O$^{2-}$-to-F$^-$ substitution on the quasi-two-dimensional quantum antiferromagnet (CuCl)LaNb$_2$O$_7$

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Abstract. We present the preparation of the electron-doped quasi-two dimensional quantum antiferromagnet (CuCl)LaNb$_2$O$_7$ by two step-wise topochemical reactions. The first step involves a reductive fluorination of the insulating layered perovskite RbLaNb$_2$O$_7$ using polytetrafluoroethylene that allows electric conduction in the perovskite blocks. The product RbLaNb$_2$O$_6$F was then ion-exchanged with copper dichloride to yield (CuCl)LaNb$_2$O$_6$F. The synchrotron x-ray diffraction study indicates that the structure of the final compound is different from that of the pure (CuCl)LaNb$_2$O$_7$.

1. Introduction

The Dion-Jacobson perovskite phases $A'$,$A_{n-1}B_nO_{3n+1}$ ($A'$ = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$,...; $A$ = La$^{3+}$, Nd$^{3+}$, Eu$^{3+}$, Sr$^{2+}$, Ca$^{2+}$, Ba$^{2+}$,...; $B$ = Nb$^{5+}$, Ta$^{5+}$, Ti$^{4+}$, $n = 2, 3, 4,...$) consist of negatively charged, non-magnetic perovskite slabs [$A_{n-1}B_nO_{3n+1}$] with the B site being occupied by a $d^0$ transition metal that is separated by a monovalent cationic ($A'$) unit.[1-3] The interlayer site, the $A'$ site, can be modified using a variety of low-temperature reactions such as intercalation and ion-exchange to give various new chemical compositions.[4]

Wiley and coworkers modified the $A'$ site with the metal-halide array ($MX$)$^+$ ($M$ = Co$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Mn$^{2+}$,... and $X$ = Cl$^-$, Br$^-$) through ion-exchange reaction using corresponding metal dihalides.[5-10] The resulting structure consists of the magnetic $MO_2X_4$ octahedra layers separated by the nonmagnetic $AB_2O_7$ arrays with the B cation remaining in the $d^0$ electronic configuration. The original structural analysis showed that the $M^{2+}$ ions form an ideal two-dimensional square lattice. These compounds exhibit interesting magnetic features due to competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions within the Cu$X$ layer. For instance, the magnetism of (CuCl)LaNb$_2$O$_7$ is characterized by a spin singlet ground state with a spin gap of 2.3 meV.[11] Under magnetic fields, the Bose-Einstein condensation of triplet magnons occurs at around 10 T.[12] Recently, its structure was refined using powder and single crystal neutron diffraction and x-ray diffraction (XRD) revealing that this material corresponds to the otherwise solely theoretical ferromagnetically coupled Shastry-
Sutherland model, where the four next-nearest neighbour Cu$^{2+}$ ions forming spin-singlets are arranged orthogonally in the $ab$ plane ($J_4$) and ferromagnetically coupled with respect to each other.[13]

How itinerant electrons behave in the frustrated lattice has recently been attracting considerable attention. Examples include the anomalous Hall effect related to chiral magnetic structures,[14,15] heavy fermion behaviour in the spinel oxide LiV$_2$O$_4$ [16] and anisotropic superconductivity in the triangular lattice Na$_{0.35}$CoO$_2$.1.3H$_2$O.[17] Up till now, however, most experimental studies were performed on triangle-based frustrated lattices. Although several theoretical investigations of the Shastry-Sutherland lattice demonstrated anisotropic superconductivity when moderate carriers are introduced, no experimental report on metallization exists on a Shastry-Sutherland system either in the ferromagnetic case, or even the antiferromagnetic Shastry-Sutherland SrCu$_2$(BO$_3$)$_2$.[18-21] In light of the fact that a ferromagnetically coupled Shastry-Sutherland compound has now been realized, it would be very interesting to inject electrons or holes into (CuCl)LaNb$_2$O$_7$. Recently, Kobayashi et al.[22] performed the reaction of RbLaNb$_2$O$_7$ with polytetrafluoroethylene (PTFE) and succeeded to reduce partially the valence of the niobium centre from Nb$^{5+}$ to Nb$^{4+}$, yielding RbLaNb$_2$O$_7$F$_x$ ($0 < x < 1$). Remarkably, this reductive fluorination induces electronic conductivity in the Nb$_2$O$_7$ blocks while preserving the ion-exchangeable Rb$^+$ layer. The present study combines the aforementioned ion-exchange reaction with the reductive fluorination of RbLaNb$_2$O$_7$ to finally obtain (CuCl)LaNb$_2$O$_7$F.

2. Experimental

RbLaNb$_2$O$_7$ was synthesized using high temperature synthesis. Powders of Rb$_2$CO$_3$ (99.99%), La$_2$O$_3$ (99.99%) and Nb$_2$O$_5$ were mixed in an agate mortar. The mixture was heated in an alumina crucible at 800 ºC for 12 hours. Next, the powder was ground and sintered at 1050 ºC for 24 hours. Finally, the obtained sample was washed using water and heated at 1050 ºC for 24 hours. The quality of the sample was checked using a Bruker AXS (D8 Advance) XRD apparatus.

Fluorination was performed by mixing RbLaNb$_2$O$_7$ with PTFE (99.9%). A 1:0.5 mol mixture was ground thoroughly in an agate mortar and pelleted. The pellets were inserted in a Pyrex tube, sealed under dynamic vacuum (1.3×10$^{-8}$ MPa) and heated at 400 ºC for 24 hours. Following this, fluorinated samples were mixed with CuCl$_2$ (99.999%) in a 1:3 molar ratio in an Ar-filled glove box, pelleted, inserted in pyrex tubes and sealed under dynamic vacuum (< 1.3×10$^{-8}$ MPa). The tubes were heated at 325 ºC for one week. Finally the powders were washed using methanol to remove RbCl and excess CuCl$_2$ byproducts. Chemical composition was determined by combustion ion chromatography.

The synchrotron powder XRD experiments were performed at 293 K on the large Debye–Scherrer camera installed at the Japan Synchrotron Radiation Research Institute SPring-8 BL02B2 by using an imaging plate as a detector. Incident beams from a bending magnet were monochromatized to 0.77709 Å. The synchrotron XRD data were collected in a 2$\theta$ range from 0º to 75º with a step interval of 0.01º.

The crystal structure was refined using the Rietveld method (RIETAN-2000).[23] The peak shape model used was a modified split-pseudo-Voigt function. The agreement indices are $R$-weighted pattern, $R_w = \left[ \sum w_i (y_{io} - y_{ic})^2 / \sum w_i (y_{io})^2 \right]^{1/2}$, $R$-pattern, $R_p = \sum |y_{io} - y_{ic}| / \sum y_{io}$, and goodness of fit (GOF), $\chi^2 = \left[ R_w^2 / R_{wp} \right]^2$, where $R_{wp} = (N-P) / \sum w_i (y_{io} - y_{ic})^2$, $y_{io}$ and $y_{ic}$ are the observed and calculated intensities, $w_i$ is the weighting factor, $I_d(h_k)$ and $I(h_k)$ are the observed and calculated integrated intensities, $N$ is the total number of $y_{io}$ data when the background is refined, and $P$ is the number of adjusted parameters.
3. Results and discussion

The synthesis of (CuCl)LaNb₂O₇ occurs in two steps: the reductive fluorination of the niobium layer of RbLaNb₂O₇ and the ion-exchange of the interlayer cation Rb⁺ with CuCl⁺. The colour of the sample changes from white to black in the first reaction. After the fluorination, we observed a larger change of the lattice parameters, i.e. the increase of the c axis (≈0.26 Å) is greater than ≈0.21 Å reported earlier [22] (see Table 1). This indicates that a larger amount of fluorine was inserted in the sample, despite the fact that less PTFE was used in our preparation compared to ref. 22. This difference may be due to the difference in the fluorination method. The fluorination was performed previously under flowing N₂, while in the present study the RbLaNb₂O₇:PTFE mixture was inserted in a vacuum sealed pyrex tube. The a axis decreases only slightly, which comes from the preferential occupation of the fluorine atoms at the apical site as pointed out in [22].

| Space Group   | a (Å)     | b (Å)     | c (Å)     | V (Å³) |
|---------------|-----------|-----------|-----------|--------|
| RbLaNb₂O₇     | 3.89170(9)| 3.89170(9)| 11.0072(4)| 166.71 |
| RbLaNb₂O₆F   | 3.86575(16)| 3.86575(16)| 11.2135(7)| 167.58 |
| RbLaNb₂O₇     | 3.8894(8) | 3.8894(8) | 10.9870(2)| 166.05 |
| RbLaNb₂O₆F   | 3.8685(4) | 3.8685(4) | 11.243(8) | 168.27 |
| (CuCl)LaNb₂O₇| 3.8807(4) | 3.8807(4) | 11.7337(9)| 176.70 |
| (CuCl)LaNb₂O₆F| 3.8711(8) | 3.8711(8) | 11.863(5) | 177.77 |

* ref. 22
Figure 3. Rietveld refinement of \((\text{CuCl})\text{LaNb}_2\text{O}_6\)F. Dark crosses, the black line, black ticks and the bottom line indicate the observed pattern, calculated pattern, peak positions and difference between observed and calculated pattern, respectively.

The second reaction led to a colour change from black to dark green. Elemental analysis showed that the average content of fluorine is approximately 1.1(7) in \(\text{RbLaNb}_2\text{O}_6\)F and 1.4(4) in \((\text{CuCl})\text{LaNb}_2\text{O}_6\)F, indicating no loss of fluorine during the ion-exchange reaction. Unfortunately, the electric conductivity was lost. The unit cell of the final product was calculated to be tetragonal with \(a = 3.8711(8)\) Å and \(c = 11.863(5)\) Å. The \(c\) axis increase of \(\approx 0.13\) Å with respect to the previously reported non-fluorinated \((\text{CuCl})\text{LaNb}_2\text{O}_7\) indicates both the successful intercalation of CuCl and the preservation of the fluorine. We first refined the structure using the simple tetragonal unit cell and the space group \(P4/mmm\). The refinement gave reasonable agreement values of \(R_{wp} = 7.09\%\) and \(\chi^2 = 3.43\). However, several peaks were not fitted well and high anisotropic displacement parameters (ADP) values were observed for both Cu (3.64 \(\times\) 10\(^{-2}\) Å\(^2\)) and Cl (8.56 \(\times\) 10\(^{-2}\) Å\(^2\)). From this, we tried a disordered model with copper and chlorine shifting from their ideal (0, 0, 0.5) and (0.5, 0, 0.5) positions, respectively. The agreement values consequently decreased to \(R_{wp} = 5.97\%\) and \(\chi^2 = 2.48\) (Figure 3); the position of copper remained within the ideal position but chlorine drifted to (0.094, 0.056, 0.4999) (Table 2). The refinement of the ADP led to similar values for copper and better values for chlorine. The occupation factor of copper and chlorine was refined and gave reasonable values \(g_{\text{Cu}} = 0.98(2)\) for copper and \(g_{\text{Cl}} = 1.00(6)\) for chlorine indicating that the ion exchange was complete.

The genuine structure of \((\text{CuCl})\text{LaNb}_2\text{O}_7\) is orthorhombic \(Pbam\) \(2a \times 2b \times c\) with a pseudo tetragonal unit cell \((a = 7.7556(5)\) Å and \(b = 7.7507(5)\) Å\).[13,24] When we applied this distorted model to the obtained data, however, the refinement did not lead to better values \((R_{wp} = 6.33\%\) and \(\chi^2 = 2.72\)). While the ADP parameters for copper decrease significantly from the disordered model (Table 3), the occupancy factors for both elements are not satisfactory \((g_{\text{Cu}} = 0.95(2)\) and \(g_{\text{Cl}} = 0.90(2)\)). The refinement results based on the non-distorted structure \((P4/mmm)\) and the superstructure \((Pbam)\) indicate that although the structure of \((\text{CuCl})\text{LaNb}_2\text{O}_6\)F is possibly distorted, the structure is different from that of \((\text{CuCl})\text{LaNb}_2\text{O}_7\) and the FM Shastry-Sutherland model. Complementary analysis of these materials using other techniques (electron and neutron diffraction) will be necessary to understand their genuine structure.

The valence state of the transition metal elements (i.e., copper and niobium) in the final product is not clear yet. A possible reason for the loss of the electronic conductivity after the ion-exchange
reaction is that mobile carriers in the perovskite blocks in RbLaNb₂O₇F become frozen out as a consequence of the CuCl layer insertion. The insertion of such a covalent network may induce the deformation of oxygen octahedral in NbO₆ and the tilting and rotation of octahedra, both of which would strongly modulate the transfer integral between Nb 3d and O 2p orbitals. Another plausible reason is the case, where all conducting electrons in the perovskite blocks are transferred to the CuCl layer, leaving no partially occupied d-electrons for both Cu (d¹⁰) and Nb (d⁰). Then an interesting challenge toward metallization would be controlling F/O ratio. It was already demonstrated that the F/O ratio in RbLaNb₂(O₆+xFₓ) can be tuned in the range of 0 ≤ x ≤ 1.[22] It would be thus possible to obtain (CuCl)LaNb₂(O₆+xFₓ). In any case, band calculations would be helpful to know whether the chemical potential is located closer to the Cu 3d band or to the Nb 4d band.

Table 2. Structural parameters obtained from Rietveld refinement CuCl)LaNb₂O₆F.

| Atom | site | sof | x   | y   | z   | 100Biso (Å²) |
|------|------|-----|-----|-----|-----|--------------|
| Cu   | 1d   | 0.97(7) | 0.5 | 0.5 | 0.5 | 3.64(3)      |
| Cl   | 8    | 0.125(6) | 0.094(3) | 0.056(5) | 0.5 | 3.96(8)      |
| La   | 1a   | 1     | 0   | 0   | 0   | 1.29(2)      |
| Nb   | 2h   | 1     | 0.5 | 0.5 | 0.193(6) | 0.28(1) |
| O(1) | 4i   | 1     | 0   | 0.5 | 0.152(3) | 1.13(9) |
| O(2) | 2h   | 1     | 0.5 | 0.5 | 0.333(2) | 1.27(4) |
| O/F(3) | 1c | 1     | 0.5 | 0.5 | 0   | 2.67(2)      |

P4/mmm, a = 3.8711(8) Å, c = 11.863(5) Å, Rwp = 5.97 %, Rp = 4.07 %, and χ² = 2.48.

Table 3. Structural parameters obtained from Rietveld refinement of (CuCl)LaNb₂O₆F, distorted model.

| Atom | site | sof | x   | y   | z   | 100Biso (Å²) |
|------|------|-----|-----|-----|-----|--------------|
| Cu   | 4h   | 0.95(2) | 0.492(7) | –0.220(7) | 0.5 | 2.09(8)      |
| Cl   | 4h   | 0.90(2) | 0.737(2) | –0.057(8) | 0.5 | 4.83(6)      |
| La   | 4g   | 1     | 0.750(5) | –0.505(2) | 0   | 1.24(8)      |
| Nb   | 8i   | 1     | 0.500(8) | –0.248(3) | 0.192(5) | 0.44(8) |
| O(1) | 4f   | 1     | 0.5   | 0   | 0.152(3) | 1.48(5) |
| O(2) | 4e   | 1     | 0.5   | 0.160(2) | 0.374(6) | 0.37(4) |
| O(3) | 8i   | 1     | 0.761(8) | –0.251(6) | 0.148(7) | 0.87(3) |
| O/F(4) | 4g | 1     | 0.519(7) | –0.265(9) | 0   | 1.82(5) |
| O(5) | 8i   | 1     | 0.500(1) | –0.257(1) | 0.322(7) | 1.09(2) |

Pbam, a = 7.7419(5) Å, b = 7.7426(2) Å, c = 11.863(5) Å, Rwp = 6.33 %, Rp = 4.25 %, and χ² = 2.72.

4. Conclusion

We prepared (CuCl)LaNb₂O₆F by two successive topotactic reactions. The first consisted in the substitution of O²⁻ by F⁻ and the second the ion-exchange of Rb⁺ with (CuCl)⁺ to yield (CuCl)LaNb₂O₆F from RbLaNb₂O₇. By using synchrotron powder diffraction, we were able to show that the structure of the fluorinated (CuCl)LaNb₂O₆F appears to be different from (CuCl)LaNb₂O₇. Distortions from the ideal model are common in these layered perovskites and have been observed in
(FeCl)LaNb$_2$O$_7$, having a $\sqrt{2}a \times \sqrt{2}b \times c$ monoclinic cell [25], and (CuCl)LaNb$_2$O$_7$ having a $2a \times 2b \times c$ orthorhombic cell.[13,24] In the same way, the detailed structures of the fluorinated phases RbLaNb$_2$O$_6$F and (CuCl)LaNb$_2$O$_6$F are unknown; i.e. RbLaNb$_2$OF has been demonstrated to have a $4a \times 4b \times c$ superstructure, but the details are not clear yet.[22] Although the electronic conductivity was lost after the ion-exchange reaction, further synthetic efforts such as controlling the fluorine content may eventually change the unfortunate situation. The synthesis pathway and structure analysis developed here will allow the systematic study of new fluorinated ion-exchanged perovskite $(MX)_n A_{n-1} B_n O_{3n+1}$ which we hope will provide crucial hints to understand and realize new structures with novel magneto-electric properties.

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