Magnetic Properties of Geometrically Frustrated Double Perovskites, $\text{Ba}_2\text{YRuO}_6$, $\text{Ba}_2\text{YMoO}_6$ and $\text{La}_2\text{LiReO}_6$

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We have carried out neutron diffraction measurements on $\text{La}_2\text{LiReO}_6$, $\text{Ba}_2\text{YMoO}_6$, and $\text{Ba}_2\text{YRuO}_6$ using the C2 powder diffractometer at the Canadian Neutron Beam Centre. We expected that no magnetic peaks would appear in the first two compounds, since there were no signatures of long range ordering according to magnetic susceptibility measurements. On the other hand, $\text{Ba}_2\text{YRuO}_6$ was expected to show some feature of antiferromagnetic long range ordering since the heat capacity data shows a very sharp $\lambda$-type peak around 37 K, which is consistent with magnetic susceptibility results.

$\text{Ba}_2\text{YRuO}_6$ crystallizes in the cubic space group Fm-3m [1]. The refinement for the crystal structure with the data collected using longer neutron wavelength and FULLPROF program [2] was done and the cell constant is determined to be $8.332(1)$ Å at room temperature and $8.3194(7)$ Å at 2.7 K. R-factors in the refinements for each temperature are: $R_p = 4.90$, $R_{wp} = 6.45$ for room temperature, and $R_p = 4.54$, $R_{wp} = 6.88$, magnetic R-factor $= 20.5$ for 2.7 K. These factors are reasonably low, meaning these are good refinements.

The magnetic susceptibility results collected at McMaster University using SQUID magnetometer (Quantum Design) show two shoulder-like peaks at 47 K and 37 K for this compound, which may be the transition temperatures, and the Curie-Weiss constant is calculated to be $\theta = -522$ K. However the heat capacity measurement shows a $\lambda$-type peak around 37 K only. This could be explained as antiferromagnetic short range ordering occurring first around 47 K, following by the formation of complete antiferromagnetic long range ordering at 37 K.

The evolution of magnetic peaks in the diffraction patterns of $\text{Ba}_2\text{YRuO}_6$ is shown in Figure 1. As one can see, two magnetic peaks appear around $2\Theta = 16^\circ$ and $23^\circ$ below about 35 K. The magnetic structure was also refined and the two magnetic peaks at $2\Theta = 16^\circ$ and $23^\circ$ could be indexed as $k = (0, 0, 1)$, and $(1, 1, 0)$, respectively. According to this result, the actual transition temperature of $\text{Ba}_2\text{YRuO}_6$ is determined to be 37 K. The magnetic structure of this compound was confirmed to be face-centered cubic and Type I structure, which was reported by Battle et al. [1].

As well as $\text{Ba}_2\text{YRuO}_6$, $\text{Ba}_2\text{YMoO}_6$ also crystallizes into the same cubic symmetry (space group Fm-3m) [3]. Since the magnetic susceptibility result shows the lack of long range ordering in the temperature region from 300 K to 2 K and Curie-Weiss constant was determined to be $\theta = -394$ K, there should not be any new magnetic peaks appearing. This result was confirmed based on the comparison of diffraction patterns collected using longer neutron wavelength (2.37Å) at 2.7 K and room temperatures. The absence of antiferromagnetic long range ordering also agreed with the result of heat capacity collected at McMaster University. The crystal structures at 298 K and 2.7 K were refined and determined to have a cubic structure with cell constants, $8.3904(5)$ Å and $8.3784(5)$ Å, respectively. R factors are: $R_p = 4.87$, $R_{wp} = 6.36$ and $\chi^2 = 2.87$. Since the Mo$^{5+}$ ion has $d^3$ electronic structure, it could result in Jahn-Teller distortion and transform to a lower symmetry. However, the refinement with cubic symmetry shows good agreement and it is reasonable to say that $\text{Ba}_2\text{YMoO}_6$ remains cubic structure at 2.7 K.

We also have performed neutron diffraction measurements on the compound, $\text{La}_2\text{LiReO}_6$. The structure is monoclinic with space group P2$_1$/n. The magnetic susceptibility result shows a ZFC/FC divergence around 50 K, a broad maximum in the ZFC curve at 33 K and the Weiss temperature is $\theta = -163$ K. Therefore, antiferromagnetic interaction exists. However, the heat capacity data did not show any peaks or shoulders. Thus, there are not any features indicating the presence of antiferromagnetic long or short range ordering. The comparison of two diffraction patterns collected at room and base temperatures supports the absence of antiferromagnetic long range ordering. Crystal structure refinement with the data collected at 298 K determined the structure parameters to be a = 5.5819(6) Å, b = 5.6743(6) Å, c = 7.8840(8) Å, $\beta = 90.243^\circ$ and total cell volume is 249.7117 Å$^3$. R factors are: $R_p = 3.39$, $R_{wp} = 4.47$ and $\chi^2 = 3.01$. The structure refinement was also done with the data collected at 2.7 K and determined the cell parameters to be a = 5.5801(6) Å, b = 5.6859(6) Å, c = 7.8421(9) Å, $\beta = 90.479^\circ$ and total cell volume is 248.8079 Å$^3$. R factors are: $R_p = 4.17$, $R_{wp} = 5.72$ and $\chi^2 = 6.10$.

In summary, the neutron diffraction experiment confirmed the presence of antiferromagnetic long range ordering and revealed the transition temperature in $\text{Ba}_2\text{YRuO}_6$ and the absence of long range ordering with $\text{Ba}_2\text{YMoO}_6$ and $\text{La}_2\text{LiReO}_6$ is confirmed, as expected.
Fig. 1  Evolution of magnetic peaks of Ba$_2$YRuO$_6$.

Fig. 2  Crystal structure refinement of Ba$_2$YMoO$_6$ at 2.7 K (upper) and the intensity difference of the diffraction patterns at 2.7 K and 298 K (lower). There is no difference between two patterns.

Fig. 3  Crystal structure refinement for La$_2$LiReO$_6$ (298 K)

References