  60   12  95  94    4 227 228   H,K=  8, -3   3  93  94   H,K= 10, -8   9  57  55   H,K= 12, -9  H,K= 13, -6
12 101 103   H,K=  0, 12  H,K=  1,  9  H,K=  2,  6   3 136 140    1 539 539   12 128 131   H,K=  5,  8  H,K=  6,  4   7 121 122    2 352 353    6 203 202    3  23  25*  H,K= 11, -9   3  24  26*   1  29  38
15 105 100    3  13  18*   1  91  93    2 207 206    6 295 294    4 309 303   H,K=  5, -3   0  82  87    2 216 218   10 118 117    5 115 116    9   7  12*   6 166 166    2 159 159    6  53  58    4  86  86
H,K=  0,  1   6  58  57    4 146 147    5 115 118    9  19  25*   7  22  21*   2 371 370    3  16  20*   5  13  17*  13  12  17*   8 134 135   12  73  73    9  25  29    5  26  18   H,K= 12, -8   7  15  26*
 2 740 740   H,K=  0, 13   7  16  18*   8 148 150   12 126 125   10 131 130    5 135 136    6  80  78    8 121 119   H,K=  7,  1  11  48  48   H,K=  9, -5  H,K= 10, -7   8  56  56    2 154 149   H,K= 13, -5
 5 355 349    2  55  55   10  80  82   11  56  59   H,K=  3,  4  13  53  56    8 152 148   H,K=  5,  9  11  39  38    0 214 215   H,K=  8, -2   2 202 201    2 107 106   H,K= 11, -8   5  12  23*   3  43  43
 8 452 453   H,K=  1,  0  H,K=  1, 10  H,K=  2,  7   2 182 179   H,K=  4,  1  11  36  43    2  76  76   H,K=  6,  5   3  84  81    1  12  15*   5  93  95    5  74  76    1  37  36    8  49  46    6  77  78
11  38  39    1 108 121    0 142 141    1 138 139    5 279 283    0 466 471   14 122 120    5  33  31    1 110 106    6 114 116    4 253 257    8 157 158    8  87  90    4 177 176   H,K= 12, -7  H,K= 13, -4
14  75  74    4 152 133    3  20  13*   4 205 204    8 155 154    3 211 208   H,K=  5, -2  H,K=  6, -5   4 113 114    9  47  48    7  86  87   11  42  38   11  35  31    7  46  40    1  63  63    2 111 106
H,K=  0,  2   7 284 282    6  79  81    7  43  40   11  11  11*   6 359 361    1 143 141    2 407 407    7  54  52   12 109 109   10 117 116   H,K=  9, -4  H,K= 10, -6  10  56  54    4 118 118    5  21  27*
 1  50  51   10 318 322    9  41  38   10 116 116   H,K=  3,  5   9 109 109    4 479 477    5  45  47   10  71  72   H,K=  7,  2  13  28  26    1  85  82    1  71  70   H,K= 11, -7   7  34  29   H,K= 13, -3
 4 507 505   13  43  41   H,K=  1, 11  H,K=  2,  8   1  44  44   12  62  65    7  69  69    8 249 250   H,K=  6,  6   2 290 294   H,K=  8, -1   4 160 160    4 143 143    3  21  25*  H,K= 12, -6   1  25  24
 7 162 161   H,K=  1,  1   2  87  88    0 113 115    4 225 227   H,K=  4,  2  10 111 113   11  27  14    0 127 129    5  51  50    3  11  14*   7  32  33    7  42  45    6 130 131    3  20  26*   4  77  82
10 229 228    0 821 841    5  43  45    3 101 102    7  61  61    2 241 237   13  62  58   14  77  76    3   9   9*   8  86  87    6 188 190   10 134 133   10  75  74    9  43  39    6 111 108   H,K= 13, -2
13  40  41    3 409 396   H,K=  1, 12   6 115 114   10 113 114    5 138 135   H,K=  5, -1  H,K=  6, -4   6 102 103   11  60  57    9  30  31   H,K=  9, -3  H,K= 10, -5  H,K= 11, -6   9  41  42    3  45  41
H,K=  0,  3   6 201 201    1  19  12*   9  57  51   13  60  61    8 252 253    3 190 188    1 143 144    9  49  46   H,K=  7,  3  12 104 105    3  61  62    3  47  48    2 118 118   H,K= 12, -5  H,K= 13, -1
 3  69  68    9  79  78    4  58  56   H,K=  2,  9  H,K=  3,  6  11  19  24*   6 397 398    4 271 267   H,K=  6,  7   1 102 105   H,K=  8,  0   6 158 159    6 152 151    5   3  10*   2 105 106    2  70  74
 6 303 298   12 149 152   H,K=  2, -1   2 124 124    0 191 192   14  89  88    9  85  87    7 134 133    2 105 106    4 175 177    2 230 231    9  34  33    9  52  50    8 120 119    5  10   9*  H,K= 13,  0
 9 154 154   15  35  36    3 121 120    5  30  33    3 131 130   H,K=  4,  3  12  84  84   10 179 182    5  24  27*   7   9  10*   5  90  94   12  83  80   H,K= 10, -4  H,K= 11, -5   8  96  96    1   0   7*
12 186 185   H,K=  1,  2   6 383 384    8  75  77    6 158 159    1 111 114   H,K=  5,  0  13  13  18*   8  54  53   10 110 109    8  75  74   H,K=  9, -2   2 151 152    1 128 129   H,K= 12, -4  H,K= 14,-11
15  18  10*   2 904 930    9  27  27   H,K=  2, 10   9  28  24    4 243 241    2 199 197   H,K=  6, -3  H,K=  6,  8  H,K=  7,  4  11  36  28    2 161 162    5  19  22    4  89  88    1  75  76    1  12  18*
H,K=  0,  4   5  41  37   12 147 148    1  18   9*  12  80  80    7 135 136    5  35  38    3 228 233    1  16  24*   0 121 121   H,K=  8,  1   5 111 109    8 144 144    7  50  46    4 103 103   H,K= 14,-10
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11  45  46   H,K=  1,  3   5 298 289    0  85  84    8 109 110    0 292 289   H,K=  5,  1  H,K=  6, -2  H,K=  7, -6  H,K=  7,  5  10 102 102    1  17  19*   4 171 169    6 133 131    6  62  66    5  22  30*
14 113 114    1 358 346    8 319 316    3  32  34   11  47  46    3  87  90    1 259 260    2 378 380    1 133 134    2  96  98   H,K=  8,  2   4 235 236    7  63  61    9  43  47   H,K= 12, -2  H,K= 14, -8
H,K=  0,  5   4 672 674   11  67  70   H,K=  3, -2  H,K=  3,  8   6 206 205    4 107 102    5  95  94    4 116 113    5  21  25*   0 103 104    7  78  77   10  63  62   H,K= 11, -3   2 119 120    1  12  10*
 1 276 274    7  58  58   14  98  96    2 305 305    1  55  61    9  28  30    7 138 139    8 196 196    7  98 102    8  83  78    3 110 108   10  52  57   H,K= 10, -2   2 124 126    5  27  28    4  74  73
 4 243 238   10 198 198   H,K=  2,  1   5 283 285    4 137 134   12 115 116   10 145 146   11  70  72   10 138 139   H,K=  7,  6   6 114 114   H,K=  9,  0   3  23  19    5  16  27*   8  73  66   H,K= 14, -7
 7 227 230   13   4  11*   1 498 494    8 166 163    7  43  43   H,K=  4,  5  13  18  17*  14  69  69   13  30  34    1  32  25    9  41  38    0 117 118    6 165 162    8  84  84   H,K= 12, -1   3  29  29
10 164 165   H,K=  1,  4   4 559 558   11  44  46   10  54  57    2 198 198   H,K=  5,  2  H,K=  6, -1  H,K=  7, -5   4 104 102   H,K=  8,  3   3  42  40    9  13  22*  H,K= 11, -2   1  33  36   H,K= 14, -6
13  25  24*   0 368 371    7  92  95   14 144 145   H,K=  3,  9   5 102 105    0 432 433    1 277 279    3 141 145    7  21  26*   2 102 103    6 147 149   H,K= 10, -1   1  59  54    4  51  58    2  61  60
H,K=  0,  6   3  41  47   10 229 231   H,K=  3, -1   0 100  99    8 136 134    3  71  70    4 180 180    6 157 155   H,K=  7,  7   5  21  26*   9  25  28    2 113 113    4 119 122    7  18  24*   5  43  40
 3  24  22    6 233 225   13  53  57    1  88  94    3  15  14*  11  27  28*   6 193 195    7  91  90    9  33  35    0  69  69    8  94  97   H,K=  9,  1   5  50  49    7  27  25   H,K= 12,  0  H,K= 14, -5
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H,K=  0,  7   2 336 330    6 253 246   13  97  94    5  68  62    7  51  53    2 280 279    0 515 519    5 151 151   H,K=  8, -7   7  32  24   H,K=  9,  2   4  91  93    9  35  32   H,K= 12,  1   3  38  32
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 8 208 209   11   2  12*  15  24  20    3 433 422   H,K=  4, -3   0 153 153   11  14  15*   9 107 107   H,K=  7, -3   9   9  10*   3  34  33    7   6  16*  H,K= 10,  1   5  23  14*   1  16  18*  H,K= 15, -8
11  41  36   14  76  79   H,K=  2,  3   6 529 530    1  30  27    3  10  10*  H,K=  5,  4  12  66  69    1 100  95   12  65  67    6  98  93   H,K=  9,  3   0 148 144    8 103 100    4  50  49    2  50  53
H,K=  0,  8  H,K=  1,  6   2 523 525    9  39  40    4 655 659    6 125 128    1  22  25   H,K=  6,  1   4 273 273   H,K=  8, -6  H,K=  8,  6   0  96  93    3  38  37   H,K= 11,  1  H,K= 13,-11  H,K= 15, -7
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 4 201 201    4 169 165    8 158 159   15  14  13*  10  99  98   H,K=  4,  8   7  66  65    5  81  83   10 216 213    5 152 154    5  48  43    6 127 125    9  30  31    4  48  47   H,K= 13,-10
 7  25  19*   7  51  56   11  89  91   H,K=  3,  1  13  13  26*   2  95  96   10 122 121    8 185 185   13  33  29    8 183 182   H,K=  8,  7  H,K=  9,  4  H,K= 10,  2   7  34  29    2 111 111
10  98  98   10 144 145   14  88  87    2 344 352   H,K=  4, -2   5  38  37   H,K=  5,  5  11  17  12*  H,K=  7, -2  11   9  21*   1   3  14*   2  45  50    2  61  58   H,K= 11,  2   5  26  24*
H,K=  0,  9  13  43  38   H,K=  2,  4   5  40  41    3  38  28    8  70  71    0 223 223   H,K=  6,  2   3 164 167   H,K=  8, -5  H,K=  9, -8   5  53  52    5  23  24*   0  91  92   H,K= 13, -9
 3  81  85   H,K=  1,  7   1  40  36    8 272 272    6 559 563   H,K=  4,  9   3  20  21    1  40  40    6 135 136    1  45  45    2 120 120   H,K=  9,  5   8  92  93    3  17  25*   1  29  30
 6 135 133    0 182 185    4 333 329   11 154 152    9  35  34    1  14   8*   6 127 127    4 219 217    9  65  65    4 167 167    5  65  67    1   7   7*  H,K= 10,  3  H,K= 11,  3   4  99  98
 9  59  54    3 215 215    7 137 137   14  76  79   12 164 160    4  96  92    9  71  67    7  68  69   12 106 110    7  35  33    8 102 105    4  69  72    1  22  22*   2  79  76    7  21  16*
H,K=  0, 10   6 168 168   10 139 142   H,K=  3,  2  15  15  25*   7  35  35   H,K=  5,  6  10 149 148   H,K=  7, -1  10 160 160   11  48  43   H,K=  9,  6   4  71  70   H,K= 12,-11  H,K= 13, -8
 2 154 156    9  21  27*  13  36  35    1 375 373   H,K=  4, -1  H,K=  4, 10   2 156 151   13  20  23*   2 319 319   13  52  46   H,K=  9, -7   0  75  72   H,K= 10,  4   2 101 103    3  43  48
 5   3   9*  12  76  77   H,K=  2,  5   4 387 381    2  47  42    0  73  69    5  21  19   H,K=  6,  3   5  83  84   H,K=  8, -4   1  13  13*  H,K= 10, -9   0  78  76    5  17  22*   6  53  54
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tion of unit weight = 1·33. In the last cycle, no parameter shifted more than 1 % of its standard deviation. Slight variation of the occupancy ratio did not result in any significant improvement.

In the otherwise straightforward refinement of the structure of $ZnSiF_6.6H_2O$ we were confronted with the interesting fact that in this centric space group ($R\overline{3}$) different values of the coordinates must be assigned to identical structures if opposite choices are made for the positive direction of the unique axis. By chance, the same choice was made for the Co and Ni crystals, but the opposite choice for the Zn crystal. Thus the Zn structure was determined without the knowledge that it was so nearly the same as the others. The coordinates and indices had to be transformed by the matrix

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

to yield the results reported here. No meaningful improvement was gained when the occupancy ratio was changed from F(1)/F(2) = 0·33/0·67, and with this ratio $R = 0{\cdot}018$ excluding reflections with $I < \sigma(I)$; $R = 0{\cdot}023$ (all reflections), $R_2 = 0{\cdot}021$; standard deviation of an observation of unit weight = 1·07. In the last cycle no parameter shifted by more than 4 % of its standard deviation.

The final parameters are given in Table 1. Observed and calculated structure factors are listed in Table 2. Some interatomic distances and angles appear in Tables 3, 4 and 5.

Table 3. *Interatomic distances* (Å)

Values in parentheses are corrected for thermal motion, assuming that the lighter atom rides on the heavier atom. Distances involving disordered positions F(1) and F(2) are designated by (1) and (2) respectively.

(*a*) $CoSiF_6.6H_2O$			
Co–O		2·081 ± 0·001	(2·092)
Si–F	(1)	1·674 ± 0·001	(1·695)
	(2)	1·678 ± 0·002	(1·697)
O–H(1)		0·874 ± 0·026	(0·888)
O–H(2)		0·805 ± 0·032	(0·822)
(*b*) $NiSiF_6.6H_2O$			
Ni–O		2·047 ± 0·001	(2·055)
Si–F	(1)	1·671 ± 0·006	(1·701)
	(2)	1·683 ± 0·003	(1·698)
O–H(1)		0·862 ± 0·029	(0·881)
O–H(2)		0·709 ± 0·026	(0·737)
(*c*) $ZnSiF_6.6H_2O$			
Zn–O		2·078 ± 0·001	(2·088)
Si–F	(1)	1·671 ± 0·003	(1·693)
	(2)	1·680 ± 0·003	(1·698)
O–H(1)		0·778 ± 0·020	(0·790)
O–H(2)		0·775 ± 0·020	(0·797)

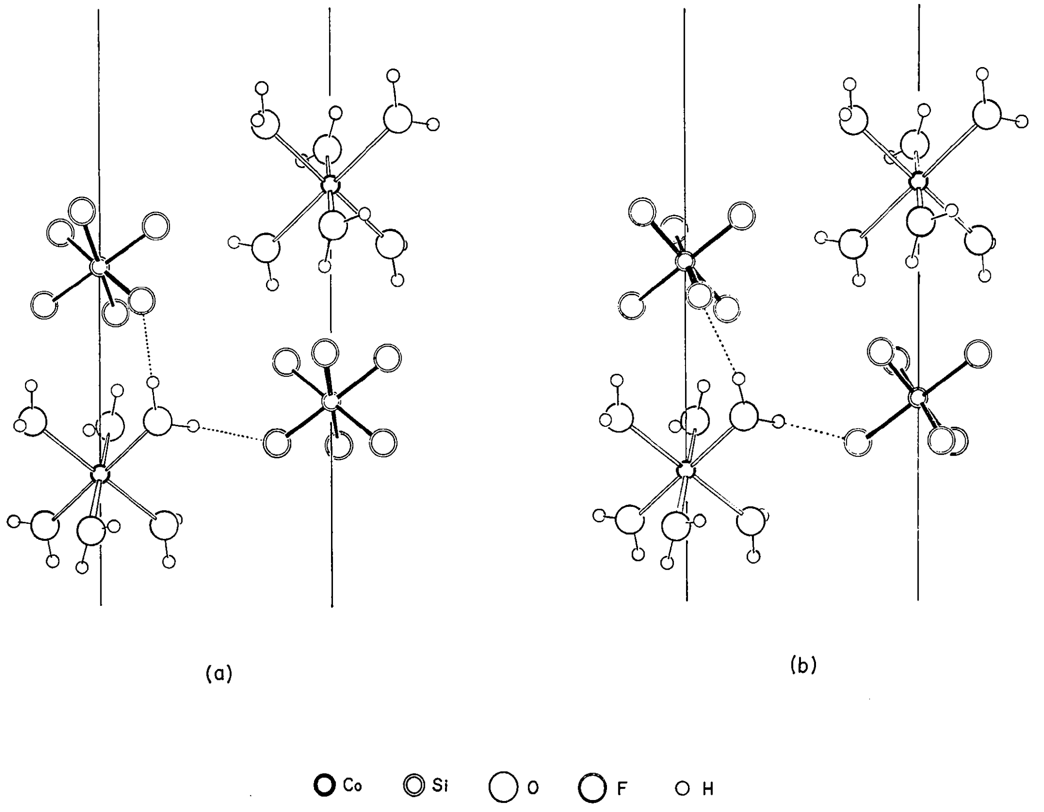

Fig. 1. Two neighboring columns in the structure of $CoSiF_6.6H_2O$. Fluorine atoms are shown in (*a*) according to the F(1) positions and in (*b*) according to F(2).

Table 4. *Distances involved in hydrogen bonds* (Å)

F|| and F⊥ refer respectively to bonds approximately parallel and perpendicular to the threefold axis.

(*a*) $CoSiF_6.6H_2O$		
O—F‖	(1) 2·711 ± 0·003	(2) 2·888 ± 0·003
H(1)-F‖	(1) 1·861 ± 0·026	(2) 2·037 ± 0·029
O—F⊥	(1) 2·721 ± 0·004	(2) 2·759 ± 0·003
H(2)-F⊥	(1) 1·961 ± 0·031	(2) 1·957 ± 0·033
(*b*) $NiSiF_6.6H_2O$		
O—F‖	(1) 2·718 ± 0·007	(2) 2·863 ± 0·004
H(1)-F‖	(1) 1·862 ± 0·031	(2) 2·017 ± 0·031
O—F⊥	(1) 2·683 ± 0·007	(2) 2·782 ± 0·003
H(2)-F⊥	(1) 2·021 ± 0·028	(2) 2·082 ± 0·027
(*c*) $ZnSiF_6.6H_2O$		
O—F‖	(1) 2·710 ± 0·004	(2) 2·868 ± 0·002
H(1)-F‖	(1) 1·948 ± 0·020	(2) 2·104 ± 0·021
O—F⊥	(1) 2·713 ± 0·003	(2) 2·766 ± 0·002
H(2)-F⊥	(1) 1·979 ± 0·020	(2) 1·995 ± 0·021

Table 5. *Bond angles* (°)

(*a*) $CoSiF_6.6H_2O$		
O—Co—O	89·4 ± 0·1	
O—Co—O′	90·6 ± 0·1	
F—Si—F	(1) 89·6 ± 0·2	(2) 89·6 ± 0·2
F—Si—F′	(1) 90·4 ± 0·2	(2) 90·4 ± 0·2
H(1)-O—H(2)	108·7 ± 3·0	
O—H(1)···F	(1) 163·7 ± 1·0	(2) 162·7 ± 1·0
O—H(2)···F	(1) 157·0 ± 1·0	(2) 174·0 ± 0·8
F····O······F	(1) 110·7 ± 0·1	(2) 123·5 ± 0·1
(*b*) $NiSiF_6.6H_2O$		
O—Ni—O	90·5 ± 0·1	
O—Ni—O′	89·5 ± 0·1	
F—Si—F	(1) 90·1 ± 0·4	(2) 89·4 ± 0·2
F—Si—F′	(1) 89·9 ± 0·4	(2) 90·6 ± 0·2
H(1)-O—H(2)	107·4 ± 3·0	
O—H(1)···F	(1) 171·9 ± 1·0	(2) 166·4 ± 0·7
O—H(2)···F	(1) 155·6 ± 1·0	(2) 169·5 ± 0·7
F····O······F	(1) 111·5 ± 0·2	(2) 123·1 ± 0·1
(*c*) $ZnSiF_6.6H_2O$		
O—Zn—O	89·9 ± 0·1	
O—Zn—O′	90·1 ± 0·1	
F—Si—F	(1) 89·8 ± 0·2	(2) 89·6 ± 0·1
F—Si—F′	(1) 90·2 ± 0·2	(2) 90·4 ± 0·1
H(1)-O—H(2)	108·1 ± 2·6	
O—H(1)···F	(1) 166·3 ± 0·7	(2) 167·0 ± 0·5
O—H(2)···F	(1) 157·8 ± 0·7	(2) 170·8 ± 0·6
F····O······F	(1) 110·9 ± 0·1	(2) 123·2 ± 0·1

Discussion

Except for minor numerical details the three salts have the same crystal structure. An unusual feature of this structure, for which we have no satisfactory explanation, is the disorder of F between two sites, unrelated by any symmetry element and with unequal occupancy factors. The distances between alternate sites are 0·71, 0·60 and 0·66 Å, respectively, in the Co, Ni and Zn salts. We assume that all the F atoms in a particular SiF_6^{2-} ion are in the same type of site because otherwise there would be unsatisfactory F–F distances. According to this model, the disorder involves two orientations of the fluosilicate ion about 30° apart with respect to rotation about the threefold axis. The F atoms are at the corners of regular or nearly regular octa-

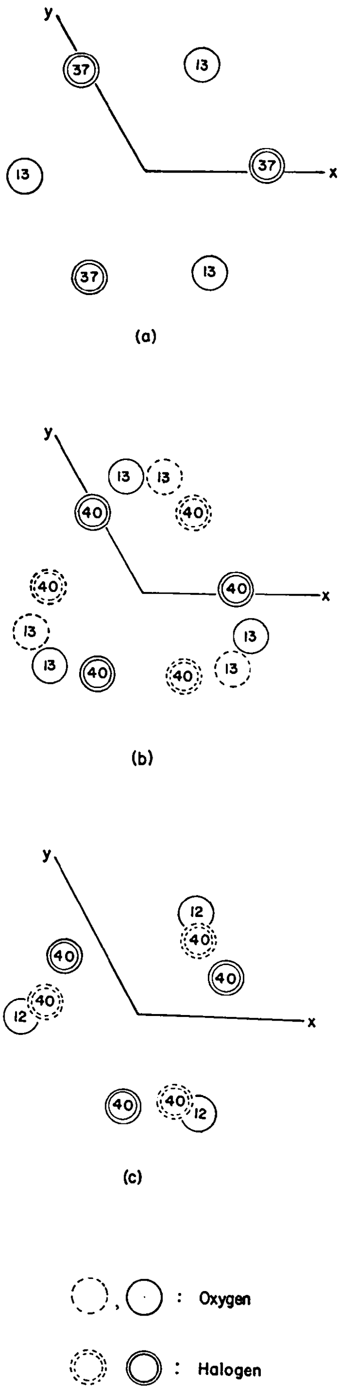

Fig. 2. Relative orientation of oxygen atoms on the top face of a water octahedron and halogen atoms on the bottom face of the adjacent octahedron in (*a*) $NiSnCl_6$ $6H_2O$ (Pauling, 1930), (*b*) $FeSiF_6$ $6H_2O$ (Hamilton, 1962) and (*c*) $CoSiF_6$ $6H_2O$ (this study). The numbers indicate values of the *z* coordinates (× 100), and broken circles indicate the alternate sites according to the disorder models.

hedra; for the F(1) sites in the Ni and Zn compounds the octahedra are regular within the experimental accuracy, while in the other cases there is a slight elongation in the direction of the threefold axis of two to four standard deviations. All six results are within about one standard deviation of an average shape with F–Si–F = 89·7°, as is also the result found by Hamilton (1962) for the Fe salt.

The water molecules are also at the corners of nearly regular octahedra, but these octahedra are not so consistent in shape. In the Zn salt the octahedron is regular, while for Co it is elongated and for Ni it is compressed, but by amounts which change bond angles only about half a degree. Hamilton (1962) observed a greater elongation [O–Fe–O = 88·6 (3)°] in the Fe salt.

These octahedra are packed according to a rhombohedrally distorted CsCl-type structure. The densest packing is in columns of alternate cations and anions along the threefold axis (Fig. 1). Three hydrogen bonds connect each pair of adjacent octahedra in a column, while one hydrogen bond connects an octahedron to each of its six neighboring octahedra in other columns. This topology of hydrogen bonding is the same for either F site and is also the same as that which Hamilton (1962) deduced for each component of his structure. It would not exist in the Pauling (1930) structure because in that arrangement each O would have two equidistant F neighbors in the same column (Fig. 2). This latter arrangement permits closer packing of spherical atoms, but provides too many acceptors for hydrogen bonds. Any rotation of one kind of octahedron relative to the other makes one neighbor closer than the other, with a rotation of 60° giving the maximum difference. In the $FeSiF_6.6H_2O$ structure, the oxygen atoms are twisted about 40° from the Pauling (1930) structure, in each component of the disorder model. In the present structures it is the fluorine atoms which are twisted, F(1) about 50° and F(2) about 20°.

Note added in proof: – Lynton & Siew (1973) describe the structure of the cobalt salt with fluorine in a single site with large and very anisotropic thermal motion. Their measurements ended at $2\theta = 40°$ with Mo $K\alpha$ radiation, while ours extended to 70°. This model is similar to the one which we found to be inadequate to fit our more extensive data.

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