Two-dimensional Frustrated Antiferromagnets (MCl)LaNb$_2$O$_7$ ($M = \text{Mn, Co, Cr}$)

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Abstract. Magnetic susceptibility and specific heat measurements have been performed on two-dimensional spin systems (M$^{2+}$Cl)LaNb$_2$O$_7$ ($M = \text{Mn (S = 5/2), Cr (S = 2), Co (S = 3/2)}$), prepared via a topotactic ion-exchange reaction. All three compounds establish antiferromagnetic order at $T_N = 53$ K, 61 K and 52 K, respectively for $M = \text{Mn, Co, Cr}$.

Together with $T_N = 78$ K for $M = \text{Fe (S = 2)}$, this result indicates that the $T_N$ is not simply scaled by the magnitude of spin. In particular, the presence of strong spin-orbit interactions is suggested for (CoCl)LaNb$_2$O$_7$.

1. Introduction

Geometrically frustrated magnets have been received considerable interests over the last several decades. Among the models comprising of squares with some diagonal interactions are the $J_1$-$J_2$ model Li$_2$VO(Si, Ge)O$_4$ [1], the checkerboard model $A_2$Fe$_2$Fe$_2$O$_2$Q$_2$ ($A = \text{Sr and Ba; Q = S and Se}$) [2] and the Shastry-Sutherland SrCu$_2$(BO$_3$)$_2$ [3]. These materials show intriguing magnetic properties such as spin-disordered state and quantized magnetization plateaus to name only a few [3, 4].

Soft chemical methods offer promising routes to explore low-dimensional magnetic compounds, as thermodynamically metastable phases. Recently $S = 1/2$ layered copper oxyhalides (CuX)$_{A_{n-1}}B_nO_{3n+1}$ (where $X = \text{Cl, Br}$; $A = \text{La}^{3+}, \text{Ca}^{2+}, \text{Na}^+, ...$; $B = \text{Nb}^{4+}, \text{Ta}^{5+}, \text{Ti}^{4+}, ...$; $n = 2, 3$) were obtained by topotactic ion-exchange reactions, where the magnetic CuCl$_2$O$_2$ octahedral layers are separated by magnetically inert perovskite blocks [5-7]. Various exotic quantum magnetic phenomena have emerged from these quasi-two-dimensional magnets. The properties range from spin-singlet ground states based on quantum dimers in (CuCl)LaNb$_2$O$_7$ [8-12], stripe magnetic order with reduced magnetic moments in (CuBr)LaNb$_2$O$_7$ and (CuCl)LaTa$_2$O$_7$ [13, 14], quantum phase separation in the solid solution system (CuCl)La(Nb, Ta)$_2$O$_7$ [14, 15], to successive phase transitions and 1/3 magnetization plateaus in (CuBr)A$_2$B$_3$O$_{10}$ [16]. These interesting magnetic behaviors were interpreted...
as due to the presence of competing antiferromagnetic and ferromagnetic interactions within the CuX layer.

This ion-exchange strategy was expanded by replacing the copper by other transition-metal elements, yielding (MCl)LaNb2O7 (S = 3/2 for V2+ and Co2+, S = 2 for Cr2+ and Fe2+, and S = 5/2 for Mn2+) [17-19], (FeCl)Ca2Ta3O10 (S = 2) [7] and (NiCl)Sr2Ta3O10 (S = 1) [20]. However, only a little is still known about the spin number dependence of the magnetic properties of (MX)A+n−1BnO3n+1. In (NiCl)Sr2Ta3O10 magnetic long-range-order is significantly suppressed down to 50 K despite a large Weiss temperature $\theta$ of $-125$ K. Additionally, $\mu$SR measurements of (NiCl)Sr2Ta3O10 revealed the coexistence of the magnetically ordered and disordered states for 20 K < $T$ < 50 K [20]. The antiferromagnetic transition temperatures $T_N$ of (FeCl)LaNb2O7 and (MnCl)LaNb2O7 are suggested to be 78 K and 54 K [18, 19]. In this paper we report on the magnetic properties of (MCl)LaNb2O7 (M = Mn, Co, Cr).

2. Experimental

2.1. Synthesis

The synthesis of (MCl)LaNb2O7 (M = Mn, Co, Cr) is expressed as the following two-step ion-exchange reactions [17]:

$$RbLaNb2O7 + LiNO3 \rightarrow LiLaNb2O7 + RbNO3$$

$$LiLaNb2O7 + MCl2 \rightarrow (MCl)LaNb2O7 + LiCl$$

First, RbLaNb2O7 was prepared via a conventional high-temperature route, using stoichiometric amount of La2O3 (99.99% purity) and Nb2O5 (99.99%) and 25% molar excess of Rb2CO3 (99.9%). Second, LiLaNb2O7 was obtained from LiNO3 and RbLaNb2O7 in 10:1 molar ratio through the ion-exchange reaction (1) at 300 °C for 24 hours in air. The product was washed with warm water and then dried at 120 °C overnight. Third, LiLaNb2O7 was mixed with two-fold molar excess of ultradry MCl2 (M = Mn, Co, Cr; 99.9%) and pressed into pellets in an Ar-filled glove box (<1ppm O2/H2O). The ion-exchange reaction (2) was carried out in sealed, evacuated (<10-3 Torr) Pyrex tubes at 390 ~ 400 °C for 7 days, followed by washing with distilled water for $M$ = Mn, Co and with ethanol for $M$ = Cr to eliminate the excess MCl2 (M = Mn, Co, Cr) and LiCl, and dried at 120 °C overnight. The schematic structure is represented in figure 1.

2.2. Characterization

In-house X-ray diffraction study at room temperature confirmed the tetragonal symmetry with room-temperature cell constants: $(a, c) = (3.899 \text{ Å}, 12.04 \text{ Å}), (3.908 \text{ Å}, 11.63 \text{ Å}),$ and $(3.899 \text{ Å}, 11.97 \text{ Å})$ for $M$ = Mn, Co and Cr, respectively, in good agreement with those previously reported [17]. Magnetic susceptibilities were studied using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS) for a temperature range $T = 2$ – 300 K in a magnetic field $H = 0.1$ T. Specific heat measurements were performed by the thermal relaxation method in a $T$ range between 4 K and 100 K in the absence of magnetic field using Physical Property Measurement System (PPMS, Quantum Design) at Institute for Solid State Physics, University of Tokyo. Hand-pressed pellets were attached to an alumina platform with a small amount of Apeizon N grease.

3. Results and Discussions

Figure 2(a) shows the temperature dependence of magnetic susceptibility $\chi_{raw}$ for (MnCl)LaNb2O7. A Curie-tail is seen below 30 K, which is most likely due to impurities and/or defects of Mn2+ ions in (MnCl)LaNb2O7, as was also present in the previous report [19]. Using the Curie equation $\chi_{imp} = C_{imp}/T$, we fitted the raw data $\chi_{raw}$ below 30 K and the best fit gave a small $C_{imp} = 0.12$ emu K$^{-1}$ mol$^{-1}$, corresponding to about 2.7% of noninteracting $S = 5/2$ Mn2+ ions. After subtracting this upturn, one obtains the intrinsic susceptibility $\chi_{spin}$, where a broad maximum characteristic of low-dimensional magnet was centered at $T_{\chi_{max}} = 65$ K. Above 160 K, the inverse susceptibility $\chi_{spin}^{-1}$ (figure 2(b)) obey
a Curie-Weiss law, and the fitting gave the Curie constant $C = 4.38$ emu K$^{-1}$ mol$^{-1}$ together with $\theta = -131$ K with a slight temperature-independent impurity term of $\chi_0 = -4.0 \times 10^{-4}$ emu K$^{-1}$ mol$^{-1}$. The value of $T^\alpha_{\text{max}}$ is comparable with that previously reported (63 K) [19]. Moreover, the value of $C$ obtained in this study is in excellent agreement with the theoretical value for 1 mol of $S = 5/2$ Mn$^{2+}$ ions (4.375 emu K$^{-1}$ mol$^{-1}$), while the one obtained in the previous study was a little larger (4.467 emu K$^{-1}$ mol$^{-1}$) [19]. However, the value of $\theta$ obtained in this study is somewhat smaller than the one obtained in the previous study ($-145.7$ K) [19]. This is probably because the value of $C$ largely depends on the fitting range and the value of $\chi_0$. It is also to be noted that $C$ and $\theta$ are influenced by the way in which the Curie-tail at low temperature is subtracted from the raw data. The specific heat $C_p$ at zero field is shown in figure 3. A tiny anomaly at around 53 K being located 15 K below $T^\alpha_{\text{max}}$ strongly indicates the occurrence of the antiferromagnetic phase transition. Indeed, this temperature is in excellent agreement with $T_N = 54$ K estimated from $d\chi/dT$ [19]. The anomaly in the specific heat is not so obvious probably because of the use of polycrystalline sample. We could not estimate magnetic specific heat $C_m$ by subtracting lattice contribution $\beta T^3$ because this approximation should be valid up to around 30 K. The large difference between $\theta$ and $T_N$ manifests two-dimensionality of the magnetic system and also certain frustrated interactions.

The specific heat $C_p$ of $M = \text{Co}$ and Cr at zero field (figures 4 and 5) has a slight anomaly at 61 K and 52 K, respectively. As shown in figures 6(a) and 7(a), each magnetic susceptibility has, as in the case of $M = \text{Mn}$, a broad maximum at a slightly higher temperature of 67 K for $M = \text{Co}$ and 55 K for $M = \text{Cr}$, indicating that the anomaly in the specific heat is due to the magnetic phase transition. As is the case with $M = \text{Mn}$, we could not estimate magnetic specific heat $C_m$ by subtracting lattice contribution $\beta T^3$. In the lower temperature region below this transition, the susceptibility grows considerably with decreasing temperature. However, in contrast to the case of $M = \text{Mn}$ as
demonstrated above, both materials exhibit another anomaly in a different manner: in (CoCl)LaNb2O7, a hysteresis behavior is observed below about 6 K, while in (CrCl)LaNb2O7 a cusp without hysteresis is observed at 3 K (see the insets of figures 6(a) and 7(a)). The low-temperature anomaly featured by the hysteresis between zero-field and field cooling processes is also seen in (FeCl)LaNb2O7 and was attributed to the second magnetic transition [18]. We would consider, however, that these low-temperature anomalies likely come from the defect of the magnetic ions in the crystal (and thus being extrinsic to the pure system) because the magnitude of the Curie-like tail has sample dependence. The estimation of the defect amount is not straightforward because of the presence of low-temperature anomalies. However, since the Co-, Cr- and Mn-samples have a similar size of the Curie-like tail, the amount of the magnetic defect should be roughly the same.

Figure 3. Temperature dependence of $C_p$ for $M = $ Mn showing magnetic order at 53 K.

Figure 4. Temperature dependence of $C_p$ for $M = $ Co showing magnetic order at 61 K.

Figure 5. Temperature dependence of $C_p$ for $M = $ Cr showing magnetic order at 52 K.

Figure 6. (a) Temperature dependence of the susceptibility for $M = $ Co. Inset: enlarged plot of the susceptibility below 35 K. (b) Inverse susceptibility. The dotted line represents the Curie-Weiss fit.

Figure 7. (a) Temperature dependence of the susceptibility for $M = $ Cr. Inset: enlarged plot of the susceptibility below 30 K. (b) Inverse susceptibility. The dotted line represents the Curie-Weiss fit.
Given the lower temperature anomaly in these two materials, subtracting the Curie-like tail from the raw data would not be appropriate. Accordingly, the raw data were fitted to the Curie-Weiss formula in the temperature range above 90 K (Co) and 175 K (Cr). We obtained, for \(M = \text{Cr}, C = 3.24 \text{ emu K}^{-1} \text{ mol}^{-1}\), which agrees reasonably with the theoretical value for 1 mol of \(S = 2 \text{ Cr}^{2+}\) ions (3.0 \text{ emu K}^{-1} \text{ mol}^{-1}), indicating the completion of the ion-exchange reaction. Interestingly, the obtained value of \(C\) for \(M = \text{Co}\) is 2.775 \text{ emu K}^{-1} \text{ mol}^{-1}, which is significantly larger than the theoretical value for 1 mol of \(S = 3/2 \text{ Co}^{2+}\) ions (1.875 \text{ emu K}^{-1} \text{ mol}^{-1}), where \(g = 2\) is assumed. Thus orbital angular momentum should sizably contribute to the \(g\)-factor, resulting in a strong anisotropy in the Co moment due to spin-orbit interactions. Such a strong anisotropy has been observed in the \(\text{Co}^{2+}\)-containing compounds [21, 22]. The values of \(\theta\) for \(M = \text{Co and Cr}\) were, respectively, \(-77.95 \text{ K, -61 K}\), the magnitude of which is only slightly higher than \(T_N (61 \text{ K and 52 K})\). Here we would like to stress that the proximity between \(|\theta|\) and \(T_N\) does not mean that the frustration effect is negligible because when competing antiferromagnetic and ferromagnetic interactions are present (which is the case of the related systems), \(|\theta|/T_N\) cannot be a measure of frustration. Notably, recent reinvestigations of the structure of \((\text{CuCl})\La\text{Nb}_2\text{O}_7\) using a single crystal X-ray diffraction and the state-of-the-art structural analysis revealed the superstructure in the space group \(Pbam\), which accounts for the spin-singlet formation [12]. We suppose that there will be also a possibility that \(M\) and Cl atoms in the present compounds displace from the vertices of square lattice in an ordered manner, which might result in complex relationship between \(|\theta|\) and \(T_N\).

4. Conclusion
The two-dimensional antiferromagnets (\(M\text{Cl})\La\text{Nb}_2\text{O}_7\) \((M = \text{Mn} (S = 5/2), \text{Co} (S = 3/2) \text{ and Cr} (S = 2))\) obtained via a topotactic ion-exchange reaction are found to exhibit antiferromagnetic long range ordering at 53 K, 61 K and 52 K, respectively, indicating that the \(T_N\) is not simply scaled by the spin quantum number but affected by competing magnetic interactions and a possible formation of superstructure. A strong anisotropy was indicated in \((\text{CoCl})\La\text{Nb}_2\text{O}_7\), where the orbital degrees of freedom may affect the magnetic property. Further magnetic study is needed such as powder neutron diffraction.

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