Crystal Structure and Long Range Magnetic Order in the Novel Rock Salt Structure Type Ruthenate: $Li_3Mg_2RuO_6$

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Antiferromagnetic (AFM) compounds, which comprise triangular cationic sub-lattices, have the potential to exhibit geometric magnetic frustration [1]. Within the family of ordered sodium chloride type transition metal oxides, a number of compositions and structures present triangle-based topologies and therefore are they very attractive for they study of geometric magnetic frustration.

4d and *5d* ions have more extended *d* orbitals relative to the *3d* compounds and they also exhibit a broader range of oxidation states, especially ≥ +5. The large difference in formal charge between the magnetic cations on one hand and the nonmagnetic alkali and alkali earth cations on the other hand is the driving force towards crystallographic cation ordering in such systems. This allows precise design of the magnetic exchange pathways and interactions.

The title compound, which is iso-structural with $Li_3Mg_2NbO_6$ [2], was synthesized via solid state reaction and the phase purity was examined by the XRD method, employing a Guinier-Hägg camera with Cu Kα_1 radiation and Si as an internal standard. The magnetic susceptibility as well as the heat capacity data reveals that there is a long range AFM order below 17 K.

Variable temperature powder neutron diffraction measurements were performed on the C2 diffractometer at the Canadian Neutron Beam Centre at Chalk River, Ontario. The room temperature data were collected using two different wavelengths of 1.3307 Å and 2.3724 Å. Low temperature data collections (4, 6, 8, 10, 12, 14, 16, 17, 18 K) were carried out for investigation of the ordering temperature and the magnetic structure. For this purpose the long wavelength, 2.37197 Å in the range 4° ≤ 2θ ≤ 84° with 0.1° intervals was utilized.

Rietveld refinements, using the GSAS program [3,4], on the room temperature neutron diffraction data sets were performed to verify the crystal structure. The structural model was initially taken from that proposed for $Li_3Mg_2NbO_6$. A pseudo-Voigt peak shape profile was chosen and the parameters were refined to obtain the best fit to the experimental data. The overall residual factors of Rp = 0.0306, wRp = 0.0384 and χ^2 = 3.2 are rather low, which indicate a good quality refinement.

$Li_3Mg_2RuO_6$ crystallizes in the orthorhombic *Fddd* space group in an ordered rock salt structure type. The dimensions are: *a* = 5.8759 (2) Å, *b* = 8.4206 (1) Å and *c* = 17.6455 (5) Å. The structure is composed of edge-shared octahedra with eight formula units per unit cell (Figure 1).

There are four independent cationic positions in the unit cell. The oxidation state and size of the Ru^{5+} cations are significantly different from the other cations (Li+ = 0.76 Å, Mg^{2+} = 0.72 Å and Ru^{5+} = 0.565 Å) [5] and therefore they tend to reside in separate crystallographic positions. However, Li and Mg occupy the other three cationic sites with different fractions, M1 being magnesium rich while M2 and M3 are lithium rich sites. When the thermal displacement factors of M2 and M3 sites were refined together, divergence occurred. To stabilize the refinement, their U_{iso} values were constrained to a reasonable value, 0.015. This is due to the very small total scattering length in these sites. In fact, the scattering lengths of Li and Mg have opposite signs, b_{Li} = -1.900 and b_{Mg} = 5.375, and the Li:Mg occupancy ratio being close to 4:1 results in a small total negative scattering length, approximately -0.45. The crystallographic details and the atomic positions are summarized in Tables 1 and 2, respectively.

Low temperature neutron diffraction data were collected to probe the magnetic structure as shown in Figure 2. There are at least five additional peaks in the low temperature data that correspond to the magnetic structure. Subtracting the 18 K data from those of the 4 K their positions are identified as shown in Figure 2. They clearly disappear by 18 K, Figure 3, consistent with both the susceptibility and specific heat data. The two major peaks were indexed using a LeBail approach which required a magnetic cell of dimensions 2a × 2b × 3c relative to the chemical cell, giving indices (½ 1) and (½ ½ 2). Thus, the magnetic cell is 12 × the volume of the chemical cell and involves 8 × 12 = 96 Ru spins. Attempts to solve the magnetic structure are on-going but this is clearly a difficult and highly underdetermined problem. While the details of the magnetic structure are not known in detail, the large dimensions of the magnetic unit cell are consistent with a high level of frustration in three dimensions. As well, the symmetric shape of the magnetic diffuse scattering at 18 K, seen clearly in Figure 3, is not consistent with short range 2D magnetic correlations for which the highly asymmetric "Warren" line shape is expected.
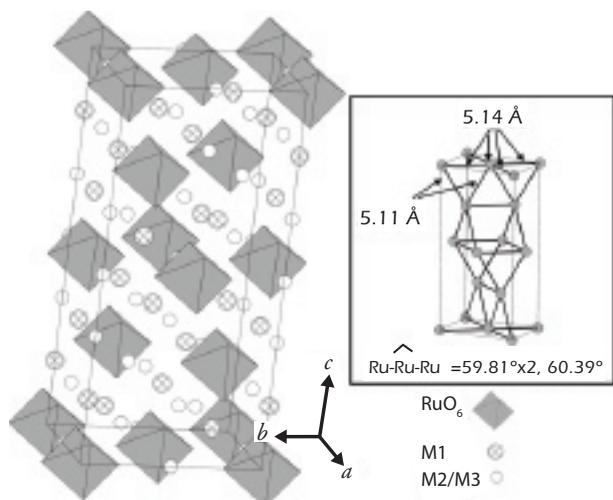
Fig. 1 The crystal structure of Li_3MgRuO_6. The grey octahedra represent $[RuO_6]^{7-}$ the crossed circles are magnesium rich (M1) positions and small empty circles are Li rich (M2 and M3) positions. The Ru—Ru distances and Ru—Ru—Ru angles are presented in the inset.

Inset labels: 5.14 Å, 5.11 Å, Ru-Ru-Ru =59.81°x2, 60.39°
RuO_6, M1, M2/M3
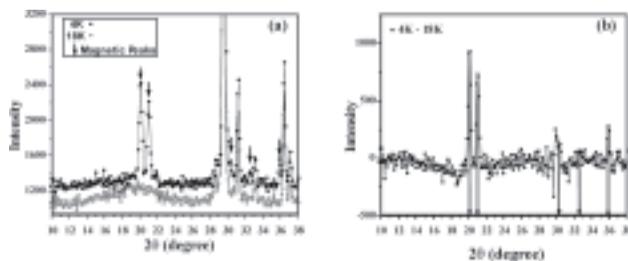
Fig. 3 (a) Comparison between diffraction patterns at 4 K and 18 K. (b) The magnetic peaks obtained by subtracting the 18 K data from 4 K data.

	a (Å)	b (Å)	c (Å)	Rp	wRp	z

Table 1. Some selected structural parameters of Li3Mg2RuO6.

	x	y	z	Occ. Li/ Mg	U_{iso} (Å^2)
Ru	0.125	0.125	0.125		0.007(1)
M1	0.125	0.125	0.2939(4)	0.33(1)/ 0.67	0.005(2)
M2	0.125	0.625	0.299(4)	0.78(1)/ 0.22	0.015
M3	0.125	0.625	0.125	0.82(1)/ 0.18	0.015
O1	0.125	0.3576(4)	0.125		0.007(1)
O2	0.1114(3)	0.3747(3)	0.2961(2)		0.0069(6)

Table 2. Atomic coordinates, occupancy factors and equivalent isotropic displacement parameters for $Li_{3.06(1)}Mg_{1.94}RuO_6$.
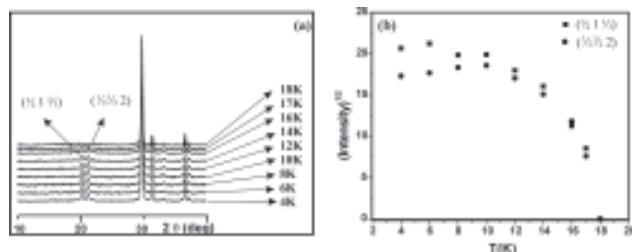
Fig. 2 (a) Low temperature powder neutron diffraction data. (b) Integrated area for magnetic peaks as a function of the temperature.

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