

Synchrotron X-ray diffraction study on the square-lattice antiferromagnets (CuCl)LaNb₂O₇ and (FeCl)LaNb₂O₇

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Abstract

High resolution synchrotron X-ray diffraction methods have been used to study the crystal structure of the two-dimensional square-lattice antiferromagnets (CuCl)LaNb₂O₇ and (FeCl)LaNb₂O₇. While the structure of the former is of tetragonal symmetry with simple perovskite unit cell dimensions in the *a, b* plane (*a* × *a*), the latter exhibits a tiny orthorhombic distortion with a *2a* × *2a* × *c* superstructure, providing a first example of modulation in the family of transition-metal oxyhalides prepared from topotactic ion-exchange reactions. Possible arrangement in the FeCl layer is proposed.

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1. Introduction

It has recently been recognized that ion-exchange reaction is a useful tool for designing magnetic materials. Starting from double- and triple-layered (*n* = 2, 3) perovskites RbLaB₂O₇ and RbA₂B₃O₁₀ (A²⁺ = Ca²⁺, Sr²⁺; B⁵⁺ = Nb⁵⁺, Ta⁵⁺), a new family of two-dimensional square-lattice antiferromagnets expressed as (MX)LaB₂O₇ and (MX)A₂B₃O₁₀ (M²⁺ = Fe²⁺, Co²⁺, Cu²⁺...; X⁻ = Cl⁻, Br⁻) has been prepared [1–4]. In the final products, the [MX]⁺ layers are sandwiched by the nonmagnetic perovskite slabs (Fig. 1(a)). The magnetic properties of several materials have been examined so far. (FeCl)LaNb₂O₇ with *S* = 2 undergoes a conventional antiferromagnetic order at 78 K, though there is an anomaly in the magnetic susceptibility at around 8 K [5]. An unusual behavior characterized by the *spin liquid*

has been found in an *S* = ½ system (CuCl)LaNb₂O₇, where no long-range magnetic order exists even at 0 K and there is an energy gap of 2.3 meV between the spin-singlet ground state and the first excited triplet state [6,7]. Such a spin-liquid state on the square lattice is interesting in connection with the RVB state predicted by Anderson after the discovery of high *T_c* superconductivity [8].

Previous powder X-ray and neutron diffraction studies on all the materials in this family revealed that the structure was described simply by a tetragonal symmetry (space group *P4/mmm*) with an approximate dimension of *a* = *b* ~ 3.9 Å and *c* ~ 12 Å for *n* = 2 and *c* ~ 16 Å for *n* = 3. However, to understand the nature of the spin liquid in (CuCl)LaNb₂O₇, a more precise determination of the crystal structure and comparison with those of related materials is highly desired. Here, we report on the results of high resolution synchrotron X-ray diffraction (XRD) for (CuCl)LaNb₂O₇ and (FeCl)LaNb₂O₇.

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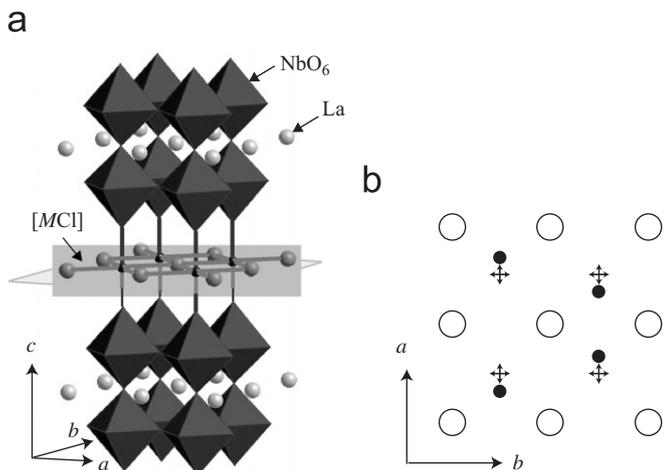


Fig. 1. Schematic view of the crystal structure of $(MCl)LaNb_2O_7$ ($M = Cu, Fe$). (b) Possible ordered pattern of the FeCl layer in $(FeCl)LaNb_2O_7$, where open and closed circles represent chlorine and iron atoms. Arrows denote the disordering of irons suggested by Viciu et al. [5].

2. Experiments

Polycrystalline samples of $(MCl)LaNb_2O_7$ were prepared by ion-exchange reaction between $RbLaNb_2O_7$ and MCl_2 at $320^\circ C$ for $M = Cu$ and $350^\circ C$ for $M = Fe$ in a sealed, evacuated Pyrex tube for one week. The final products were washed with water to eliminate unreacted MCl_2 and $RbCl$ byproduct. Synchrotron X-ray powder diffraction experiments were carried out at 300 K on the large Debye-Scherrer camera installed at BL02B2 in SPring-8. The sample powder with homogeneous granularity prepared by precipitation method was sealed in a glass capillary of 0.2 mm in diameter.

3. Results and discussion

Fig. 2 shows the synchrotron XRD profiles for $(CuCl)LaNb_2O_7$ and $(FeCl)LaNb_2O_7$, where the wavelength was calibrated at 0.776532 \AA . The observed peaks for both compounds are fairly sharp and nearly symmetric. This is an indication of successful ion-exchange reactions and good crystallinity of the specimens. All the peaks for $(CuCl)LaNb_2O_7$ are indexed by a tetragonal unit cell and from the least-square fitting the lattice constants for $(CuCl)LaNb_2O_7$ are determined as $a = 3.88005(6) \text{ \AA}$ and $c = 11.7337(3) \text{ \AA}$, consistent well with those reported previously [1]. For $(FeCl)LaNb_2O_7$, observed peaks basically coincide with those for $(CuCl)LaNb_2O_7$. However, a closer look at the data revealed the splitting of some reflections together with the appearance of several new discrete peaks. A small peak shown in the inset of Fig. 2, for example, is the superstructure reflection that is indexed as $(\frac{1}{2} \frac{1}{2} 0)$. The analysis led us to the conclusion that the crystal structure is orthorhombic with cell parameters being $a = 7.76213(8) \text{ \AA}$, $b = 7.74218(8) \text{ \AA}$ and $c = 11.8508(1) \text{ \AA}$. Note that this is the

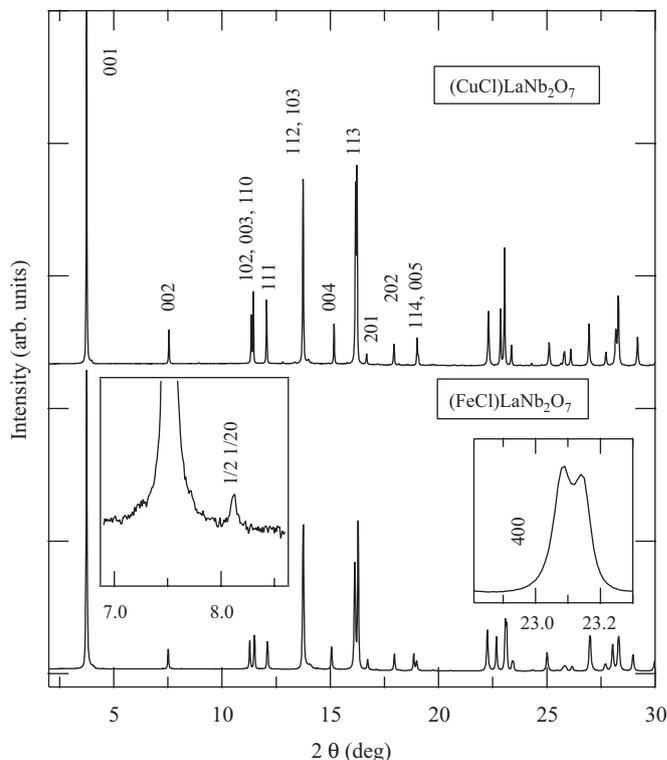


Fig. 2. Synchrotron X-ray diffraction patterns of (upper) $(CuCl)LaNb_2O_7$ and (lower) $(FeCl)LaNb_2O_7$. The insets show the enlarged plots for $(FeCl)LaNb_2O_7$, highlighting the superreflection assigned as $(\frac{1}{2} \frac{1}{2} 0)$ and the splitting of the (400) reflection.

first experimental observation of nontetragonal symmetry and the superstructure in the family of $(MX)LaB_2O_7$ and $(MX)A_2B_3O_{10}$.

The observed $2a \times 2a \times c$ modulation in the present study must be related to the structural mismatch between perovskite slabs and FeCl layers. A plausible model is that irons in the FeCl layer are ordered as shown in Fig. 1(b). In fact, Viciu et al. claimed based on the data taken by a laboratory X-ray diffractometer that the ions are statistically disordered being located at the 4o site in the space group $P4/mmm$ [5], resulting in an averaged structural description. It is worth noting that such ordering could be accompanied by the tilting and/or distortion of the NbO_6 octahedra.

4. Summary

High resolution of the SPring-8 X-ray diffractometer allows us to detect a tiny orthorhombic distortion in $(FeCl)LaNb_2O_7$. A possible model to explain the $2a \times 2a \times c$ superstructure of the FeCl layer was proposed. On the contrary, no superstructure reflection was found for $(CuCl)LaNb_2O_7$ within the experimental accuracy. The refinements of both materials are in progress. From the viewpoint of inorganic structural chemistry, this study offers an interesting subject to investigate structural modulation and instability as a function of M , X , A , B and n .

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