Synthesis and Magnetic Characterization of Double Perovskites

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Abstract

Geometric magnetic frustration[1] occurs when magnetic ions are arranged spatially in such a way that inhibits the development of magnetic order. Frustrated magnetic materials are of interest to the research community due to their rich phase diagrams with a wide variety of magnetic ground state, resulting in exotic physics and high sensitivity to parameters such as doping and structural distortion.

We have successfully synthesized and performed magnetic susceptibility measurements[2] (using a SQUID magnetometer) on the following compounds: Ba_2YbMoO_6, Ba_2YWO_6, Ba_2LuWO_6, Ba_2ScMoO_6, and Sr_2ScMoO_6. Susceptibility measurements were also conducted on the non-magnetic niobate equivalents.

Magnetic susceptibility measurements provide a useful probe into how much frustration compounds exhibit. Double perovskites, of the form $A_2BB'O_6$, tend to exhibit frustration in the presence of antiferromagnetic correlations, and their frustration index can be determined from fitting the susceptibility data. In our measurements, the compounds Ba_2YbMoO_6, Ba_2YWO_6, Ba_2LuWO_6, Ba_2ScMoO_6, and Sr_2ScMoO_6, exhibited Curie-Weiss behavior with no evidence of magnetic transition down to 2K.

Measurements were conducted under zero-field-cooled and field-cooled conditions, and from fits to the data, the nature of magnetic interactions may be determined. All of the compounds had large and negative Curie-Weiss temperatures, indicating antiferromagnetic correlations. Our data also indicates high frustration indices, given their high Curie-Weiss temperatures, and that no irreversibility or other evidence of magnetic ordering was observed to 2 Kelvin.

Theory

Fig. 1: Frustration of antiferromagnetically-correlated (AF) moments on a tetrahedron, favoring antiparallel nearest-neighbor alignment. No arrangement of the moments allows all interactions to be satisfied at once. This causes magnetic order to be suppressed to lower temperatures, or altogether, and leads to rich phase diagrams featuring exotic magnetic ground states, as moments attempt to relieve the frustration.

Magnetic susceptibility is a proportionality constant that provides the degree to which a material responds to an applied magnetic field. It is determined from the following relation:

$$\boldsymbol{B} = \mu_0(1+\chi)\boldsymbol{H}$$

where **B** is the resulting magnetic field, **H** is an applied magnetic field, μ_0 is the permeability of free space constant, and χ is the magnetic susceptibility. The temperature dependence of the susceptibility may be fit to the Curie-Weiss model:

$$\chi(T) = \frac{C}{T - \Theta_{cw}}$$

where C is the Curie constant, T is the temperature, and Θ_{cw} is the Curie-Weiss temperature. These parameters may be used to determine the strength and the nature of magnetic interactions present in the material. In particular, negative values of Θ_{cw} indicate antiferromagnetic correlations, in the presence of which geometric frustration occurs. The value of C can be used to determine the effective magnetic moment size μ_{eff}.

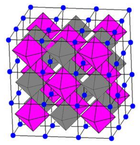


Fig. 2 (left): The ideal face-centered double perovskite structure $A_2BB'O_6$[3], as exemplified by Ba_2YMoO_6[4,5]. In this structure, the A cation (Ba) is shown in blue, the non-magnetic B cation (Y) is at the center of the gray YO_6 octahedra, and the magnetic B′ cation (Mo) is at the center of the magenta MoO_6 octahedra.

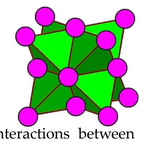


Fig. 3 (right) The magnetic ions in the above structure comprise a face-centered cubic lattice, or, equivalently, a network of edge-sharing tetrahedra, which exhibit frustration in the presence of AF correlations.

The Curie-Weiss temperature relates to the strength of interactions between moments at high temperatures. In general, magnetic order in a material is expected at a temperature approximately equal to the magnitude of the Curie-Weiss temperature. Typically, order arises when the energy of thermal fluctuations, of order k_BT become comparable to strength of correlations between moments. In frustrated systems, this is not the case, as correlations between moments are cancelled out, reducing the temperature at which order occurs by a factor known as the frustration index:

$$f = |\Theta_{CW}| / T_{order}$$

Ba_2ScMoO_6 Susceptibility

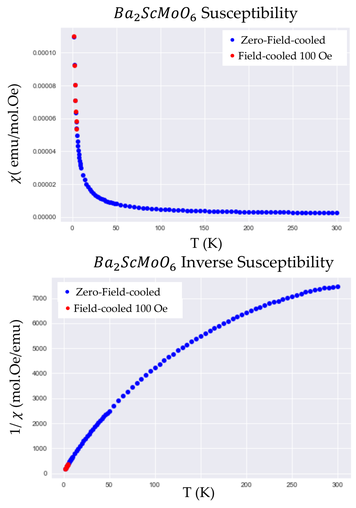


Fig. 4 (left): Susceptibility data for Ba_2ScMoO_6. Field-cooled data (red) and zero field cooled (blue). Field-cooled refers to cooling the sample in a magnetic field, and zero-field cooled means the sample was cooled with no field applied.

Fig. 5 (below left): Inverse susceptibility data for Ba_2ScMoO_6.

Fig. 6. (below right): linear fit to Curie-Weiss model at high temperature regime between 200K and 300K. Fit parameters given in table below.

Ba_2YbMoO_6 Susceptibility

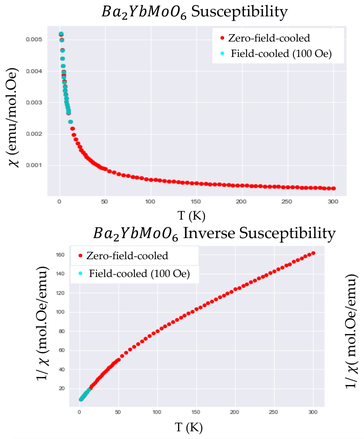


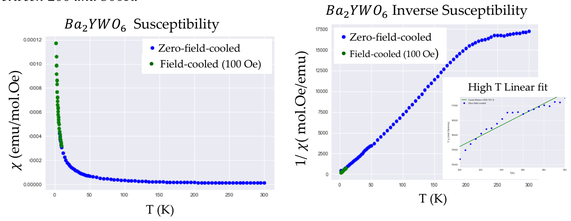
Fig. 7 (left): Susceptibility data for Ba_2YbMoO_6[6]. Field cooled data (blue) and zero field cooled (red), with H = 100 Oe.

Fig. 8 (below left): Plotting inverse susceptibility data for Ba_2YbMoO_6.

Fig. 9. (below) Curie-Weiss temperature determined from linear fit to high temperature regime from 180 to 300 K.

Ba_2YWO_6 Susceptibility

Fig. 10 (left): Susceptibility data for Ba_2YWO_6[7]. Zero field cooled (green) and field cooled (blue). Fig. 11 (right): Inverse susceptibility data for Ba_2YWO_6. Linear fit between 200 and 300K.



Sr_2ScMoO_6 Susceptibility

Fig 12. (left) Susceptibility data for Sr_2ScMoO_6[8] under zero field cooled (blue) and field cooled (red) conditions, with H = 100 Oe.

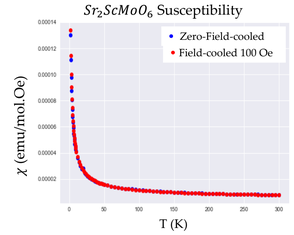
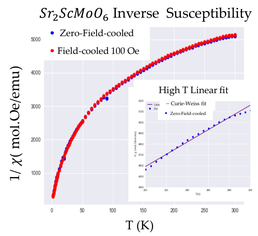


Fig 13. (right) Inverse susceptibility data with linear fit between 200 and 300 K.



Ba_2LuWO_6 Susceptibility

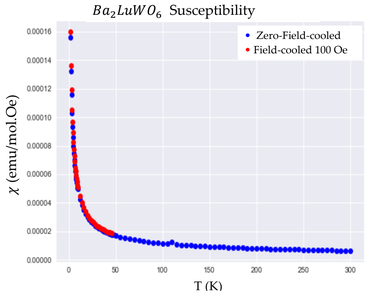
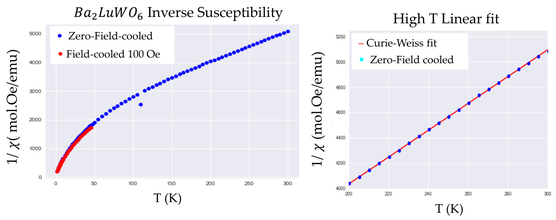


Fig. 14 (left): Susceptibility data for Ba_2LuWO_6. Zero-field cooled (blue) and field cooled data (red) collected in a field H = 100 Oe.

Fig. 15 (bottom left): Plotting inverse susceptibility data for Ba_2LuWO_6 under zero-field-cooled and field-cooled configurations with H = 100 Oe.

Fig. 16. (bottom right) Curie-Weiss fit to inverse susceptibility 200K and 300K.



Magnetic Moments and Curie-Weiss Temperatures

Below we include our results in a table with the calculated effective moment sizes and Curie-Weiss temperatures, both formulated from our high temperature fits. We calculate the effective magnetic moment, μ_{eff}, from the following relation:

$$\mu_{eff} = \sqrt{\frac{3k_BC}{N_A}}$$

Compound	C(emu·K/mol.Oe)	Effective Magnetic Moment (μ_B)	Θ_{cw} (K)
Ba_2YbMoO_6	2.58	4.54	-120
Ba_2LuWO_6	0.094	0.867	-180
Ba_2ScMoO_6	0.088	0.840	-386
Sr_2ScMoO_6	0.174	1.18	-606
Ba_2YWO_6	0.054	0.656	-655

Table 1 (top): Our measured values of Curie constant, effective magnetic moment, and Curie-Weiss temperature. For a nominal s=1/2 system, the spin-only moment size is 1.73 μ_B. Smaller values are expected in the presence of significant spin-orbit coupling, typical for 4d and 5d systems. The larger value for Ba_2YbMoO_6 is due to large paramagnetic Yb^{3+} moments. Moment sizes are expressed in units of Bohr magnetons, where

$$1\,\mu_B = 9.274 \times 10^{-24}\left(\frac{J}{T}\right)$$

Results & Conclusions

Magnetic frustration in double perovskites is an area that is currently attracting significant research. Double perovskites are of particular interest due to the potential for systematic investigation into frustration physics, made possible by the versatility of the perovskite structure.

We have successfully synthesized and conducted magnetic susceptibility measurements on the following compounds: Ba_2YbMoO_6, Ba_2YWO_6, Ba_2LuWO_6, Ba_2ScMoO_6, and Sr_2ScMoO_6. Structural analysis indicated that all the compounds, with the exception of Sr_2ScMoO_6, crystallize in the simple cubic perovskite structure, whereas Sr_2ScMoO_6 crystallizes in a tetragonal structure.

Our susceptibility results indicate large and negative Curie-Weiss temperatures for all of our specimens, with no irreversibility or other indications of magnetic ordering down to 2K. This is indicative of antiferromagnetic nearest neighbor correlations, and highly frustrated ground states.

The effective moments determined are consistent with expectations for nominal S=1/2 ($4d^1$ and $5d^1$) systems (with the S=1/2 expected $\mu_{eff} = 1.73\,\mu_B$), with reduction expected in the presence of moderate to significant spin orbit coupling. Similarly reduced values have been seen in other $4d^1/5d^1$ systems[4,6,7,8]. The exception is the Yb sample, in which large paramagnetic moments from the Yb^{3+} ions complicate the analysis.

In the Ba_2LuWO_6 data, there is an indication of a slight, nearly temperature independent difference between field-cooled and zero-field cooled data, indicating either a small ferromagnetic impurity phase or a potential instrumental issue.

We encountered some difficulty in fitting the high temperature behavior of Ba_2YWO_6, potentially due to instrumental error, or because we were unable to reach temperatures high enough for magnetic moments to be uncorrelated.

Further measurements including neutron scattering, heat capacity, and muon spin relaxation will provide the opportunity to get a fuller picture of magnetic behavior of these compounds, which is necessary for a fuller characterization of this "family" of double perovskites.

References

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Acknowledgments

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