to *z*. The way in which the layers of $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units are stacked above each other, corresponds very well to a three-dimensional hexagonal close packing if one considers only a pair of layers at $z \sim 1/4$ and $z \sim 3/4$. This means that each unit at $z \sim 3/4$ is stacked almost perfectly above a void between three units at $z \sim 1/4$ when viewed down **c*** (deviation only ~0·2 Å). This relationship is not valid, however, between layers at $z \sim 1/4$ and $z \sim -1/4$. Compared with close-packing they are displaced relative to each other by about 2·6 Å parallel to [560]. Owing to this displacement, the pseudo-trigonal triclinic unit cell is distinctly skew in a view perpendicular to the given direction (angle between **c** and **c*** is 8·37°). Trigonal pseudosymmetry, which stems from the arrangement of the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units, is further diminished by the irregular arrangement of the alkali cations at $z \sim 0$ and $z \sim 1/2$, by the water molecules $H_2O(30w)$–$H_2O(32w)$, and by the asymmetric conformation of the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ unit. The macroscopic result of this is that crystals of the title compound do not show obvious trigonal or hexagonal aspects in habit.

The title compound differs distinctly in architecture from the monoclinic phases β-$K_5Fe_3O(SO_4)_6.10H_2O$, $Rb_5Fe_3O(SO_4)_6.5H_2O$ and $K_{2\cdot64}Tl_{2\cdot36}Fe_3O(SO_4)_6.5H_2O$, but shows close relationships to salt *X*, $(Na,K,H_3O^+)_5Fe_3O(SO_4)_6.8\cdot5H_2O$, trigonal, space group $P\overline{3}$, $a = 9\cdot643$, $c = 18\cdot018$ Å, $Z = 2$ (Scordari & Milella, 1984), and to the mineral metavoltine, $KNa_3Fe^{2+}_{0\cdot5}Fe_3O(SO_4)_6.9H_2O$, trigonal, space group *P*3 or $P\overline{3}$, $a = 9\cdot58$, $c = 18\cdot17$ Å, $Z = 2$ (Giacovazzo, Scordari, Todisco & Menchetti, 1976). In their structures $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units are centered at $x = \pm 1/3$, $y = \pm 2/3$, $z \sim \pm 1/4$, and thus adopt an almost perfect hexagonal close-packed arrangement, not violated by displacements as in the title compound. In salt *X* one potassium ($x = \pm 1/3$, $y = \pm 2/3$, $z = \pm 0\cdot78$), a sodium ($x = \pm 1/3$, $y = \pm 2/3$, $z = \pm 0\cdot52$) and a Fourier peak interpreted as an H_3O^+ ion ($x = y = 0$, $z = \pm 0\cdot86$) correspond in positions and function to *A*(1), *A*(2) and $H_2O(29w)$ in the title compound. The remaining cations (Na, K and postulated H_3O^+) and water molecules in salt *X* are located near $z \sim 0$ and $z \sim 1/2$, as in the title compound, but show a complicated disorder.

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Structure of $Ag_{0\cdot6}NbS_2$

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Abstract. Silver niobium sulfide, $Ag_{0\cdot6}NbS_2$, $M_r = 223\cdot48$, hexagonal, $P6_3/mmc$, $a = 3\cdot354\,(1)$, $c = 14\cdot431\,(1)$ Å, $V = 140\cdot59\,(6)$ Å^3, $Z = 2$, $D_x = 5\cdot279$ g cm^{-3}, $\lambda(\text{Mo } K\overline{\alpha}) = 0\cdot71073$ Å, $\mu = 93$ cm^{-1}, $F(000) = 203\cdot9$, $T = 295$ K, $R_F = 0\cdot037$ for 335 observed reflections with $I \geq 3\cdot0\sigma(I)$. This single-crystal study confirms the space-group symmetry known from powder data. The structure is based on NbS_2 sandwiches, between which Ag is statistically distributed in the tetrahedral holes.

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Introduction. Phases $M_x\mathrm{Nb}X_2$ ($M = \mathrm{Ag,Cu}$; $X = \mathrm{S,Se}$; $0{\cdot}1 \le x \le 0{\cdot}8$) have been extensively studied by X-ray powder diffaction (Koerts, 1962), electron diffraction (de Ridder, Van Tendeloo, Van Landuyt, Van Dyck & Amelinckx, 1976; Boswell, Prodan & Corbett, 1976, 1980; Curzon & Rajora, 1985), electrochemical, magnetic and electrical measurements (Rajora & Curzon, 1986; Bouwmeester, 1985, 1988). The structure of the phases $\mathrm{Cu}_x\mathrm{NbS}_2$ and $\mathrm{Ag}_x\mathrm{NbS}_2$ ($\sim 0{\cdot}6 \le x \le 0{\cdot}8$), determined from powder data (Koerts, 1962), is described in space group $P6_3/mmc$ with the atoms in special positions: S at 4(f) with coordinates $z \simeq \frac{1}{8}$, Cu (Ag) statistically distributed at 4(f) with $z \simeq 0{\cdot}437$ and Nb at 2(c). In this paper the refinement of the structure of $\mathrm{Ag}_{0{\cdot}6}\mathrm{NbS}_2$ at 295 K is described.

Table 1. *Final fractional atomic coordinates and mean-square amplitudes* (Å^2) *with e.s.d.'s in parentheses*

$$F(\mathbf{h}) = F_o(\mathbf{h}) \exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j a_i^* a_j^* U_{ij}\right).$$

	x	y	z	S.o.f.	U_{11}	U_{33}
Ag	$\frac{1}{3}$	$\frac{2}{3}$	0·4801 (1)	0·308 (3)	0·049 (1)	0·0081 (4)
Nb	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1·000	0·0047 (1)	0·0074 (2)
S	$\frac{2}{3}$	$\frac{1}{3}$	0·14277 (8)	1·000	0·0080 (2)	0·0081 (3)

Note: $U_{11} = U_{22} = 2U_{12}$; $U_{13} = U_{23} = 0$.

Experimental. Polycrystalline samples of $\mathrm{Ag}_{0{\cdot}7}\mathrm{NbS}_2$ were prepared by synthesis from the elements in evacuated quartz tubes at temperatures of 1073–1273 K for six days. The samples obtained were powdered and annealed at 1123 K for one day. Single crystals could be grown by vapour transport (1223–1023 K) with a polycrystalline sample as starting material, using chlorine [from $(\mathrm{NH_4})_2\mathrm{PbCl_6}$] as transport agent. A suitable plate-shaped crystal (0·15 × 0·12 × 0·03 mm) was glued on the top of a glass fibre and mounted on an Enraf–Nonius CAD-4F diffractometer [295 K; graphite-monochromated Mo $K\bar{\alpha}$ radiation; 5900 reflections scanned; $\omega/2\theta$ scan, $\Delta\omega = (0{\cdot}85 + 0{\cdot}35\tan\theta)°$; $1{\cdot}14 < \theta < 49{\cdot}9°$; $(\sin\theta/\lambda)_{\max} = 1{\cdot}0768$ Å^{-1}; h: $-7 \rightarrow 7$; k: $-7 \rightarrow 7$; l: $-31 \rightarrow 31$]. Unit-cell dimensions and their standard deviations were determined from the setting angles of 12 reflections in the range $32{\cdot}01 < \theta < 34{\cdot}00°$ in four alternate settings (de Boer & Duisenberg, 1984). The three standard reflections were measured every 2 h of X-ray exposure (014: r.m.s. deviation 0·77%; 100: r.m.s. deviation 0·53%; 102: r.m.s. deviation 0·76%); these showed no decay during the 77·4 h of X-ray exposure time. A 360° ψ scan for the reflection 110 showed an intensity variation up to 31% about the mean value. The intensity data were corrected for the scale variation, Lorentz and polarization effects and for absorption using a Gaussian-integration method (Spek, 1983; grid: 8 × 8 × 8, corrections in the range 1·27 to 2·91). Preliminary refinements showed indications of the occurrence of extinction, and therefore the intensities of all reflections, along with the values of the absorption-weighted mean path length (T_{bar}), were used to obtain extinction correction factors [Zachariasen formalism (Coppens & Hamilton, 1970), Gaussian distribution, $g = 0{\cdot}181\ (4) \times 10^4$]. The refinements were performed by full-matrix least squares on F; the coordinates determined by Koerts (1962) were used as starting values. In addition anisotropic temperature factors for all atoms, one occupancy factor for Ag and one scale factor were refined. After applying the obtained extinction correction factors, averaging of symmetry-related reflections was performed in Laue classes $\bar{3}m$ and $6/mmm$, resulting in 626 and 369 reflections respectively satisfying the $I \ge 3{\cdot}0\sigma(I)$ criterion of observability, the internal consistency factor being $R_I = \sum_k[\sum_j(\bar{I}_k - I_j)^2]/\sum_k\sum_j(I_j^2)_k = 0{\cdot}026$ (0·030 without extinction correction) and 0·026 (0·029) respectively. The final refinements were performed with these two unique sets. The space group $P6_3/mmc$ (No. 194; *International Tables for Crystallography*, 1983) was obtained as the most probable one. The refinements converged at $R_F = 0{\cdot}037$, $wR = 0{\cdot}039$, $S = 0{\cdot}917$; $w = 1$; ten parameters refined; $\langle\Delta/\sigma\rangle < 0{\cdot}001$, max. $\Delta/\sigma < 0{\cdot}001$. The final difference Fourier map revealed maximum and minimum densities of $-3{\cdot}2$ and $4{\cdot}9$ e Å^{-3}, both near the silver sites. Final fractional atomic coordinates, occupancies and anisotropic thermal parameters for the atoms are given in Table 1.* Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on the CDC-Cyber 170/760 computer of the State University of Groningen with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983), and calculation of geometrical data was carried out with *EUCLID* (Spek, 1982).

Discussion. The present study confirms the approximate structure proposed by Koerts (1962). Inspection of the structure-factor list however shows that reflection conditions required by space-group symmetry $P6_3/mmc$ and atoms in special positions 4(f) and 2(c) are not completely fulfilled. Although we did not check it experimentally, we do not believe that the 'Umweganregung' effect could be responsible for the presence of all these reflections (the crystal was mounted arbitrarily on the diffractom-

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* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52674 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

eter). Instead we have tried to explain the presence of three different sets of nearly extinct reflections $[3\sigma(I) < I \leq 10\sigma(I)]$, *viz.* (1) *hhl* with *l* odd; (2) 00*l* with *l* odd; (3) $h—k = 3n$ with *l* odd and $h \neq k$, by employing different structural models.

Reflections of set (3) may be present in the case of pronounced anharmonicity, as can be shown by applying Dawson's structure-factor formalism (Dawson, 1967; Willis & Pryor, 1975). Silver intercalates of the transition metal dichalcogenides are known for high diffusion coefficients of Ag. In diffraction, one finds in such cases significant anisotropic and anharmonic thermal vibration as was shown in the case of $AgCrSe_2$ (van der Lee & Wiegers, 1989). The addition of three third-order tensor elements $[C_{111} = 0{\cdot}16\,(2) \times 10^{-3}$, $C_{333} = 0{\cdot}14\,(6) \times 10^{-6}$ and $C_{113} = 0{\cdot}017\,(1) \times 10^{-3}]$, using the Gram–Charlier expansion of the temperature factor (Zucker & Schulz, 1982), lowered the agreement factors significantly ($R_F = 0{\cdot}024$, $wR = 0{\cdot}030$), but still gave too low calculated structure factors in set (3). Adding fourth-order tensor elements did not improve the fit, so only the third-order tensor elements are considered to be significant. A study of anharmonicity in $Ag_{0\cdot6}NbS_2$ and related compounds as a function of temperature will be presented elsewhere. A refinement of a model with different occupancies of silver sites in layers *c*/2 apart (space group $P\bar{3}m1$) did not give better results. In this space group, there are no general or special reflection conditions, but the calculated structure factors in the three sets were still systematically too low. Moreover, the difference Fourier synthesis did not improve much and still showed peaks and holes near the silver sites. Some other space groups were tried ($P6_3$, $P3m1$), with different occupancies of the silver sites, with and without anharmonic temperature factors, but none gave satisfactory results, especially with respect to the difference Fourier synthesis.

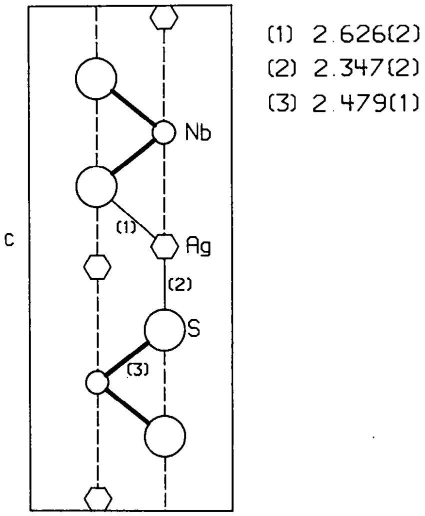

Fig. 1. ($1\bar{1}20$) section of the structure of $Ag_{0\cdot6}NbS_2$. Large open circles are S atoms, Nb atoms are small open circles, the hexagon denotes Ag. Bond lengths in Å with e.s.d.'s in parentheses.

Because none of the alternative models could explain the occurrence of the weak reflections in the three sets, we retain $P6_3/mmc$ as the most probable space-group symmetry. The structure is shown in Fig. 1. Ag is statistically distributed over the available tetrahedral sites between the NbS_2 sandwiches with a refined occupancy of 0·309 (3). The equal occupancy of the silver sites is what one would expect from theoretical calculations. Sato & Kikuchi (1971) calculated the phase diagram of the *hc* lattice using the cluster variation method in the pair approximation and found that long-range order is not possible for $x < 2/3$ in the case of stage-1 phases, *i.e.* phases with all van der Waals gaps occupied by silver. A renormalization group approach given by Sabbaswamy & Mahan (1976), as well as a Monte Carlo simulation by Ishikawa, Taguchi & Ozeki (1987) shows this to be the case for $x \leq 0{\cdot}84$ in stage-1 phases. There is no indication of an occupation of the octahedral sites in the van der Waals gap.

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Structural Instability of the Water Molecule in $Sr(IO_3)_2.H_2O$, a Neutron Diffraction Study

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Abstract. Strontium diiodate(V) monohydrate, $Sr(IO_3)_2.H_2O$, $M_r = 455{\cdot}44$, monoclinic, $I2/c$, $a = 8{\cdot}9003\,(6)$, $b = 7{\cdot}748\,(1)$, $c = 9{\cdot}6496\,(8)$ Å, $\beta = 90{\cdot}230\,(8)°$, $V = 665{\cdot}47\,(9)$ Å^3, $Z = 4$, $D_x = 4{\cdot}546\,(1)$ Mg m^{-3}, neutron radiation, $\lambda = 0{\cdot}8494$ Å, μ(calc.) $= 0{\cdot}0124$ mm^{-1}, $F(000) = 202{\cdot}93$ fm, $T = 295$ K, $R = 0{\cdot}042$ for 977 observed unique reflections. The water molecules exhibit strong librational motion perpendicular to the H_2O plane, shown by a large anisotropy of the O(4) thermal ellipsoid. The O—H bond length is 0·942 (2) Å, the H—O—H angle 114·4 (3)° and the hydrogen-bond length (H···O) is 1·864 (2) Å.

Introduction. As part of spectroscopic and structural studies on alkaline earth halate hydrates (Lutz & Klüppel, 1975; Lutz, Klüppel & Kesterke, 1976; Eckers & Lutz, 1985; Lutz, Alici & Buchmeier, 1985) with special respect to the water of crystallization in these compounds, we performed a neutron diffraction study on $Sr(IO_3)_2.H_2O$. The crystal structure of $Sr(IO_3)_2.H_2O$, which is isostructural to the $Ba(ClO_3)_2.H_2O$ (Kartha, 1952*a*,*b*) type halates $M(XO_3)_2.H_2O$ (M = Sr, Ba, Pb; X = Cl, Br, I), was determined by Manotti Lanfredi, Pellinghelli, Tiripicchio & Tiripicchio Camellini (1972) (hereafter MPTT) by X-ray single-crystal methods.

Experimental. Single cyrstals of $Sr(IO_3)_2.H_2O$ were grown by interdiffusion of $SrCl_2$ and HIO_3 solutions in an H-shaped tube with an intermediate layer of pure water at room temperature. The cell parameters were refined from Guinier powder data (Huber FR601 camera, Cu $K\alpha_1$ radiation, 52 reflections, α-quartz as internal standard, $a = 4{\cdot}9136$, $c = 5{\cdot}4054$ Å) by least-squares methods.

A suitable crystal (elongated monoclinic prism, $3{\cdot}90 \times 0{\cdot}65 \times 0{\cdot}55$ mm) was mounted in a sealed quartz capillary on an Enraf–Nonius CAD-4 diffractometer in order to obtain the orientation matrix. It was then mounted on the D9 four-circle diffractometer now equipped with a two-dimensional detector system (Lehmann, Kuhs, McIntyre, Wilkinson & Allibon, 1989) at the Institut Laue–Langevin, Grenoble. A beryllium (110) monochromatized neutron beam was used. The intensities of 1263 reflections, of which 1112 were unique, were collected in the range $2 \leq 2\theta \leq 80°$; range of hkl: $-13 \leq h \leq 13$, $0 \leq k \leq 11$, $0 \leq l \leq 14$. Data reduction was performed according to Wilkinson, Khamis, Stansfield & McIntyre (1988). A numerical absorption correction did not improve the results, an intensity decrease of the standard reflection ($\bar{4}00$) was not observed during data collection.

The Sr, I and O positions obtained from X-ray data (MPTT) were used as starting values for the refinement. Scattering lengths for all atoms were taken from Sears (1986). The iodine position reported by MPTT turned out to be incorrect, possibly due to a misprint; it was therefore determined from a difference Fourier synthesis, as were the hydrogen positions. Full-matrix least-squares refinement (modified *SHELX*; Sheldrick, 1976) of positional and anisotropic thermal parameters, extinction coefficient, and scale factor based on F magnitudes of 977 reflections with $F \geq 2\sigma_F$ gave a final $R = 0{\cdot}042$ [$wR = 0{\cdot}035$, $w = 2{\cdot}07/\sigma^2(F)$] and an extinction coefficient of $4{\cdot}9\,(2) \times 10^{-7}$. The ratio of

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