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X-ray single-crystal study of the low-temperature structure of KNiCl_3

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Abstract. A single-crystal x-ray study on the low-temperature structure of KNiCl_3 proves the existence of two different crystal structure distortions, as originally found by neutron scattering. One phase is hexagonal and does not differ much from the room temperature structure. It appears through a second-order phase transition. The other phase is orthorhombic and appears through a first-order phase transition. A model is proposed for the orthorhombic phase, which fits our x-ray measurements on KNiCl_3 as well as on RbMnBr_3 . The model gives rise to a magnetic configuration that maps on to the row model of Zhang *et al.*

1. Introduction

It is well known that some of the ABX_3 -family hexagonal perovskites exhibit crystal structure distortions. Different types of distortion have been found at sufficiently low temperatures in KNiCl_3 , RbMnBr_3 , RbVBr_3 , RbVI_3 , RbTiI_3 and RbFeBr_3 . An interesting issue is the influence of the nuclear distortion on the magnetic properties of the crystals. Generally, the magnetic structure of ABX_3 -family hexagonal perovskites is triangular or close to triangular and is determined by a delicate balance of the sign and relative magnitude of the exchange interaction and the anisotropy [1]. Even a small movement of atoms, of order 0.5 Å, may cause dramatic changes in the magnetic properties. In RbVBr_3 the magnetic structure remains commensurate and deviates only slightly from the perfect 120° triangular configuration [2], while in RbMnBr_3 the magnetic structure is incommensurate [3]. Moreover, in some materials there are indications that chemically similar crystals grown by different workers (usually by an ordinary Bridgman technique) have different crystal structures. This implies that the difference in energy between two or more possible phases is small, so even minor deviations in crystal preparation result in a change of crystal structure and consequently in a change of magnetic structure.

It has been found recently by neutron scattering measurements [4] that KNiCl_3 has two different modifications of low-temperature crystal structure, denoted by phases A and B. In this report we present the results of x-ray single-crystal measurements on KNiCl_3 using a triple-axis diffractometer at McMaster University. The x-ray study is a logical extension of our previous ESR [5], neutron scattering and magnetization measurements [4, 6]. It allows us to explore both of the low-temperature crystal phases of KNiCl_3 in more detail and to propose a model for the unusual phase B. Less extensive x-ray measurements on RbMnBr_3 indicate that the same distortion occurs there at low temperature.

KNiCl_3 crystallizes from the melt to a high-symmetry space group, $P6_3/mmc$. The features of the high-temperature (HT) structure are linear chains of face-sharing octahedra of NiCl_6 along the c -axis which are arranged triangularly in the ab -plane. Phase transitions to lower symmetry appear on cooling. Dielectric anomalies indicating structural phase transitions are found exclusively along the c -axis at 274 K, 285 K, 561 K and 762 K [7] (such uniqueness of the c -axis is common for ABX_3 crystals; the majority of them are found to be one-dimensional in both the crystal and magnetic sense, with the crystal bonding and the magnetic interactions much stronger along the c -axis than in the perpendicular direction). The nature of the first transition at 762 K is still unclear [8]. At 561 K the crystal undergoes a second phase transition to a hexagonal structure with a unit cell increased by a factor of $\sqrt{3}$ by $\sqrt{3}$ in the basal plane. The symmetry group has been found to be $P6_3cm$ [9]. The phase transition leaves two of the NiCl_3 chains fixed while the third is shifted along the c -direction. Fitting to the intensities of x-ray single-crystal scattering indicates that in different parts of the crystal the amplitude of the shift varies from 0.21 to 0.93 Å [9]. Additional evidence for such disorder in the crystal structure was obtained by electron diffraction [10]. We will refer to this structure, associated with the 561 K phase transition, as the room temperature (RT) structure.

Passage through the two successive phase transitions at 285 K and 274 K for large samples results in an inhomogeneous sample with different parts showing different crystal structures. From the low-temperature neutron scattering measurements [4] it was concluded that in a phase A the unit cell is rotated through 90° about the c -axis from the room temperature unit cell and enlarged to $\sqrt{3}a$, $\sqrt{3}a$ and c , and that the distortion is small, so the structure does not differ much from the structure at room temperature. In contrast, in phase B the change of crystal structure is more substantial with new peaks appearing at $(\frac{3}{4}h, 0, l)$. Based on our x-ray results we will argue that our crystals have a multidomain B phase with orthorhombic symmetry.

2. Experimental procedures

X-ray measurements were performed on a triple-axis rotating-anode diffractometer at McMaster University. A vertically focusing pyrolytic graphite monochromator was used to select the $\text{Cu K}\alpha$ wavelength. The scattering was measured from single crystals in a two-stage closed-cycle helium refrigerator. The diffractometer used was not configured for crystal structure determination, but rather in a manner close to that of a neutron scattering triple-axis spectrometer. In an attempt to employ the best features of the diffractometer we have used a typical neutron scattering approach: instead of automatic collection of a few thousand reflections necessary for a proper structure refinement, we have performed a number of long scans along key directions in reciprocal space. This approach is not geared to precise crystal structure determination, but rather to giving an understanding of the nature of the concurrently appearing structures

The sample of KNiCl_3 was prepared by the Bridgman technique from a stoichiometric mixture of KCl and NiCl_2 . Crystals approximately 0.4–0.5 mm in diameter and 1 mm in length were chipped out of much larger crystals previously used for neutron scattering experiments. All operations on the crystals were performed in an argon-filled glovebox or in a petri dish filled with paraffin oil in order to prevent exposure to the air since KNiCl_3 is highly hygroscopic. The crystals were examined using a polarized microscope and were subsequently placed in small glass capillaries. The ends of the capillaries were then sealed.

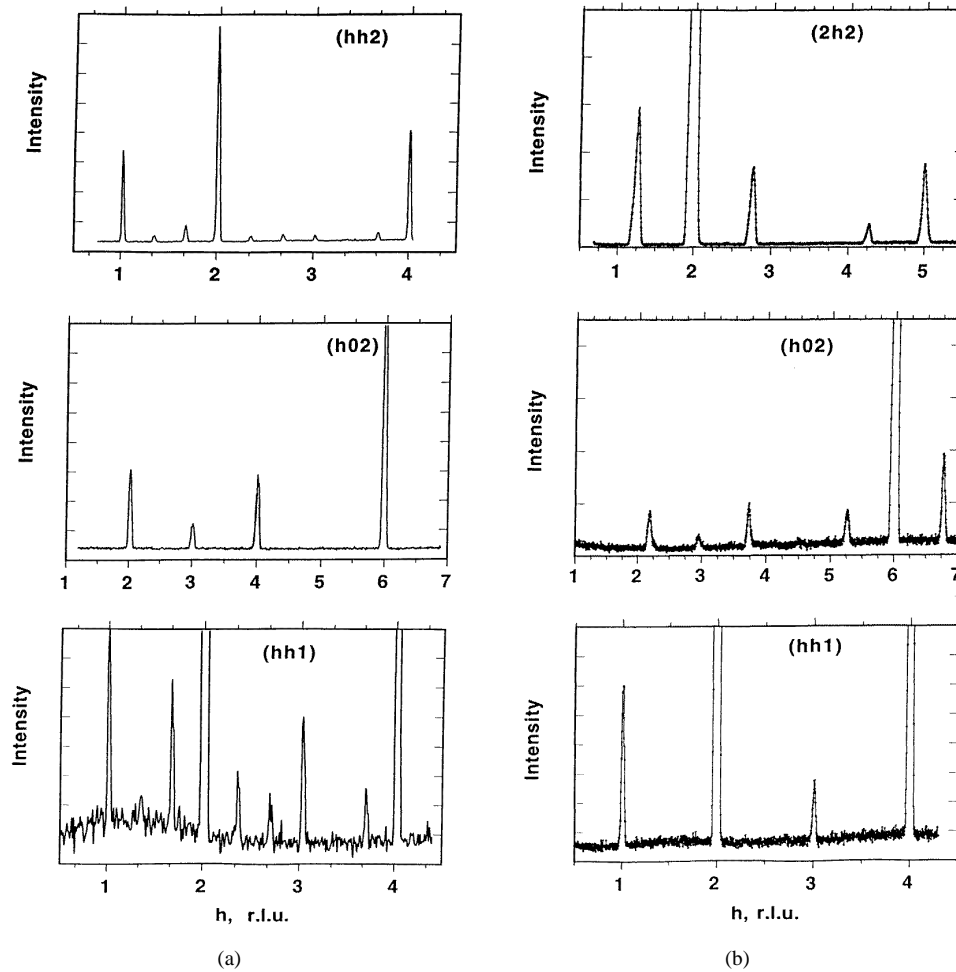


Figure 1. X-ray scattering scans in reciprocal space at $T = 7.2$ K in phase A (a) and in phase B (b), indexed in units of the room-temperature structure. In phase A additional small peaks can be indexed as $(h/3, h/3, l)$, while in phase B low-temperature peaks are shifted from the room temperature position by a quarter of a reciprocal-lattice vector. Intensity is in arbitrary units.

3. Experimental results

We have investigated half a dozen crystals of KNiCl_3 in our x-ray scattering experiments. At room temperature all of them showed identical scattering patterns consistent with the space group $P6_3cm$. We found no way that we could predict what phase, A or B, a particular crystal would take at low temperature. In one of the crystals a mixture of the two phases was found.

Figure 1 shows some examples of scans in reciprocal space, which illustrate the difference between the two low-temperature (LT) phases. In agreement with neutron scattering results, in phase A (figure 1(a)) additional weak peaks were observed at the position $(h/3, h/3, l)$ with l a nonzero integer; the intensity of all RT peaks remained unchanged within experimental accuracy. In a phase-B crystal (figure 1(b)), all peaks

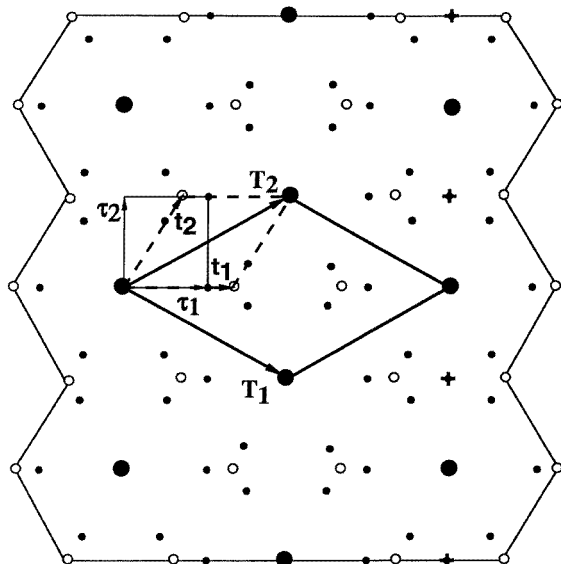


Figure 2. X-ray scattering in the plane $(hk2)$ for phase B. Big circles represent reflections in the high-temperature (HT) phase, open circles correspond to reflections observed at room temperature (RT) and small solid circles are reflections at low temperature (LT). Unit-cell vectors are denoted as $T_{1,2}$ (thick solid lines), $t_{1,2}$ (dashed lines) and $\tau_{1,2}$ (thin solid lines) for HT, RT and LT phases respectively. Crosses show the position of additional, weak reflections (see the text for details).

corresponding to the highly symmetric HT phase with space group $P6_3/mmc$ (for example, peaks $(3h, 0, l)$ and (h, h, l)) change intensity slightly, while a triplet of new peaks was detected in place of each peak corresponding to the RT structure distortions. These new peaks are shifted from the original position towards the nearest HT peak by a quarter of the reciprocal-lattice vector. The overall picture of the Bragg reflections in the $(hk2)$ plane is shown in figure 2 to illustrate the splitting of room temperature reflections into a low-temperature triplet. In figure 2 we show the unit cell for the HT and RT structures, as well as the unit cell for the proposed model of the phase-B LT structure.

In addition to the peaks described above, extra Bragg peaks have been seen at some higher (hkl) indexes, although they are very weak in intensity. Figure 3 is an example of a scan where these very weak peaks have been seen. Positions of these peaks in reciprocal space are marked by crosses on figure 2.

Remarkable differences between phases A and B have been seen in the temperature dependence of the intensity of the new peaks. In phase A it increased gradually as the temperature decreased, while in phase B the appearance of new peaks and disappearance of room temperature ones was sharp and had hysteresis in temperature. Figure 4 gives a comparison between the temperature dependencies of the peak intensity for the two crystal phases.

4. Discussion

Both from a crystallographic and from a magnetic point of view phase B is more interesting and unusual. While in phase A the magnetic structure is similar to the 120° triangular spin

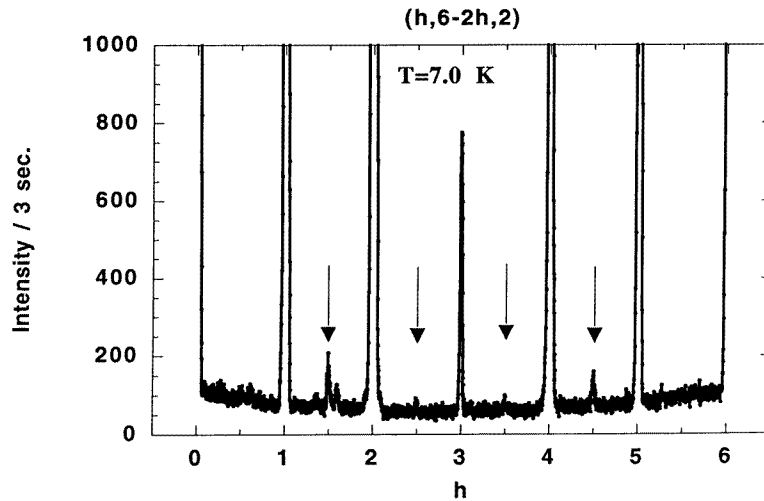


Figure 3. The $(h, 6 - 2h, 2)$ scan at $T = 7.0$ K. Arrows indicate weak peaks, which are not seen at lower (hkl) . The intensity of RT peaks with integer indexes reaches 25 000 counts on the same scale.

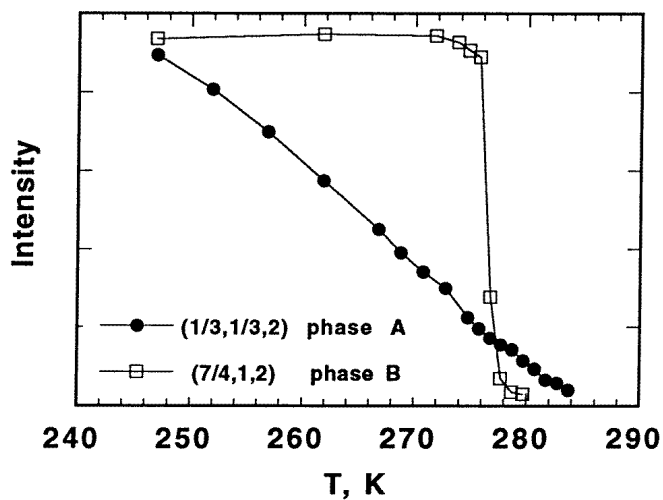


Figure 4. Temperature dependence of the intensity of the peak $(\frac{1}{3}, \frac{1}{3}, 2)$ in phase A and of the peak $(\frac{7}{4}, 1, 2)$ in phase B. Solid lines are guides for the eyes.

structure, in phase B the magnetic structure is more complex. Hence, we focus our attention on phase B. The results may be summarized as follows:

- (1) the transition between LT and RT is a first-order phase transition;
- (2) all peaks corresponding just to the RT structure disappeared in passing through the phase transition, while all peaks corresponding to the HT structure change intensity, but only slightly;
- (3) reasonably strong new peaks appeared as triplets around former RT peaks in all

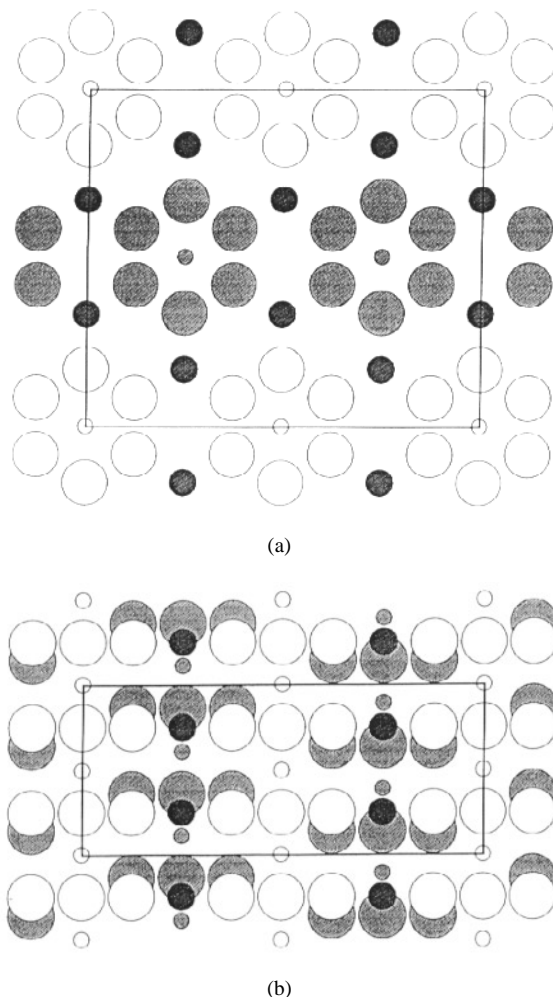


Figure 5. The proposed model of the low-temperature structure for a phase B of KNiCl₃. Small and big circles are Ni and Cl ions; shadowed circles correspond to ions shifted up or down from the basal plane. Intermediate solid circles are K ions. The unit cell is shown by solid lines.

(*hkl*) planes with even *l* (except *l* = 0); they are shifted from the RT peak positions by a quarter of a reciprocal-lattice vector;

(4) other new peaks are systematically very weak; special efforts have to be made in order to observe them.

We propose a model of the LT-structure distortion in phase B (see figure 5), which is self-consistent and which matches all the conditions given above.

The observed tripling of some reflections suggests a splitting of the sample into domains and the loss of hexagonal symmetry. In order to describe all reflections found in one domain, the reciprocal unit cell has to be orthorhombic with $|\tau_1| = \sqrt{3}|T|/4$ by $|\tau_2| = |T|/2$, where $|T| = |T_1| = |T_2|$ is the size of HT unit cell. The direction of τ_1 coincides with one of the hexagonal axes at RT. In real space, the LT unit cell has size $|a_1| = 2a$ and $|a_2| = \sqrt{3}a$, where *a* is the lattice parameter of the HT unit cell. Thus the LT structure is four times

larger in volume than the HT structure.

The main feature of the model is a sinusoidal modulation of the ion chains in the basal plane: instead of the RT sequence 0–0–UP–0–0–UP–0–0, where ‘0’ means an ion in the basal plane and ‘UP’ means an ion slightly shifted above the basal plane along the c -axis, in our model the sequence is 0–UP–0–DN–0–UP–0–DN–0, where ‘DN’ means that the ion is shifted to below the basal plane. In this sequence some reflections are absent or very weak: in the scan ($h02$), for example, the intensity of the reflections $(1.5, 0, 2)$, $(4.5, 0, 2)$, $(7.5, 0, 2)$ and so on is below the background level, while in the scan $(h, 6 - 2h, 2)$ the intensity of the reflections $(1.5, 3, 2)$, $(2.5, 1, 2)$, $(3.5, -1, 2)$ and $(4.5, -3, 2)$ is just above the background level. The absence of new peaks for $l = 0$ at low temperature shows that distortion manifests itself as a shift of ions chains along the c -axis rather than rotation around the c -axis or a shift in the x - or y -components of the atomic positions (the same was true in the RT structure).

As can be seen from figure 5, the model’s unit cell contains four pairs of Ni ions. Ions in each pair are in the same chain, separated by the distance $c/2$. Two of these pairs still lie in the original basal plane, while the other two are shifted by a small distance Z below and above the basal plane. Ions of Cl are located such that they still form face-sharing octahedra with Ni ions. The position of K ions in the model coincides with their position in the HT phase. After fixing the position of all ions we calculated the dependence of the x-ray scattering intensity for the proposed model on Z . The results of the calculation show that in order to fit the experimental data, Z is $(0.09 \pm 0.01)c$, that is $Z \approx 0.5 \text{ \AA}$, which is very similar to the value of the distortions found in other ABX_3 compounds.

The problem of determining the space group is complicated by the fact that the former hexagonal c -axis is not special any more and may not necessarily coincide with the c -axis of the new orthorhombic unit cell. The systematic absences indicate space group $Pca2_1$ or $Pbcm$.

Both LT and RT structures can be obtained from the HT structure by shifting one half or one thirds of the NiCl_3 chains along the c -axis. A rearrangement of the structure is required to go from the RT to the LT phase, which explains the first-order nature of this transition. It also may give us a clue about different proportion of phases A and B in large samples—extremely small amounts of impurities or even differences in sample shape are capable of ‘stabilizing’ the RT structure (or similarly the A-phase structure) and prevent transitions to a symmetrically different B phase. Apparently, the energy gap between two phases is very small.

In reference [4] we drew the analogy between LT structures of KNiCl_3 and RbMnBr_3 . The analogy becomes even more obvious after measurements of the x-ray scattering profile using the same instrument and method. We have investigated the LT structure of RbMnBr_3 and found that it is identical to phase B of KNiCl_3 . A first-order phase transition between RT and LT was found at $T = 219 \text{ K}$.

The neutron measurements on RbMnBr_3 of Heller *et al* [3] show a crystal which seems to contain both the A and B phases, while the measurements of Kato *et al* [12] show a crystal where only the B phase is present. The B phase shows an incommensurate magnetic structure below 8.3 K, while the phase transition seen at 10.0 K corresponds to the onset of a commensurate magnetic structure in the A phase which is the same as that found in the A phase in KNiCl_3 . No additional peaks were observed in the x-ray profile of RbMnBr_3 at low temperature, which proves the magnetic nature of the phase transition at 10 K.

The identity of structure makes it hard to explain difference in magnetic structure in the B phase. From a symmetry point of view the proposed model for the B phase corresponds to the ‘row model’ of Zhang *et al* [11], and consequently incommensurate magnetic structure

should appear at sufficiently low temperature. In RbMnBr_3 the magnetic structure is incommensurate at low magnetic fields and only if the magnetic field exceeds 3 T does it become commensurate [3]. The overall H - T phase diagram, which is very complicated and includes two incommensurate phases, two commensurate phases and paramagnetic one, can be explained in terms of Landau theory using a 'row model' [13]. In KNiCl_3 the magnetic structure is commensurate even in zero magnetic field [4] and identical to the high-field structure of RbMnBr_3 . What causes the stabilization of the commensurate spin configuration in KNiCl_3 remains unknown. However, the commensurate B-phase magnetic structure is unique to these two materials; this increases confidence in the picture that we have put forward. It is the only known realization of the row model, and it is pleasing that the magnetic structures have been anticipated theoretically.

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