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Profile Structure Refinement of $\text{SrCl}_2 \cdot 2\text{D}_2\text{O}$ by Neutron Powder Diffraction

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Abstract

The structure is built up of $\text{SrCl}_4(\text{D}_2\text{O})_4$ polyhedra forming parallel layers (100). The water molecules are strongly distorted, which results from the different strengths of the hydrogen bonds formed by D(1) and D(2) to adjacent Cl^- ions. The respective D...Cl distances are 2.159 (4) and 2.424 (3) Å, and the O—D bond lengths are 0.980 (5) and 0.959 (4) Å (300 K). (The JCPDS File Nos. for strontium chloride deuterate are 43-1493 and 43-1494.)

Comment

$\text{SrCl}_2 \cdot \text{H}_2\text{O}$ crystallizes in its own structure type. It can serve as a model system for studying solid hydrates with highly asymmetric force fields of the water molecules and isotope effects involved (Lutz, 1982, 1988). This is due to the presence of only one kind of strongly distorted H_2O molecule in the structure (Lutz, Pobitschka, Christian & Becker, 1979). For such studies (Möller, 1993) knowledge of the crystal structure including the true H-atom positions is necessary. We therefore performed a neutron powder diffraction study (see Fig. 1) on fully deuterated strontium chloride dihydrate at 300 and 1.5 K (for the latter temperature data are given in parentheses). The only structure determination (single crystal, X-ray) known so far is based on film methods and estimated intensities (Jensen, 1942).

The final profile parameters are given in Table 1, the structural parameters in Table 2. The results obtained confirm the crystal structure of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ as determined by Jensen (1942) with respect to the positions of the heavy atoms. The setting chosen is different from that originally used by Jensen (1942), but consistent with that in *Structure Reports* (Jensen, 1942). The structure is built up of parallel layers (100), which are held together by the rather weak hydrogen bonds formed by D(2) (see Fig. 2). This explains the platelet-like habit of the $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ crystals. For a more detailed description of the struc-

ture see Jensen (1942) and Möller (1993). On cooling, contraction of the lattice constants and bond lengths mainly takes place in the (100) plane. This is shown by comparing interlayer distances such as $\text{D}(2)^0$ — $\text{D}(2)^{\text{viii}}$ of 3.158 (4) Å at 300 K and 3.157 (5) Å at 1.5 K with intralayer distances such as $\text{D}(2)^0$ — $\text{D}(2)^{\text{ii}}$ of 3.394 (5) and 3.368 (5) Å. No phase transition is observed between 1.5 and 300 K.

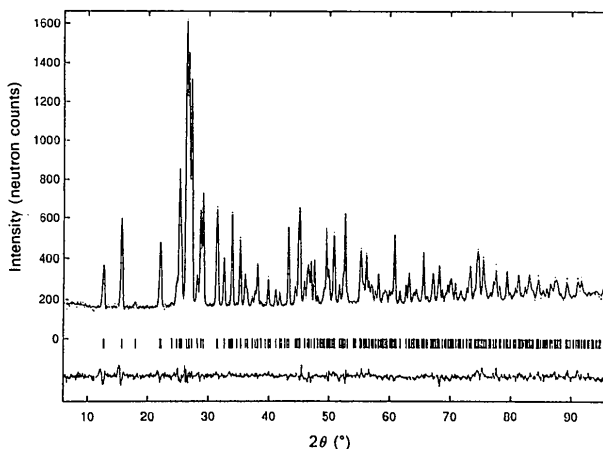


Fig. 1. Observed, calculated and difference profiles of $\text{SrCl}_2 \cdot 2\text{D}_2\text{O}$ at 300 K. Vertical bars indicate the calculated reflection positions.

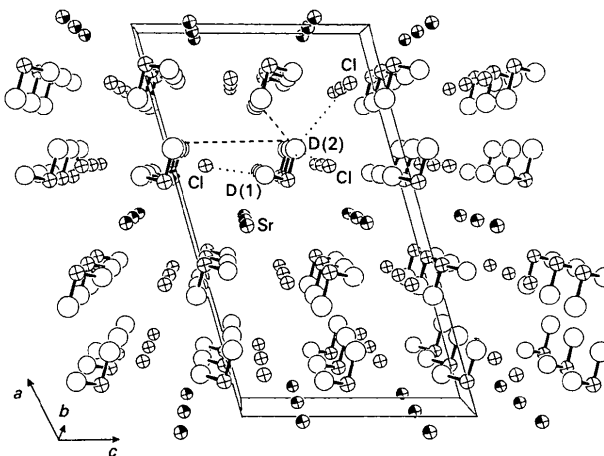


Fig. 2. Structure of $\text{SrCl}_2 \cdot 2\text{D}_2\text{O}$ (300 K data), viewed along [010]. Intralayer and interlayer D(2)—D(2) distances (see text) are represented by —, hydrogen bonds by ...

The hydrogen-bond system is also shown in Fig. 2. The OH and OD stretching modes recorded by IR and Raman spectroscopy of isotopically dilute samples (Lutz, Pobitschka, Christian & Becker, 1979) can now be undoubtedly assigned, viz.

O—H/D(1) [3256, 2422 cm⁻¹; $r_{D(1)\cdots Cl} = 2.159$ (2) Å] and O—H/D(2) [3430, 2539 cm⁻¹; $r_{D(2)\cdots Cl} = 2.424$ (3) Å]. The shorter hydrogen bond of OD(1) is nearly linear [O—D \cdots Cl angle 172.0 (1)°], while the longer one of OD(2) is strongly bent as inferred from the small temperature shift of the respective OH and OD bands ($\nu_{OD}/dT < 0.03$ cm⁻¹ K⁻¹). *Ab initio* calculations of the harmonic vibrational frequencies of HDO molecules in the crystal field of the SrCl₂·2D₂O structure represented by Ewald field-consistent point charges confirmed these findings (Möller, 1993; Ojamäe & Hermansson, 1992). Neutron diffraction studies on partially deuterated samples of SrCl₂·2H₂O revealed an isotope effect, namely an enrichment of H on position H(1) (Möller, 1993).

Experimental

Crystal data at 300 K

SrCl ₂ ·2D ₂ O	$c = 6.6988$ (2) Å
$M_r = 198.58$	$\beta = 105.550$ (1)°
Monoclinic	$V = 483.44$ (1) Å ³
C2/c	$Z = 4$
$a = 11.6918$ (4) Å	$D_x = 2.673$ Mg m ⁻³
$b = 6.4070$ (2) Å	Neutron radiation
	$\lambda = 1.2268$ Å

Crystal data at 1.5 K

SrCl ₂ ·2D ₂ O	$c = 6.6477$ (2) Å
$M_r = 198.58$	$\beta = 105.978$ (2)°
Monoclinic	$V = 476.32$ (1) Å ³
C2/c	$Z = 4$
$a = 11.7008$ (4) Å	$D_x = 2.713$ Mg m ⁻³
$b = 6.3697$ (2) Å	Neutron radiation
	$\lambda = 1.2268$ Å

Table 1. Refined profile parameters for SrCl₂·2D₂O

	300 K	1.5 K
Scale factor	0.01250 (5)	0.01196 (5)
Zero point	0.073 (1)	0.070 (1)
Asymmetry parameter	1.44 (1)	1.45 (8)
Ratio Gaussian:Lorentzian	0.058	0.118
u	0.30 (1)	0.30 (1)
v	-0.35 (1)	-0.33 (1)
w	0.159 (2)	0.160 (2)

Table 2. Structure parameters for SrCl₂·2D₂O

Data for 300 and 1.5 K are given in the first and second line; fractional coordinates reported by Jensen (1942) (data and setting as given in *Structure Reports*) are given in square brackets.

	Site	x	y	z	B_{iso} (Å ² × 10 ³)
Sr	4(e)	0	0.2559 (4)	$\frac{1}{2}$	1.49 (7)
		[0	0.25 (1)	$\frac{1}{2}$]	
		0	0.2576 (5)	$\frac{1}{2}$	0.33 (7)
Cl	8(f)	0.1460 (1)	0.0927 (3)	0.6503 (2)	1.52 (3)
		[0.14 (1)	0.10 (1)	0.64 (1)]	
		0.1462 (1)	0.0921 (3)	0.6528 (3)	0.43 (3)
		0.1086 (3)	0.5804 (5)	0.4748 (4)	1.81 (7)
O	8(f)	[0.11 (1)	0.60	0.48 (1)]	
		0.1090 (3)	0.5829 (5)	0.4771 (5)	0.73 (6)
		0.1218 (3)	0.6926 (4)	0.3841 (4)	2.98 (8)
D1	8(f)	0.1223 (3)	0.6946 (4)	0.3831 (5)	1.73 (7)
		0.1885 (2)	0.5428 (4)	0.5461 (5)	3.41 (8)
D2	8(f)	0.1903 (3)	0.5426 (4)	0.5528 (5)	1.65 (7)

Table 3. Selected interatomic distances (Å) and angles (°) for SrCl₂·2D₂O

	300 K	1.5 K	
SrCl ₄ (H ₂ O) ₄ polyhedra			
Sr—Cl	2.957 (2)	2.947 (2)	(0-0, 0-v)
	2.993 (3)	2.986 (3)	(0-vi, 0-vii)
Sr—O	2.679 (4)	2.672 (4)	(0-0, 0-v)
	2.714 (4)	2.688 (4)	(0-i, 0-ii)
D ₂ O molecule			
O—D(1)	0.980 (5)	0.987 (5)	(0-0)
O—D(2)	0.959 (4)	0.980 (5)	(0-0)
D(1) \cdots D(2)	1.501 (4)	1.533 (4)	(0-0)
O \cdots O	2.843 (5)	2.854 (5)	(0-i)
	3.379 (4)	3.374 (4)	(0-v)
D(1)—O—D(2)	101.5 (4)	102.4 (4)	(0-0-0)
Hydrogen bonds			
D(1) \cdots Cl	2.159 (2)	2.122 (4)	(0-ii)
O \cdots Cl	3.132 (4)	3.105 (4)	(0-ii)
D(2) \cdots Cl	2.424 (3)	2.351 (4)	(0-iv)
O \cdots Cl	3.269 (3)	3.222 (4)	(0-iv)
O—D(1) \cdots Cl	172.0 (1)	173.3 (1)	(0-0-ii)
O—D(2) \cdots Cl	146.8 (1)	147.7 (1)	(0-0-iv)
Cl \cdots O \cdots Cl	105.1 (1)	104.7 (1)	(ii-0-iv)
Other intralayer and interlayer distances			
D(1) \cdots D(1)	2.931 (4)	2.922 (5)	(0-v)
	3.074 (4)	3.047 (5)	(0-viii)
D(1) \cdots D(2)	2.731 (4)	2.697 (5)	(0-viii)
	2.993 (5)	2.949 (5)	(0-ii)
D(2) \cdots D(2)	3.394 (5)	3.368 (5)	(0-ii, 0-iii)
D(2) \cdots D(2)	3.158 (4)	3.157 (5)	(0-viii)

Symmetry code: (0) x, y, z ; (i) $-x, 1-y, 1-z$; (ii) $x, 1-y, z-\frac{1}{2}$; (iii) $x, 1-y, z+\frac{1}{2}$; (iv) $\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$; (v) $-x, y, \frac{1}{2}-z$; (vi) $-x, -y, 1-z$; (vii) $x, -y, z-\frac{1}{2}$; (viii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

Polycrystalline samples of SrCl₂·2D₂O were prepared by annealing stoichiometric amounts of the anhydrous salt and D₂O in sealed glass ampoules at 353 K. The deuterium content was >98% as shown by IR spectroscopy. The product was ground under argon and transferred to a vanadium container. The neutron diffraction intensities were measured at the high-resolution powder diffractometer 3T-2 at the Laboratoire Léon Brillouin, CEN-CNRS, Saclay (ORPHEE, Paris). The powder diffraction patterns (see Fig. 1) were measured continuously over the 2 θ range 6–120° in steps of 0.05°. The wavelength used was $\lambda = 1.2268$ Å [from the (335) plane of a Ge monochromator]. As a result of the low signal:noise ratio above 100° in 2 θ , the refinement was restrained to the range 6–97 (99)°, containing 1819 (1859) points and 444 (462) reflections (data in parentheses were obtained at 1.5 K). 68 (73) points were used for linear interpolation of the background function. The scattering lengths used for Sr, O, Cl and D were 7.02, 5.805, 9.5792 and 6.674 fm, respectively (Koester & Rauch, 1983). Using the heavy-atom fractional coordinates (Jensen, 1942), successive refinement of profile, positional and isotropic displacement parameters was performed with the Rietveld program PROFIL 4.05 (Cockcroft, 1991), yielding final R values of $R_{wp} = 0.054$ (0.068) and $R_I = 0.053$ (0.063). Altogether, 31 parameters were refined: lattice constants a, b, c and β ; instrumental parameters u, v, w , scale factor, zero point; an asymmetry parameter according to Rietveld; a pseudo-Voigt function (ratio Gaussian:Lorentzian); and the fractional coordinates and isotropic temperature factors of the five atoms present.

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Lists of experimental data, refinement parameters and primary diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55807 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1018]

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Structure Determination of K_2ZnBr_4 at 291 and 144 K

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Abstract

The room-temperature phase of K_2ZnBr_4 is isomorphous with Sr_2GeS_4 ($P2_1/m$) while the low-temperature structure ($P2_1$) is slightly distorted [the phase transition occurs at 155 K]. Both structures con-

tain highly deformed tetrahedral $[ZnBr_4]^{2-}$ molecules with $Br(3)-Zn-Br(3')$ angles of 103.06 (5) and 102.49 (9)° at 291 and 144 K, respectively. This distortion is caused by the repulsion of Br atoms whose distance 3.712 (1) and 3.661 (2) Å at 291 and 144 K, respectively, is below the Br—Br van der Waals distance (3.9 Å). The phase transition is accompanied by minor shifts of cations and $[ZnBr_4]^{2-}$ tetrahedra which are simultaneously rotated about a small angle. Below the phase transition point an inversion twin develops whose twinning parameter was refined to 0.459 (65).

Comment

Among compounds of composition A_2BX_4 two families exist. The first contains structures which are isomorphous with $\beta-K_2SO_4$ and which typically exhibit phase-transition sequences (e.g. on decreasing temperature), from the prototype $\beta-K_2SO_4$ to an incommensurate structure which is followed by a transition to the lock-in ferroelectric phase. The other family is related to Sr_2GeS_4 ; either isomorphous with it ($P2_1/m$) or slightly distorted ($P2_1$). At lower temperatures transitions to a ferroelectric state sometimes occur: Rb_2ZnI_4 , Tl_2ZnI_4 (Gesi, 1984), K_2ZnBr_4 (Shimizu, Yamaguchi, Suzuki, Takashige & Sawada, 1990) and K_2CoBr_4 (Suzuki, Shimizu, Takashige, Sawada & Yamaguchi, 1990). The latter three structures are reported to undergo a $P2_1/m \rightarrow P2_1$ phase transition (Gesi, 1984; Ammlung, Scaringe, Ibers, Shriver & Whitmore, 1979; Mashiyama, Kasano & Yamaguchi, 1991).

On the other hand, there are some rare cases where the Sr_2GeS_4 isomorphs transform when heated to the $\beta-K_2SO_4$ structure, e.g. Tl_2CoBr_4 , K_2CoBr_4 (Seifert & Stäudel, 1977) and Cs_2CdI_4 (Touchard, Louër, Auffredic & Louër, 1987).

Phase transitions in K_2CoBr_4 (Suzuki, Shimizu, Takashige, Sawada & Yamaguchi, 1990) and K_2ZnBr_4 (Shimizu, Yamaguchi, Suzuki, Takashige & Sawada, 1990) have recently been studied by dielectric measurements and DTA (differential thermal analysis). These experiments revealed similar behaviour in both compounds and showed the existence of a ferroelectric phase below 143 and 155 K for K_2CoBr_4 and K_2ZnBr_4 , respectively. Mashiyama, Kasano & Yamaguchi (1991) determined their space groups and discovered the existence of an incommensurate phase [$q = (1/3 - \delta)c^*$] of the basic $\beta-K_2SO_4$ structure isomorphs ($Pm\bar{c}n$) in the region 473–555 and 473–561 K for K_2CoBr_4 and K_2ZnBr_4 , respectively. Above these temperature intervals unmodulated phases of the prototype $\beta-K_2SO_4$ structure exist. When the incommensurate phases are quickly supercooled the commensurate threefold structures appear. These are, however, thermodynamically

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