Deciphering the sequence of phase transitions in KNiCl$_3$

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ABX$_3$ halides (A=K, Rb, Cs, B=Ni, Mn, Fe, X=Cl, Br) are a large class of materials where we find ferroelectricity and magnetism. The crystal structures of these materials consist of chains of BX$_6$ octahedra separated by A ions. When the ionic radius of A$^+$ is much smaller than the radius of the X$^-$ ion, structural phase transitions can occur and consequently changes in properties. For example, a sequence of phase transitions is reported for the hexagonal perovskite KNiCl$_3$ at 763 K, 560 K and 270-260 K [1, 2] which are associated with dielectric effects and ferro-electricity above 260 K [3]. These phase transitions are prototype for distorted ABX$_3$ halides (without a Jahn-Teller effect). In KNiCl$_3$, the two high temperature phases (above 560 K) have a simple hexagonal a$\times$c unit cell [4], enlarging to an 3a$\times$3a$\times$c unit cell at 300 K. In this crystallographic phase, two out of the three octahedral chains move upwards along the c-axis, with respect to the third one [4]. The intermediate phase that exists over the narrow temperature range from 270-260 K shows a further enlargement to a 3a$\times$3a$\times$c unit cell. This phase appears essentially as a single phase near 270 K and coexists with the lowest temperature phase towards 260 K. Below 260 K, the lowest unit cell is enlarged even further to 4a$\times$4a$\times$c. This cell can be reinterpreted as being a superposition of three twin domains of an orthorhombic cell (see arrow in Figure 1). Here, we present the solution of the intermediate phase and possible solutions for the lowest temperature phase. These are augmented by electronic stability calculations within the framework of DFT + eDMFT.

Figure 1. (h, k, 2) layer of KNiCl$_3$ at 300K (left) and 250K (right) recorded with neutrons using the SXD instrument at the ISIS spallation neutron source (Oxfordshire, UK).


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