Crystal and Magnetic Structures of the Pillared Perovskites, $La_5Re_2TiMO_{16}$ (M = Mn, Fe, Co, Ni, Mg)

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Recently, an attempt was made to synthesize and study a new family of pillared perovskites. The general formula would be $La_5Re_2TiMO_{16}$, where M is a 2^+ transition metal ion (such as Mn, Fe, Co, Ni or Mg). The target structure consists of perovskite-like layers of corner-sharing $Ti^{4+}M^{2+}O_6$ octahedra, "pillared" by dimers of edge-shared $Re^{5.5+}O_6$ octahedra. Thus the dimer "pillars" would contain one unpaired electron, making them paramagnetic. The dimers connect to the M^{2+} sites in the perovskite layers only. By varying the M^{2+} ion from Mn ($S = 5/2$) to Mg ($S = 0$), the effect of the spin quantum number on the resulting magnetism of these low-dimensional compounds could be studied.

SQUID magnetometry measurements have revealed some similarities between the compounds. They all have broad features, indicative of short-range order. There is a feature that could signify long-range order at approximately 160 K, 35 K and 14 K in the Mn, Co and Ni members respectively, which is similar to the $La_5Re_3MO_{16}$ (Mn, Co, Ni) analogues previously studied [1,2,3]. The Mg member did not show any features indicative of magnetic ordering down to 2 K.

Powder neutron diffraction measurements on the C2 diffractometer at the Canadian Neutron Beam Centre in Chalk River were collected to determine the crystal structure of these compounds. Unfortunately, the samples were not very crystalline, and did not diffract well. However, these measurements did show that the samples contained significant amounts of other secondary phases that could not be identified and were difficult to detect using X-ray diffraction. Collecting low temperature data (at 3.8 K) on the samples, however, revealed some surprising results. Only the Mn member showed any evidence of new reflections. There is no evidence of any enhanced or new reflections in any other sample.

The two Mn patterns, collected at room temperature and 3.8 K, along with a difference plot are pictured in Figure 1. Some artifacts appear in the difference plot due to peak broadening at low temperature. The new peaks can be indexed to a magnetic unit cell with ordering vector, $\mathbf{k} = (0,0,1/2)$. This is similar to the structure found for $La_5Re_3MnO_{16}$, which consists of ferromagnetic intra-layer coupling between the Re^{5+} ($S = 1$) and Mn^{2+} ($S = 5/2$) moments, and antiferromagnetic coupling of the layers through the diamagnetic pillar [1]. It was expected that through substitution of Re^{5+} within the layer by Ti^{4+}, an extra unpaired electron would reside on the Re_2O_{10} pillar and cause significant changes in the resulting magnetism (i.e. if antiferromagnetic coupling along the *c*-axis is preferred, then to satisfy both layers and the dimer, the layers would be coupled ferromagnetically with respect to each other). If the substitution were successful, this does not appear to be the case. The three new magnetic reflections are consistent with a magnetic unit cell involving ferromagnetic Mn^{2+} moments within the layers, aligned parallel to the *c*-axis, and antiferromagnetic interlayer coupling. The magnitude and orientation of the dimer moment are unknown and may be too weak to observe. Ferromagnetic intra-layer coupling between the Mn^{2+} ions ($S = 5/2$) is unexpected, since the Goodenough-Kanamori rules for magnetic superexchange [4,5] predict antiferromagnetic interactions. A second interpretation is that Ti substitution did not occur and that the magnetic properties studied are actually those of $La_5Re_3MnO_{16}$. As a result, further analysis to determine whether Ti substitution did indeed occur is currently underway. In addition, the synthesis of samples with improved crystallinity and phase purity is also being attempted.

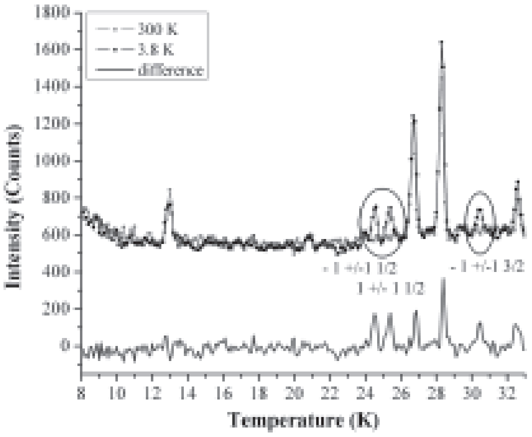

Fig. 1 Powder neutron diffraction patterns of $La_5Re_2TiMnO_{16}$ taken at room temperature (gray) and 3.8 K (black). The difference map appears below, and the magnetic reflections have been circled and indexed.

References

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