

A Neutron Powder Investigation of the Structural Changes in K_2SnCl_6

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K_2SnCl_6 is known to undergo two structural phase transitions at $T_{c1} = 261$ and $T_{c2} = 255$ K. At room temperature it has the cubic K_2PtCl_6 structure, space group $Fm\bar{3}m$ [$a = 9.9877$ (5) Å measured at 280 (10) K, $Z = 4$]. This and the low-temperature structures have been determined by the profile analysis of neutron powder diffraction data. The structural changes involve mainly two successive rotations of the Cl_6 octahedra: (1) an alternating rotation around [100] in layers perpendicular to the c axis (angle of rotation φ_1) and (2) an in-phase rotation around [110] (φ_2). The corresponding space groups are tetragonal $P4/mnc$ [at 265 (10) K $a = 7.0577$ (7), $c = 9.9784$ (16) Å, $Z = 2$] and monoclinic $P2_1/n$ [at 190 (10) K: $a = 7.024$ (1), $b = 7.013$ (1), $c = 9.988$ (1) Å, $\beta = 90.13$ (1)°, $Z = 2$]. Final profile residuals for these refinements were 8.8, 9.4 and 7.1% respectively. The angles of rotation increase with decreasing temperature [e.g. at 190 K: $\varphi_1 = 6.73$ (5) and $\varphi_2 = 6.44$ (5)°]. After correction for thermal motion the results show that the volume of the octahedra is independent of temperature, the mean Sn–Cl distance within the octahedra being 2.434 Å. The observed diffuse background in the powder diagrams can be attributed to a dynamic (at high temperatures) and a static (at low temperatures) disorder: in-phase and anti-phase rotations of the octahedra around [001] in adjacent layers perpendicular to the c axis are randomly distributed along this direction.

Introduction

The room-temperature structure modification of potassium hexachlorostannate has been determined repeatedly (Dickinson, 1922; Engel, 1935; Brill, Gearhart & Welsh, 1974; Lerbscher & Trotter, 1976; Ihringer, 1977). It belongs to the anti-fluorite type with space group $Fm\bar{3}m$. The Sn atoms occupy an f.c.c. lattice and are surrounded by Cl_6 octahedra, which are oriented according to the cubic symmetry. The K atoms form a primitive cubic lattice with $a/2$, which is shifted $\frac{1}{4}$ along the room diagonal. Two phase transitions at $T_{c1} = 261$ K and $T_{c2} = 255$ K have been observed in several experiments: specific heat (Morfee, Staveley, Walters & Wigley, 1960; only the transition at T_{c1}), NQR (Sasane, Nakamura & Kubo, 1970; Jeffrey, 1972), ITC (Winter & Rössler, 1976), Mössbauer and Raman studies (Winter, Rössler, Bolz & Pelzl, 1976; only one transition) and X-ray and neutron diffraction (Boysen, Ihringer, Prandl & Yelon, 1976). In some of these papers it has been suggested, that a rotation of the Cl_6 octahedra should play an important role in the transitions.

The present study is a part of an investigation of these phase instabilities with X-ray and neutron diffraction (Ihringer, 1977; Boysen, 1977). For a better understanding of the mechanisms involved, knowledge of the crystal structures below the transition tempera-

tures is essential. Since single-crystal methods suffer from experimental difficulties and the occurrence of domains (Boysen *et al.*, 1976) neutron powder diffraction has been chosen for the determination. The profile analysis technique as introduced by Rietveld (1967) and modified for anisotropic thermal parameters by Hewat (1973) was used to distinguish between possible structural models and to refine the parameters. Following Jeffrey (1972) the three different phases of K_2SnCl_6 will be named I ($T < T_{c2}$), II ($T_{c2} < T < T_{c1}$) and III ($T > T_{c1}$).

Experimental

K_2SnCl_6 crystals have been synthesized by standard methods from aqueous solutions of KCl and $SnCl_4$. The small clear octahedral crystals were ground to a mean diameter of about 50 μm . The measured density (pycnometrically) at room temperature was 2.72 (2) g cm^{-3} (calculated 2.737 g cm^{-3}).

Neutron diffraction data were taken at various temperatures with the powder diffractometers MAN I at the FRM in Garching and at the instrument DIA at the HFR, Institut Laue–Langevin in Grenoble, with incident wavelengths of 1.078 and 1.384 Å respectively. The powder samples were enclosed in thin-walled vanadium cans and mounted in standard cryo-

stats with temperature control, the relative accuracy being about $\frac{1}{10}$ K. Since no calibration of the absolute temperature has been made, the intermediate phase (II) has been observed at a nominal temperature of 265 K (the correct assignment can be proved by an inspection of the superlattice reflexions; the maximum deviation is -10 K). Absorption and extinction corrections could be neglected (Boysen, 1977).

Rietveld's profile-refinement program minimizes the quantity $\chi^2 = \sum_i w_i |y_i(\text{obs}) - (1/c)y_i(\text{calc})|^2$, where $y_i(\text{obs})$, $y_i(\text{calc})$, $w_i = 1/y_i(\text{obs})$ and c are the observed intensity at the position $2\theta_i$, the calculated intensity, the assigned weight and the scale factor, respectively. In addition to the profile residual

$$R_p = \sum_i |y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc})| / \sum_i y_i(\text{obs})$$

a corresponding R value for the integrated intensities $I_{\mathbf{k}}$ (\mathbf{k} specifies a reflexion hkl) is calculated for the comparison with single-crystal results:

$$R_I = \sum_{\mathbf{k}} |I_{\mathbf{k}}(\text{obs}) - \frac{1}{c} I_{\mathbf{k}}(\text{calc})| / \sum_{\mathbf{k}} I_{\mathbf{k}}(\text{obs}).$$

Here the 'observed' integrated intensity is obtained from

$$I_{\mathbf{k}}(\text{obs}) = \sum_j [w_{j\mathbf{k}} S_{\mathbf{k}}^2(\text{calc}) \cdot y_j(\text{obs}) / y_{j\mathbf{k}}(\text{calc})]$$

where $S_{\mathbf{k}}(\text{calc})$ is the calculated structure factor and the sum is taken over all $y_j(\text{obs})$ which can theoretically contribute to $I_{\mathbf{k}}(\text{obs})$. The neutron scattering lengths used were: 0.370×10^{-12} cm for K, 0.622×10^{-12} cm for Sn and 0.958×10^{-12} cm for Cl.

Structure determination and refinement

The low-temperature powder diagrams of K_2SnCl_6 exhibit two characteristic intensity changes: the occurrence of superstructure reflexions with integer indices

(in the cubic notation) at T_{c1} , corresponding to a condensation at the X point of the Brillouin zone, and the increase in intensities of reflexions with all indices odd at T_{c2} , corresponding to a condensation at the Γ point. Calculations of the structure factor involving possible rotations of the octahedra showed that these intensity changes can be attributed to an anti-phase rotation in subsequent layers and an in-phase rotation of all octahedra respectively. A number of models in different space groups (e.g. $P4_2$, $I4/m$, $Pnmm$, $Cmca$, $P2_12_12$, $C2/c$, $P2_1/c$) have been tested by the profile-refinement method (for phase I diagrams). While most of the considered models can be excluded by the insufficient fit, two structures in space groups $C2/c$ (anti-phase rotation around $[001]$ + in-phase rotation around $[010]$) and $P2_1/c$ (anti-phase rotation around $[001]$ + in-phase rotation around $[110]$) gave nearly equally good results. Distinction was made possible by a few very small deviations at high scattering angles, which could only be observed with the good resolution of instrument D1A in this region. The choice of $P2_1/c$ as the most probable space group is further supported by the observed and calculated intensity ratios of reflexions [e.g. in the splitting of the (cubic) 444 reflexion], which are not separated in the neutron diagrams, but could be measured with a high-resolution X-ray Guinier diffractometer (Ihringer, 1977). The same structure has been found by Brown (1964) for the room-temperature modification of the isomorphous K_2TeBr_6 . Group-theoretical arguments based on Landau's theory, together with the observation that the first transformation occurs at the X point, then led to a structure in space group $P4/mnc$ for the intermediate phase II.

In the following just one example for each phase will be discussed in more detail. A refinement in phase III is included for a comparison of the present neutron powder results with those from the single crystal X-ray determinations.

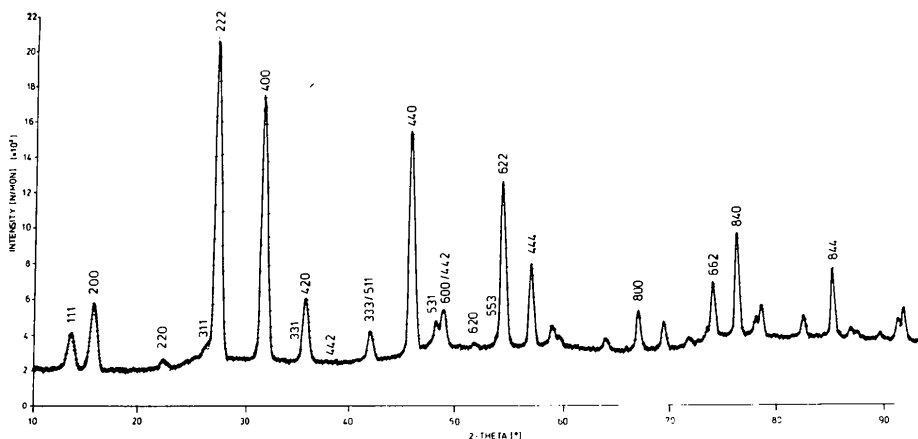


Fig. 1. The observed (crosses) and calculated (solid line) diffraction pattern of K_2SnCl_6 at 280 K. Some reflexions are denoted by their indices.

Table 1. *Positional and thermal parameters for phase III (Fm3m) at 280 K*

The anisotropic temperature factor has the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}k lb^*c^*)]$ and the isotropic temperature factor $T = \exp(-B \sin^2 \theta/\lambda^2)$. The parameters are in \AA^2 . $B_{12} = B_{13} = B_{23} = 0$.

		<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	<i>B</i>
8 K	in (<i>c</i>)	0.25	0.25	0.25	—	—	—	3.8 (2)
4 Sn	in (<i>a</i>)	0	0	0	—	—	—	1.3 (1)
24 Cl(1,2,3)	in (<i>e</i>)	0.2412 (2)	0	0	1.4 (1)	6.0 (1)	6.0 (1)	4.2 (1)

Comparison with literature

<i>x</i> (Cl)	<i>B</i> (K)	<i>B</i> (Sn)	B_{11} (Cl)	$B_{22} = B_{33}$ (Cl)	Reference
0.2415 (2)	4.85 (7)	1.97 (2)	1.81 (6)	7.34 (9)	Brill, Gearhart & Welsh (1974)
0.2411 (2)	4.26 (7)	1.91 (3)	1.73 (5)	6.48 (11)	Lerbscher & Trotter (1976)
0.2410 (2)	4.25 (9)	1.62 (2)	1.68 (8)	6.48 (14)	Ihringer (1977)
0.2412 (2)	3.8 (2)	1.3 (1)	1.4 (1)	6.0 (1)	This work

Phase III (Fm3m)

The observed and calculated intensities for a powder diagram measured at about 280 K are presented in Fig. 1. The refined parameters are given in Table 1 together with the results of some recent X-ray determinations. While the positional parameters are in excellent agreement with each other, the temperature factors of the present neutron determination are slightly lower than the X-ray results. It should be mentioned, that a refinement with isotropic thermal parameters gives some marked discrepancies between the observed and calculated diagrams. The introduction of just one additional free parameter [B_{11} and $B_{22} = B_{33}$ instead of B (iso-

tropic) for Cl] reduces the agreement index R_p from 11.8 to 8.8% and R_i from 6.8 to 2.4% (52 reflexions, 5 parameters). This is a good example showing that at least a relatively large anisotropy (perpendicular to the Sn—Cl bond, compare Table 1) can be clearly deduced from powder measurements too.

Phase II (P4/mnc)

In the intermediate phase the suggested tetragonal structure in space group $P4/mnc$ is confirmed. It consists mainly of a rotation of the octahedra around the [001] axis, where the sense of rotation is reversed in

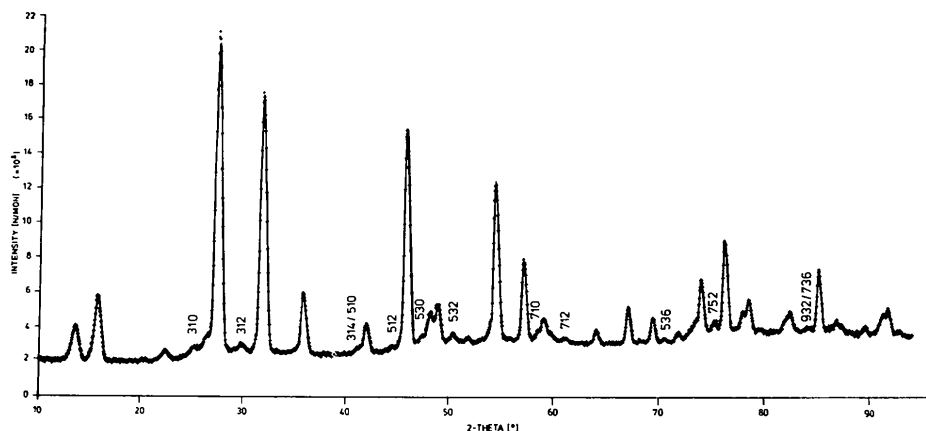


Fig. 2. The observed and calculated diffraction pattern of K_2SnCl_6 at 265 K. Some superstructure reflexions are indicated in a quasi cubic notation.

Table 2. *Positional and thermal (\AA^2) parameters for phase II (P4/mnc) at 265 K*

$$B_{13} = B_{23} = 0$$

		<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	<i>B</i>
4 K	in (<i>d</i>)	0.5	0	0.25	3.4 (1.4)	3.4 (1.4)	4.8 (3.0)	0.2 (5)	4.1 (2)
2 Sn	in (<i>a</i>)	0	0	0	0.8 (3)	0.8 (3)	2.2 (7)	0	1.2 (1)
8 Cl(1,2)	in (<i>h</i>)	0.2511 (4)	0.2217 (4)	0	2.6 (3)	2.1 (2)	6.0 (5)	-1.1 (2)	2.7 (1)
4 Cl	in (<i>e</i>)	0	0	0.2523 (5)	6.3 (6)	6.3 (6)	0.8 (3)	0	5.9 (2)

adjacent layers perpendicular to this axis. Observed and calculated profile intensities are shown in Fig. 2. Again a refinement with isotropic thermal parameters gives the same discrepancies as in phase III. R_p falls from 11.8 to 9.4% and R_f from 7.3 to 3.7% (227 reflexions, 14 parameters). The final parameters are summarized in Table 2. By the alternating rotation of the octahedra the number of molecules in the primitive unit cell is doubled, *i.e.* the old F -centred cell becomes C -centred. This is described in a primitive cell with $\mathbf{a}_p = (\mathbf{a}_c + \mathbf{b}_c)/2$, $\mathbf{b}_p = (\mathbf{b}_c - \mathbf{a}_c)/2$, $\mathbf{c}_p = \mathbf{c}_c$. In spite of the tetragonal symmetry the metric remains quasi cubic, *i.e.* $a\sqrt{2} = b\sqrt{2} \simeq c$, which agrees with the high-resolution X-ray measurements (Boysen, Ihringer, Prandl & Yelon, 1976). In addition to the rotation a small dilatation of the octahedra in the [001] direction is observed. The thermal ellipsoids for Cl have nearly the same strong anisotropy perpendicular to the Sn—Cl bond as in phase III.

Phase I ($P2_1/n$)

Below T_{c2} an additional in-phase rotation of all octahedra around the (cubic) [110] axis takes place. The octahedra become regular again (compare Table 4) and the K atoms are shifted slightly from their $\frac{1}{4}$ positions. Observed and calculated profiles are shown in Fig. 3. Here a refinement with isotropic temperature parameters yields much smaller deviations than in phases II and III. The introduction of anisotropic par-

ameters for Cl reduces R_p from 7.7 to 7.1% and R_f from 3.1 to 1.9% (684 reflexions, 29 parameters). The same procedure for Sn and K does not lead to any further improvement (compare also the large standard deviations for these atoms in phase II). The final refined parameters are presented in Table 3. The structure is described in the setting $P2_1/n$ instead of $P2_1/c$ as given in *International Tables for X-ray Crystallography* (1969) in order to maintain the cell introduced in phase II. $P2_1/n$ is derived from $P2_1/c$ by the transformation $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{a} + \mathbf{c}$.

The thermal ellipsoids for Cl still show a clear anisotropy perpendicular to the Sn—Cl bond. The metric is no longer cubic [a (pseudocubic) = b (p.c.) = 9.926, $c = 9.988$ Å] and there is a small monoclinic distortion. The relative splittings and the monoclinic angle are again in good agreement with the already cited X-ray measurements (Boysen, Ihringer, Prandl & Yelon, 1976).

Discussion of structures

The structural changes of K_2SnCl_6 are summarized in Fig. 4. Table 4 gives the absolute distances and angles in the $SnCl_6$ octahedra. In spite of the distortion in phase II a mean Sn—Cl bond length has been calculated. It seems to increase with decreasing temperature. However, the strong anisotropic vibration of the Cl atoms necessitates the correction for thermal

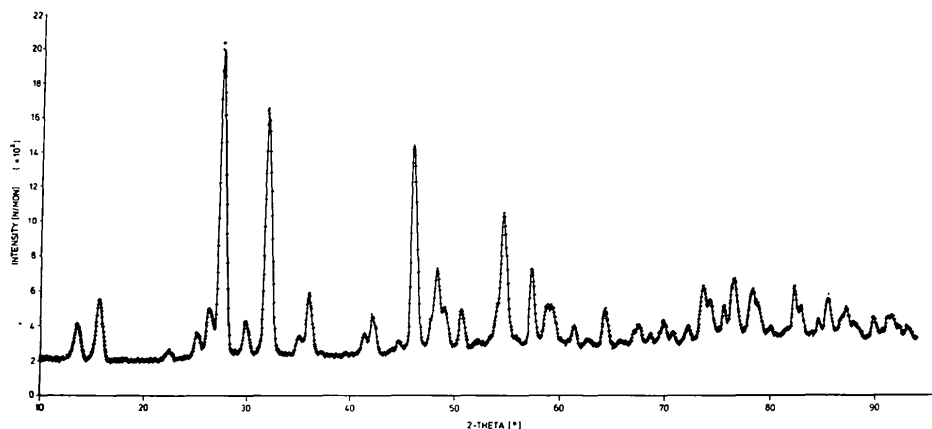


Fig. 3. The observed and calculated diffraction pattern of K_2SnCl_6 at 190 K.

Table 3. Positional and thermal (\AA^2) parameters for phase I ($P2_1/n$) at 190 K

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B
4 K in (e)	0.507 (2)	0.025 (2)	0.241 (3)	—	—	—	—	—	—	1.9 (2)
2 Sn in (a)	0	0	0	—	—	—	—	—	—	0.9 (1)
4 Cl(1) in (e)	0.271 (1)	0.211 (1)	-0.021 (1)	2.0 (4)	1.7 (3)	3.1 (4)	-0.8 (3)	0.9 (3)	-0.7 (2)	1.6 (1)
4 Cl(2) in (e)	0.218 (1)	-0.271 (1)	-0.015 (1)	2.2 (4)	1.1 (3)	2.8 (4)	0.3 (3)	0.5 (3)	0.9 (2)	2.2 (1)
4 Cl(3) in (e)	0.041 (1)	-0.001 (1)	0.240 (1)	2.4 (2)	2.3 (2)	0.5 (1)	0.5 (3)	-0.2 (2)	-1.1 (3)	1.9 (1)

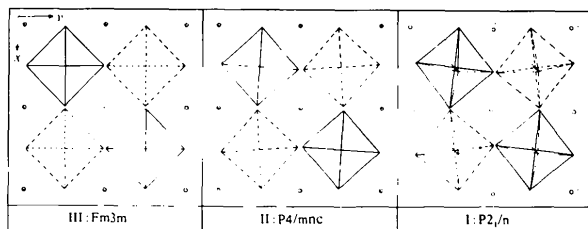


Fig. 4. Positions of Cl_6 octahedra and K atoms in the three phases of K_2SnCl_6 (projection on ab plane). The octahedra are marked by solid lines (height $0c$) and broken lines (height $\frac{1}{2}c$); K atoms are shown by points (height $\frac{1}{4}c$) and open circles (height $\frac{3}{4}c$).

motion. Assuming a libration of rigid octahedra, which was deduced from a system of diffuse streaks observed by X-ray and neutron diffraction (Boysen, Ihringer, Prandl & Yelon, 1976), this correction yields the same Sn—Cl distances in all phases, *i.e.* the volume of the octahedra is practically independent of temperature. The correction is done by splitting the thermal B matrices into a translational and a librational part (see, for example, Willis & Pryor, 1975). The (isotropic) B factors for Sn can then be compared with the translational part of those for the Cl complexes: both quantities are in excellent agreement with each other (Table 5), indicating, that the motion is indeed mainly governed by external lattice vibrations.

The angles of rotation of the octahedra around $[001]$ (φ_1) and $[1\bar{1}0]$ (φ_2) can serve as order parameters for the two-phase transitions. From the limited number of refinements only the more qualitative behaviour of φ_1 and φ_2 can be drawn (Fig. 5).

It has to be mentioned that the suggested structure for phase II seems to contradict the results of the NQR measurements of Sasane, Nakamura & Kubo (1970) and of Jeffrey (1972): the observation of three resonance lines in this temperature range demands three symmetrically independent Cl positions, whereas in space group $P4/mnc$ only two such positions are required. Moreover, the metric is found to be cubic, although the structural changes involved should produce a clearly tetragonal unit cell. On the other hand the R values obtained are of about the same magnitude as those expected from counting statistics. Usually in

similar problems a structural model is already considered to be 'correct' if $R \lesssim 2R_{exp}$.

Possible explanations are: (i) The cubic metric might be due to strains that occur when the crystals are twinned in very small regions. Very recent high-resolution X-ray measurements by Ihringer & Prandl (1977) show that indeed strains play an important role when the substance is ground to powder. Single crystals exhibit an orthorhombic splitting between T_{c1} and T_{c2} , which is absent in powdered samples. An orthorhombic structure would be consistent with the NQR results. However, a refinement within the most probable orthorhombic space group $Pnmm$, which is a subgroup of $P4/mnc$ and a supergroup of $P2_1/n$, did not yield any significant improvement of the fit. (ii) There also might be an incoherent superposition of two structures in phase II. As mentioned already a system of diffuse streaks has been observed with X-rays and neutrons, which was shown to be of inelastic origin by three-axis neutron diffraction (at room temperature). From the observed extinction rules and the intensity variation it was deduced that the streak system is due to a low-lying dispersion branch (mode A_2) between the Γ and X points of the Brillouin zone (Δ -direction) with only little dispersion along this direction (Boysen, Ihringer, Prandl & Yelon, 1976). This mode is described by a correlated rotation of the Cl octahedra in planes perpendicular to the c axis with only very weak interaction between the planes. From this behaviour it may be expected that this mode driving the phase transition at T_{c1} does not only condense at the X point (leading to space group $P4/mnc$), but partially also at the Γ point (leading to $I4/m$). Thus one would have a superposition of two structural motifs, which is consistent with the NQR results and is further supported by the interpretation of the diffuse background observed in the powder diagrams.

Table 5. Isotropic temperature factors for Sn and the centre of gravity of the Cl_6 complex

T (K)	B^{Sn} (\AA^2)	B_r^{Cl} (\AA^2)
280	1.3	1.4
265	1.2	1.1
190	0.9	0.9

Table 4. Sn—Cl bond lengths (\AA) in $SnCl_6$ octahedron before and after correction for thermal motion

The Cl—Sn—Cl angles (in phase I) all lie within 0.8° (two standard deviations) of 90° .

	280 K		265 K		190 K	
	uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
Sn—Cl(1)	} 2.409 (2)	} 2.433 (2)	} 2.364 (4)	} 2.383 (4)	2.421 (14)	2.431 (14)
Sn—Cl(2)					2.445 (13)	2.453 (13)
Sn—Cl(3)					2.416 (5)	2.425 (5)
Mean	2.409 (2)	2.433 (2)	2.415 (5)	2.437 (5)	2.427 (11)	2.436 (11)

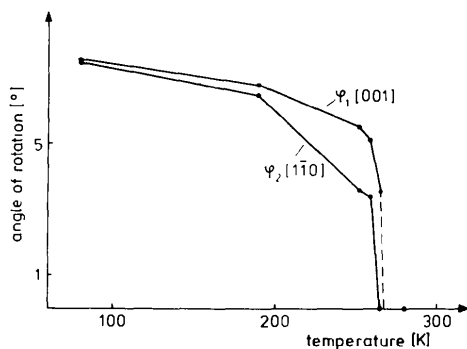


Fig. 5. Temperature dependence of the angle of rotation of the Cl octahedra. The solid line is only a guide to the eye.

The diffuse background in the powder diagrams

The powder diagrams (Figs. 1–3) exhibit a marked modulation of their background. At room temperature

this diffuse intensity may be interpreted as the inelastic scattering of the neutrons at the low-energy phonons described in the preceding section (mode A_2). The corresponding inelastic structure factor can be shown to be proportional to $F_{in} \sim (h \sin 2\pi kx_0 - k \sin 2\pi hx_0)$ independent of l , where x_0 is the Cl positional parameter in the cubic phase. The corresponding intensity measured with a two-axis diffractometer can be calculated by integrating over energy, averaging over all crystal orientations in the powder sample and folding with the resolution function of the instrument. The result of this procedure is shown in Fig. 6, together with the observed backgrounds at different temperatures. There is a qualitative satisfactory agreement between the measured and calculated curves. Since only one-phonon processes were taken into account in the calculation, there is an additional overall angular dependence in the observed diagrams due to multi-phonon processes, incoherent scattering and the background from

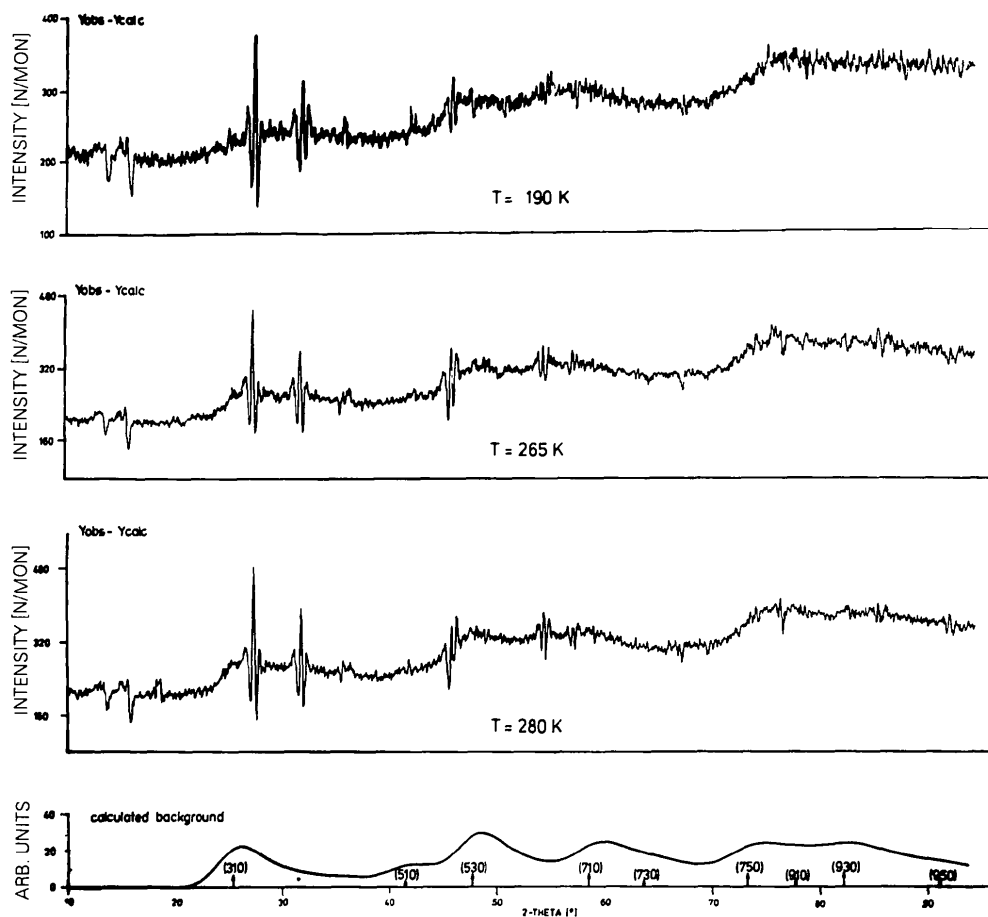


Fig. 6. The observed and calculated diffuse background in the powder diagrams. The intensity increases where the Ewald sphere cuts a diffuse streak in the $(hk0)$ plane. Some of these positions are indicated in the diagram. The strong and sharp oscillations near reflexion positions in the observed curves are due to an instrumental asymmetry of the lines at D1A. Compare the corresponding deviations in Figs. 1–3. Refinements with shortened data sets show that the calculated parameters are not affected.

the reactor hall. Furthermore, the thermal diffuse scattering from acoustic phonons has been neglected.

Now the diffuse background remains practically the same at low temperatures too. Even a diagram taken at 4 K has the same form and magnitude. Since here a dynamic interpretation is not possible because of the occupation number, some static disorder has to be taken into account. According to the model discussed at the end of the preceding section there are two structural motifs $AA = BB$ and $AB = BA$ for the sequence of two adjacent layers perpendicular to the c axis. Here A and B denote a rotation of the octahedra around $[001]$ to the right and to the left. Assuming a random distribution the corresponding diffuse intensity (see, for example, Jagodzinski, 1949) is for small angles of rotation φ proportional to $|\Delta F|^2 \sim p_1 p_2 |2\pi y \times (h \sin 2\pi kx - k \sin 2\pi hx)|^2$. Here $x = x_0 \cos \varphi$, $y = x_0 \sin \varphi$ and p_1 and p_2 are the probabilities for the occurrence of motifs AA and AB . This static diffuse scattering has the same form as the dynamic, thus giving a good hint that the suggested disorder model is indeed present at low temperatures. Because of this disorder the Bragg scattering is also affected, i.e. at low temperatures only an average structure is refined with apparently large temperature factors (depending on the values of p_1 and p_2). At high temperatures, however, the large anisotropic temperature factors are due to the librational motion of the Cl octahedra.

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The Crystal Structure of $(NH_4)_2[Cu(H_2O)_6][CuSO_3]_4$

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$(NH_4)_2[Cu(H_2O)_6][CuSO_3]_4$ is tetragonal, space group $P4_2/n$, with $a = 14.876$ (1), $c = 17.218$ (3) Å, $Z = 8$. Full-matrix least-squares calculations resulted in an R of 0.043 for 2308 independent reflexions. The structure can be described in terms of distorted $Cu^I O_3 S$ tetrahedra, the ligands being atoms from four different sulphite groups (mean distances: Cu–O 2.11, Cu–S 2.16 Å), $Cu(H_2O)_6$ octahedra implying a (4 + 2) coordination (mean distances: Cu–O 1.99 and 2.33 Å) and ammonium ions. The $Cu^I O_3 S$ tetrahedra form double layers almost parallel to (110). The average dimensions within the sulphite group are: S–O 1.52, O–O 2.42 Å and $\angle O-S-O$ 105.3°.