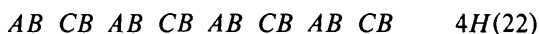
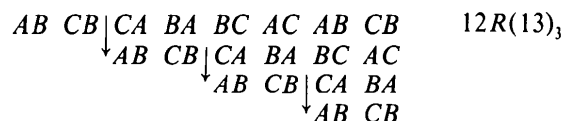
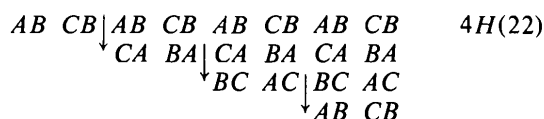
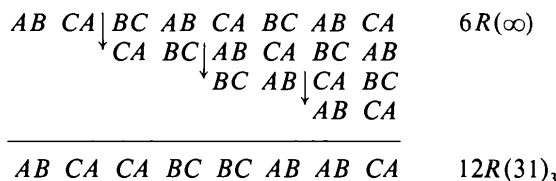


faces of the crystal. In the present case, one basal face of the crystal exhibited the reflexions of 4H, 12R and 6R (Figs. 1, 2) whereas the opposite one showed the spots of 4H, 12R and twinned 6R. The shape and size of the spots of twinned 6R were different from those of 4H and 12R; the spots of only 4H and 12R were found to be joined to each other by streaks. Also, when different regions of the basal face of the crystal were irradiated only one of the twinned 6R was found in coexistence with 4H and 12R. Therefore, it is plausible to assume that the type 12R coalesced with 4H occurred as a result of transformation of 4H or *vice versa*. This transformation can easily take place by introducing periodic slip in either of the polytypes 4H or 12R, as explained below.



Although there are two possible structures of 12R, only the one with Zhdanov symbol (13)₃ has been observed in CdBr₂, as well as in the isostructural CdI₂ and PbI₂ (Agrawal & Trigunayat, 1968; Mitchell, 1959). Recently, Agrawal (1979) has explained the non-occurrence of the other structure in CdI₂ and PbI₂ by a change in hexagonality (defined as the ratio of the number of anion layers in h.c.p. orientation to the total number of anion layers in the unit cell) of the transformed structure and through the orientation of the top and bottom layers of two successive sandwiches around the boundary of rotation coming into the same orientation after transformation. Similar argu-

ments can be given for transformation of 4H into 12R in CdBr₂. However, the most common polytype of CdBr₂ is reported to be 6R and if the periodic slip is introduced in 6R at the same interval as in 4H/12R, the other structure (31)₃ would be formed, as explained below.



Therefore, the occurrence of 12R (31)₃ as a result of a transformation of 6R is quite probable in CdBr₂. However, in this process, the hexagonality of a transformed structure is increased from 0 to 0.5 and also the top and bottom layers of two successive sandwiches around the boundary of rotation occur in different orientations whereas in 6R they are in the same orientation. For these reasons, stable polytypes may not be formed in CdBr₂ and disordered structures are observed in abundance.

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The Structure of KNiCl₃ at Room Temperature

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Abstract

The crystal structure of KNiCl₃ at room temperature has been determined by single-crystal X-ray techniques.

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The crystals are hexagonal, *P*6₃*cm*, with the cell dimensions *a* = 11.795 (1) and *c* = 5.926 (1) Å, and *Z* = 6. Full-matrix least-squares refinement of 323 observed reflexions gave a conventional index *R_w* of

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0.048. On the assumption of 33% disorder the value of R_w dropped to 0.033. A new phase transition in this compound is reported at 560 K. The room-temperature structure can be directly related to the CsNiCl_3 structure by enlarging the a axis by a factor of $\sqrt{3}$ and shifting the two inner face-sharing chains of octahedra along the c axis.

Introduction

Compounds of composition ABX_3 , with A an alkaline metal, B a first-row transition metal and X a halogen atom, crystallize in a large variety of structures. The majority of the fluorides adopt the cubic perovskite structure or a directly related one (Brandwijk, 1972; O'Keeffe & Hyde, 1977). In the chlorides (Fernandez, Tello & Arriandiaga, 1978) the hexagonal analogue of the cubic perovskite, h - BaNiO_3 (Wyckoff, 1964), e.g. CsMgCl_3 (McPherson, Kistenmacher & Stucky, 1970), is preferred. In both fluorides and chlorides mixed cubic-hexagonal stackings have been observed (Table 1). Bromides and iodides, in so far as they exist (Seifert & Flohr, 1977, and references therein; Zandbergen, 1979), crystallize in the structure types adopted by the chlorides.

The structure of CsMgCl_3 , which consists of chains of face-sharing octahedra separated by Cs ions in 12 coordination (Fig. 1), becomes less favourable when the radius of the A ion has been reduced. In this case the A ion is not able to fill the 12-coordinated polyhedron at ambient temperatures. This has been demonstrated very well in the series of compounds KBCl_3 . The result of a small A ion is an enlargement of the cell dimensions and a lower coordination number. The monoclinic or orthorhombic structures formed are

of the GdFeO_3 or NH_4CdCl_3 type (Wyckoff, 1964) (Table 1).

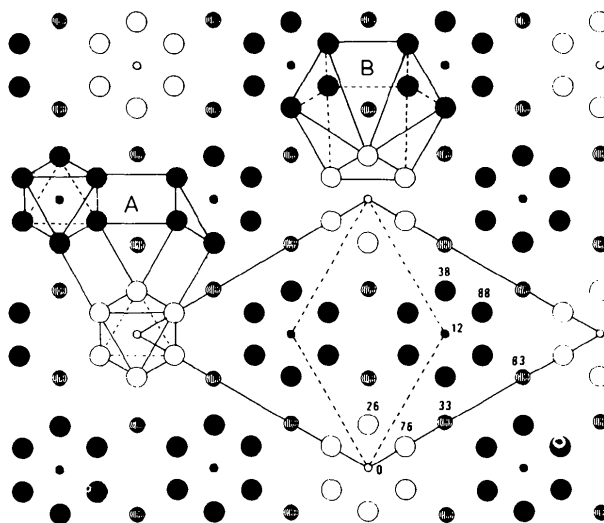


Fig. 1. Projection on the (00.1) plane showing the relation between the room-temperature cell (full lines) and the high-temperature cell (dashed lines). The large circles correspond to the Cl atoms, the small circles to the Ni atoms and the hatched circles to the K atoms. In the high-temperature structure all NiCl_3 chains are on the same height with Ni^{2+} at the origin while the K^+ ions are at 0.25 and 0.75. Polyhedron A corresponds to the cation coordination polyhedron at high temperature (twelve-coordination, twinned cuboctahedron) where the lower part coincides with the upper part. In the room-temperature structure the two different NiCl_3 chains of face-sharing octahedra have been distinguished by black and white atoms. Polyhedron B corresponds to the cation coordination polyhedron at room temperature; this is an irregular nine-coordination.

Table 1. Room-temperature cell dimensions and stacking sequences of some $ABCl_3$ compounds

| Compound | a (Å) | b (Å) | c (Å) | β (°) | Stacking sequence | References |
|-----------------------------|---------|---------|---------|-------------|-------------------|--|
| CsMgCl_3 | 7.269 | | 6.187 | | h | McPherson <i>et al.</i> (1970) |
| RbMgCl_3 | 7.090 | | 11.844 | | hc | Seifert & Fink (1975) |
| β - KMgCl_3 | 6.954 | 6.971 | 9.992 | | c | Brynstad, Yakel & Smith (1966) |
| KVCl_3 | 6.90 | | 5.98 | | h | Seifert & Ehrlich (1959) |
| KCrCl_3 | 8.68 | 3.90 | 13.85 | 95.6 | | Weenk (1976) |
| CsMnCl_3 | 7.288 | | 27.44 | | hhc | Melamud, Makovsky & Shaked (1971) |
| RbMnCl_3 | 7.164 | | 17.798 | | hcc | Melamud <i>et al.</i> (1971) |
| β - KMnCl_3 | 7.072 | 10.018 | 7.010 | | c | Seifert & Flohr (1977) |
| γ - KMnCl_3 | 8.697 | 4.015 | 14.357 | | | Visser (1980) |
| α - KFeCl_3 | 7.00 | | 5.80 | | h | Vasil'kova, Kozhina & Tronina (1969) |
| β - KFeCl_3 | 8.715 | 3.845 | 14.15 | | | Gurewitz, Makovsky & Shaked (1974) |
| KCoCl_3 | 6.870 | | 6.091 | | h | Seifert & Stäudel (1977) |
| KNiCl_3 | 6.80 | | 11.27 | | hc^* | Allamagny (1960) |
| | 6.943 | | 5.974 | | h^* | Belyaev <i>et al.</i> (1970) |
| | 13.57 | | 5.95 | | h^* | McPherson & Jin Rong Chang (1973) |
| | 11.795 | | 5.926 | | h | This work |
| KCuCl_3 | 8.715 | 4.029 | 13.785 | 97.33 | | Willett, Dwiggin, Kruh & Rundle (1963) |

* Probably incorrect cell axes; see text.

Cell enlargement in the hexagonal type was first reported for KNiCl_3 by Allamagny (1960); namely an enlargement of the c axis by a factor of 2. This indicates hc stacking, as found for RbMgCl_3 (Seifert & Fink, 1975), although Allamagny related the cell dimensions of KNiCl_3 to those of CsNiCl_3 , as found by Amussen & Soling (1956), which are in contradiction to the value from the single-crystal structure determination of CsNiCl_3 by Tischenko (1955) resulting in a normal hexagonal cell. The simple hexagonal cell has been reported by Belyaev, Lesnykh & Eikhenbaum (1970) while McPherson & Jin Rong Chang (1973) found a hexagonal cell enlarged by a factor of 2 in the ab plane. In contradiction to all these reports we established a hexagonal supercell with an enlargement factor of $\sqrt{3}$ in the basal plane, corresponding to the smallest possible hexagonal enlargement (Table 1) (Fig. 1).

The phase diagram of the system KCl-NiCl_2 has been constructed by Belyaev *et al.* (1970) and showed a structural phase transition for KNiCl_3 at 753 K. This transition has been confirmed by DTA. The DTA signal (at 772 K on heating and 763 K on cooling) showed a hysteresis of 9 K, indicating a first-order phase transition. By means of high-temperature X-ray powder diffraction we found a new phase transition at 560 K, which could not be clearly established by DTA. The axes of the two high-temperature structures of KNiCl_3 have been determined by means of neutron powder diffraction at 623 and 823 K; these are $a = 6.943$ (1), $c = 5.974$ (1) Å, and $a = 7.028$ (1), $c = 6.040$ (2) Å respectively. These axes and the intensities of the reflexions are comparable with those expected for a CsMgCl_3 -type structure. The high-temperature structures of these phases are not yet known in detail, but structure refinements will be performed (Visser, 1980). The neutron powder diffraction data at room temperature showed only a few extra reflexions corresponding to the subcell, while the intensities of all other reflexions are comparable with the high-temperature ones. Thus we expect a slightly modified CsMgCl_3 structure. In order to establish the room-temperature structure of KNiCl_3 , we carried out a single-crystal X-ray structure analysis, the results of which are reported here.

Experimental

Dry KCl was obtained by heating at 673 K and dry NiCl_2 by dehydrating $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ *in vacuo* (10^{-4} Pa) up to 823 K. Large single crystals of KNiCl_3 were grown by melting a stoichiometric mixture of KCl and NiCl_2 in an evacuated and sealed quartz tube and by lowering it in a vertical Bridgeman furnace with a temperature difference of 75 K (948–873 K) with a speed of $\frac{1}{2}$ mm per hour. Thereafter the crystal was

cooled to room temperature at a speed of 2 K per hour. All manipulations were carried out in a glovebox filled with dry nitrogen or under dry paraffin oil, since the compound is extremely hygroscopic. Single crystals suitable for X-ray diffraction were obtained by carefully crushing a large single crystal. From zero-level Weissenberg photographs around the c axis a cell with dimensions $a = 6.80$ (2), $c = 5.92$ (2) Å corresponding to the axes of CsNiCl_3 could be determined. Very few spots were seen in the first-level Weissenberg photographs. Most of these reflexions correspond to the dimensions found in the zero level. However, some superspots were observed, which could be indexed on a cell with $a' = a\sqrt{3}$.

A diamond-shaped crystal of approximate size $0.24 \times 0.32 \times 0.32$ mm was mounted on an Enraf–Nonius three-circle diffractometer with the c axis along the φ axis. From axes reflexions the cell constants were determined to be $a = 11.795$ (1) and $c = 5.926$ (1) Å. Intensities were recorded for all reflexions with θ between $4-30^\circ$, using $\text{Mo } K\alpha$ radiation monochromated by graphite. Background intensities were determined at $\theta \pm \frac{1}{2}\Delta$ where $\Delta(^\circ) = 2.3 + 0.9 \tan \theta$. The total number of reflexions measured by this method was 1779. Reflexions with intensities less than twice the standard deviation, calculated from counting statistics, were considered as not significant. Although the crystal was mounted in a sealed capillary tube it appeared to deteriorate slowly. The intensity decreased 60% during two weeks. The data were corrected by a polynome of five terms based on the intensity of three reference reflexions which were measured every 30 reflexions. Afterwards they were corrected for Lorentz and polarization effects and absorption (de Graaff, 1973) using transmission factors between 0.31 and 0.41 ($\mu = 3.895 \text{ mm}^{-1}$).

Determination of the structure

The crystal belongs to the hexagonal Laue group $6/mmm$. Together with systematic absences $h\bar{h}0l$, $l \neq 2n$ this indicates the following hexagonal space groups: $P6_3mcm$, $P\bar{6}c2$ or $P6_3cm$. Models having these space groups were refined by a full-matrix least-squares method.* Scattering factors and anomalous-dispersion corrections for the ions were taken from *International Tables for X-ray Crystallography* (1974). All intensities were reduced to F values and equivalent reflexions were averaged. This averaging procedure was carried out for each space group. The sets of symmetry-independent reflexions thus obtained were used in the refinement procedure. The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$

* All calculations were carried out on the Leiden University 370-158 IBM computer with a set of computer programs written or modified by Mrs Rutten-Keulemans and Dr R. A. G. de Graaff.

with the weighting factor $w = 1/(\sigma_F)^2$. Discrepancy values referred to are: $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The estimated standard deviation of an observation of unit weight (ERF) is given by $|\sum w_F(|F_o| - |F_c|) / (\text{NO} - \text{NV})|^{1/2}$ (where NO is the number of observations and NV is the number of variable parameters).

From the cell enlargement and space-group considerations, KNiCl_3 at room temperature is expected to maintain the chain-like character, as in the structure above the phase transition at 560 K. For the centrosymmetric space group $P6_3mcm$ the positions for the atoms can be found in *International Tables for X-ray Crystallography* (1952). The atoms lie at the following positions:

| | | | | | |
|-------|------|---------------------------------|-------|-------|---------------------|
| K | 6(g) | $\bar{x}, \bar{x}, \frac{1}{4}$ | Cl(1) | 6(g) | $x, 0, \frac{1}{4}$ |
| Ni(1) | 2(b) | 0,0,0 | Cl(2) | 12(g) | $x, y, \frac{1}{4}$ |
| Ni(2) | 4(d) | $\frac{1}{3}, \frac{2}{3}, 0$ | | | |

After refinement in this space group the resulting structure appears to be identical to that of CsNiCl_3 .

The second centrosymmetric space group $P\bar{6}c2$ gives the positions:

| | | | | | |
|-------|------|-------------------------------|-----------|------|-------------------------------|
| K | 6(k) | $x, y, \frac{1}{4}$ | Ni(3) | 2(c) | $\frac{2}{3}, \frac{1}{3}, 0$ |
| Ni(1) | 2(a) | 0,0,0 | Cl(1,2,3) | 6(k) | $x, y, \frac{1}{4}$ |
| Ni(2) | 2(b) | $\frac{1}{3}, \frac{2}{3}, 0$ | | | |

This space group allows a rotation of the NiCl_3 chains with respect to each other and adjustment of the K ions in the reduced coordination polyhedron. After refinement in this space group no rotation was found to be present.

In the noncentrosymmetric space group $P6_3cm$ the positions are:

| | | | | | |
|-------|------|-------------------------------|-------|-------|-----------|
| K | 6(c) | $x, 0, z$ | Cl(1) | 6(c) | $x, 0, z$ |
| Ni(1) | 2(a) | 0,0,z | Cl(2) | 12(d) | x, y, z |
| Ni(2) | 4(b) | $\frac{1}{3}, \frac{2}{3}, z$ | | | |

The only degree of freedom which is present in this space group is the shifting along the c axis of the two inner Ni(2)Cl_3 chains and the K ions. This will also result in a reduction of the coordination number for the K atoms. In the refinement the z coordinate of Ni(1) has been kept fixed at 0.

The positional and thermal parameters of all atoms as well as a scaling factor were refined. The final discrepancy values for the refinements in the different space groups are given in Table 2. By comparing the R and ERF values of the refinements we concluded that at room temperature the correct space group of KNiCl_3 is $P6_3cm$ with the positional parameters as given in Table 3. The reflexion conditions also allow the trigonal space groups $P\bar{3}c1$ and $P3c1$. The same model

Table 2. *Final discrepancy values*

| | R | R_w | Number of reflexions | Number of parameters | ERF |
|---|-------|-------|----------------------|----------------------|-------|
| $P6_3mcm$ | 50.23 | 50.08 | 323 | 10 | 43.78 |
| $P\bar{6}c2$ | 35.62 | 35.76 | 586 | 16 | 37.10 |
| $P6_3cm$ | 5.78 | 4.85 | 323 | 27 | 6.93 |
| With extinction correction | | | | | |
| | 5.74 | 4.74 | 323 | 27 | 6.80 |
| With disorder and extinction correction | | | | | |
| | 3.86 | 3.31 | 323 | 37 | 4.85 |

Table 3. *Positional parameters of KNiCl_3 at room temperature with the space group $P6_3cm$*

All parameters not given as fractions are multiplied by 10^3 .

| | x | y | z |
|-------|---------------|---------------|-----------|
| K | 335.3 (2) | 335.3 (2) | 329.4 (6) |
| Ni(1) | 0 | 0 | 0 |
| Ni(2) | $\frac{1}{3}$ | $\frac{2}{3}$ | 123.0 (1) |
| Cl(1) | 159.8 (1) | 0 | 260.4 (4) |
| Cl(2) | 505.6 (1) | 173.2 (1) | 385.2 (2) |

With disorder [the disorder ratio = 66.8 (7)%]

| | x | y | z |
|-------------|---------------|---------------|-----------|
| Part type 1 | | | |
| K | 336.4 (3) | 336.4 (3) | 319.4 (6) |
| Ni(1) | 0 | 0 | 0 |
| Ni(2) | $\frac{1}{3}$ | $\frac{2}{3}$ | 157.5 (3) |
| Cl(1) | 159.9 (1) | 0 | 255.9 (3) |
| Cl(2) | 505.8 (2) | 172.9 (1) | 418.2 (1) |
| Part type 2 | | | |
| K | 333.8 (6) | 333.8 (6) | 397.6 (2) |
| Ni(1) | 0 | 0 | 47.8 (1) |
| Ni(2) | $\frac{1}{3}$ | $\frac{2}{3}$ | 83.7 (2) |
| Cl(1) | 160.2 (1) | 0 | 310.4 (1) |
| Cl(2) | 505.0 (5) | 174.6 (2) | 341.3 (9) |

has been refined in these space groups but gave no better R and ERF values, hence they will not be discussed.

From the large value of the U_{33} thermal parameter for the Ni(2) chain [$66 (2) \times 10^{-3} \text{ \AA}^2$] compared to that of the Ni(1) chain [$17 (1) \times 10^{-3} \text{ \AA}^2$] and the large values of U_{33} for the K ion [$65 (2) \times 10^{-3} \text{ \AA}^2$] it may be concluded that there is a considerable amount of freedom in the z direction (Table 4). A difference Fourier analysis revealed peaks with a total intensity of 10% depicting the KNiCl_3 structure, shifted along the c axis. This explains the large thermal motion.

Disorder

No large discrepancies are found between the observed and calculated structure factors. However, the intensities of some strong reflexions are too low. This may

Table 4. *The general anisotropic temperature factors of KNiCl_3 which have the form $\exp(-2\pi^2 \sum_{ij} U_{ij} a_i^* a_j^*)$ and are given in units of 10^{-3} \AA^2*

The first line corresponds to the parameter of the overall structure and the second line to the parameters of the disordered structure; both have restrictions due to the several site symmetries in space group $P6_3cm$.

| | U_{11} | U_{22} | U_{33} | $2U_{12}$ | $2U_{23}$ | $2U_{31}$ |
|-------|----------|----------|----------|-----------|-----------|-----------|
| K | 38 (2) | 38 (2) | 65 (2) | 41 (8) | 26 (2) | 26 (2) |
| Ni(1) | 38 (1) | 38 (1) | 13 (3) | 38 (1) | 31 (6) | 31 (6) |
| Ni(2) | 21 (1) | 21 (1) | 17 (1) | 21 (1) | 0 | 0 |
| Cl(1) | 21 (1) | 21 (1) | 0 (1) | 21 (1) | 0 | 0 |
| Cl(2) | 16 (1) | 16 (1) | 67 (2) | 16 (1) | 0 | 0 |
| | 18 (1) | 18 (1) | 22 (3) | 18 (1) | 0 | 0 |
| | 23 (2) | 35 (3) | 27 (2) | 35 (3) | 0 | -3 (5) |
| | 23 (1) | 35 (2) | -4 (4) | 35 (2) | 0 | -10 (4) |
| | 20 (1) | 21 (1) | 66 (2) | 7 (2) | 4 (4) | 2 (4) |
| | 21 (1) | 22 (1) | 33 (4) | 9 (2) | 13 (5) | 9 (4) |

The reduction of the U_{33} and U_{23} thermal parameters of Ni(1) and Cl(1) to zero has to be attributed to systematic errors in the absorption corrections or in the correction for the deterioration.

Table 5. *Interatomic distances (\AA) and bond angles ($^\circ$) for KNiCl_3*

| | $P6_3cm$ with disorder | | |
|-----------------------|------------------------|-------------|-------------|
| | $P6_3cm$ | Part type 1 | Part type 2 |
| K-Cl(1) | (1×) 3.450 (2) | 3.458 (3) | 3.449 (6) |
| K-Cl(1)' | (2×) 3.287 (3) | 3.320 (6) | 3.190 (3) |
| K-Cl(2) | (2×) 3.411 (3) | 3.450 (8) | 3.392 (10) |
| K-Cl(2)' | (2×) 3.411 (3) | 3.430 (8) | 3.447 (8) |
| K-Cl(2)'' | (2×) 3.321 (3) | 3.119 (4) | 3.327 (6) |
| Ni(1)-Cl(1) | (3×) 2.436 (1) | 2.420 (6) | 2.447 (1) |
| Ni(1)-Cl(1)' | (3×) 2.359 (1) | 2.376 (6) | 2.355 (1) |
| Ni(2)-Cl(2) | (3×) 2.450 (1) | 2.444 (3) | 2.428 (4) |
| Ni(2)-Cl(2)' | (3×) 2.361 (1) | 2.366 (3) | 2.374 (4) |
| Cl(1)-Cl(1) | (3×) 3.264 (2) | 3.266 (14) | 3.272 (2) |
| Cl(1)-Cl(1)' | (6×) 3.511 (1) | 3.512 (4) | 3.514 (1) |
| Cl(2)-Cl(2) | (3×) 3.281 (1) | 3.281 (7) | 3.273 (5) |
| Cl(2)-Cl(2)' | (6×) 3.507 (1) | 3.511 (9) | 3.567 (4) |
| Cl(1)-Ni(1)-Cl(1) | (3×) 84.15 (7) | 84.90 (19) | 83.90 (3) |
| Cl(1)'-Ni(1)-Cl(1) | (6×) 94.14 (3) | 94.14 (18) | 94.02 (3) |
| Cl(1)''-Ni(1)-Cl(1) | (3×) 87.53 (7) | 86.81 (18) | 88.00 (3) |
| Ni(1)-Cl(1)-Ni(1) | (6×) 76.30 (3) | 76.29 (24) | 76.14 (3) |
| Cl(2)-Ni(2)-Cl(2) | (3×) 84.08 (4) | 84.13 (11) | 84.70 (16) |
| Cl(2)''-Ni(2)-Cl(2) | (6×) 94.24 (5) | 94.07 (32) | 95.10 (14) |
| Cl(2)'''-Ni(2)-Cl(2)' | (3×) 88.04 (4) | 87.78 (10) | 87.17 (17) |
| Ni(2)-Cl(2)-Ni(2) | (6×) 76.01 (2) | 76.01 (13) | 76.17 (10) |

indicate extinction or inaccuracies in the absorption correction. Correction for extinction yielded only a small improvement (Table 2). The peaks found in the difference Fourier analysis can be accounted for in two different ways – by twinning or disorder.

When we assume twinning to be present in the crystal it is mostly possible to detect a twin plane in the crystal in which there is enough freedom for reorientation of groups to form the different parts (Stork-Blaise, 1972). This process is inherent in the space

group. Since the space group $P6_3cm$ does not allow such a freedom, disorder is the most likely explanation. In order to check the validity of this assumption the structure of KNiCl_3 has been refined in the space group $P6_3cm$, in which two structures move freely with respect to each other; only an extra occupation parameter has been used and the thermal parameters for both structures have been kept equal. In order to avoid singularities in the determinant used in the refinement, Waser constraints (Waser, 1963) were imposed upon the Ni-Cl distances in the chains. By allowing the distances in Table 5 (column 1) to vary up to 0.0015 \AA , singularities were avoided.

The R values dropped significantly to $R_w = 3.31$ and the ERF was 4.85. The occupation parameter p turned out to be 0.0667. The difference Fourier analysis showed no peaks of significant height.

The final positional parameters for both structures are given in Table 3. The atomic distances and bond angles are given in Table 5. The U_{33} thermal parameters of the Ni(2) chain and the K ion have been reduced by this refinement to normal values: respectively $22 (3) \times 10^{-3}$ and $13 (3) \times 10^{-3} \text{ \AA}^2$ (Table 4). After this refinement we can decide if there is twinning or disorder present. We have to consider the crystal as parts of two structure types which are shifted relative to each other. In the case of twinning no phase relation between the twin parts is present. Designating F'_o and F_o as observed structure factors for the twinned and untwinned structures and F_{o1} and F_{o11} for the structure factors of the two structure parts calculated on full weight (100%), one finds that:

$$F_o'^2 = (1-p)F_{o1}^2 + pF_{o11}^2$$

and

$$p = \frac{1}{2} - \frac{1}{2} \frac{F_{o1}'^2 - F_{o11}'^2}{F_{o1}'^2 - F_{o11}'^2},$$

where p is the twinning parameter.

In the presence of disorder in the crystal there is a phase relation between the different parts. In this case there is a continuous change from one ordered part to the other. The contributions to the calculated structure factor F_c' are coherent and have to be added according to $F_c' = (1-p)F_{c1} + pF_{c11}$, where p is now the disorder parameter.

By calculating the structure factors of the reflexions for both structures with full weight, respectively F_{c1} and F_{c11} , we see by using the formulae for F_o' and F_c' in the case of twinning or disorder that the crystal showed a large amount of disorder.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34799 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

In the cubic perovskite structure (ABX_3) phase transitions associated with a reduction of the A cation polyhedron have been observed frequently (Megaw, 1973). In such a case the reduction of the volume and the coordination number is obtained by tilting the octahedra (e.g. α - β - KMnCl_3 and α - β - KMgCl_3), because the A cation is not able to fill the coordination polyhedron (cuboctahedron) at ambient temperatures. The analogous hexagonal structures (ABX_3) consist of chains of face-sharing octahedra, separated by A cation polyhedra (twinned cuboctahedra, Fig. 1). The A cation polyhedra also form a chain of face-sharing twinned cuboctahedra (e.g. CsMgCl_3). In the hexagonal systems the volume of the A cation polyhedron can be reduced by two different operations – by rotating or by shifting the face-sharing octahedra relative to each other. Only the last possibility has been observed (e.g. KNiCl_3 and RbFeBr_3 ; Eibschutz, Davidson & Cox, 1974).

The resulting structure is an $a\sqrt{3}$ enlarged cell in the basal plane (Fig. 1). In KNiCl_3 , the two inner $\text{Ni}(2)\text{Cl}_7^-$ chains are shifted over 0.21–0.93 Å along the c axis for the different refinements. The resulting hexagonal layers are puckered in the $[11.0]$ direction (Fig. 2). The A cation polyhedron has been changed into an irregular nine-coordination (Fig. 1), while there is no longer mutual interaction between them.

Concerning the bonding of the framework of these structures, it is obvious that the mutual bonding of the octahedra in the cubic perovskite (three-dimensional) is stronger than in the hexagonal case (one-dimensional) and will find expression in the phase transition. No anomaly has been observed by DTA at the phase transition at 560 K. According to Depmeier, Felsche & Wildermuth (1977) such a transition corresponds to a continuous phase transition, including a direct supergroup/subgroup relation. Such a group relation does

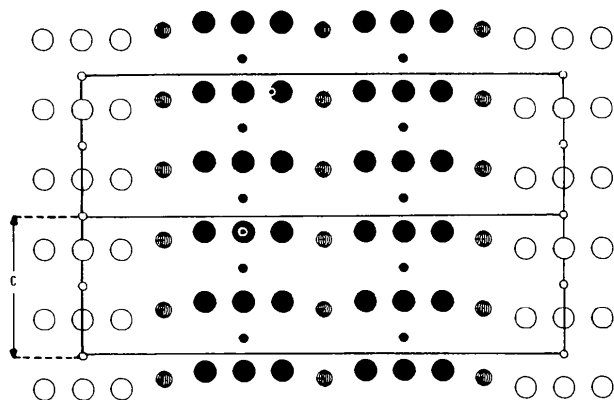


Fig. 2. Projection on the (11.0) plane showing the puckering of the anion layers due to the shifting of the two inner $\text{Ni}(2)\text{Cl}_7^-$ chains along the c axis.

not relate the structure of KNiCl_3 at room temperature ($P6_3cm$) to the space group of CsNiCl_3 ($P6_3mnc$) according to the tables of Bärnighausen, Felsche & Wondratschek (1975). A continuous phase transition in this system would imply that the chains are shifting gradually along the c axis during the decrease of temperature. By assuming that the superstructure starts to nucleate at different parts of the crystal and from the observed flexibility of the K ion coordination polyhedron we can understand the large amount of disorder in KNiCl_3 . We performed single-crystal electron microscopy and diffraction studies (Visser & Prodan, 1980), the results of which will be published in the near future.

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