# Long range magnetic order in spin-orbit coupled double perovskites $Ba_2YRuO_6$ and $Ba_2CaOsO_6$ probed with neutron scattering and muon spin relaxation


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## Abstract


Frustration manifests in the double perovskite lattice $A_2BB'O_6$ (Fig. 1), in which the antiferromagnetically correlated B' ions comprise a network of edge-sharing tetrahedra. Perovskites may be synthesized with most elements from the periodic table, enabling systematic studies of frustration as a function of structural distortion, lattice parameter, ionic size, moment size, and spin-orbit coupling (SOC), for example. The latter, in particular, has been explored by Chen et al. [1,2], who found that sizable SOC in $d^1$ and $d^2$ systems yields rich phase diagrams with diverse ground states.

Here we report inelastic neutron scattering and muon spin relaxation (μSR) experiments on the undistorted double perovskites $Ba_2YRuO_6$ [3] and $Ba_2CaOsO_6$ [5], finding evidence for long-range order in both. $Ba_2YRuO_6$ ($4d^3$ $Ru^{5+}$), orders antiferromagnetically with $T_N$ = 47K (although $\Theta_{CW} \approx -400$-500K, so $f \approx 10$) and exhibits a 5 meV gap below 36K; such a gap is unexpected for an $d^3$ orbital singlet and suggestive of exotic physics induced by SOC. $Ba_2CaOsO_6$ has been found via susceptibility, heat capacity and μSR measurements to exhibit long-range order below 50K ($\Theta_{CW}$ = -150K, $f$ = 3), consistent with theoretical expectations, although the precise long-range nature of the ground state has not yet been determined.

Both compounds are isostructural to $Ba_2YReO_6$ [7] and $Ba_2YMoO_6$ [8]. The latter ($4d^1$ $Mo^{5+}$) system possesses a singlet low-temperature state with a 28 meV gap. While $Ba_2YReO_6$ is isoelectronic to $Ba_2CaOsO_6$ ($Os^{6+}$ vs. $Re^{5+}$, both $5d^2$ and periodic table neighbors with similar $\lambda_{SOC} \propto Z^4$), the rhenate exhibits a disordered spin-frozen ground state below 50K, in contrast to theoretical predictions, despite a lack of evidence for structural disorder.


## Introduction

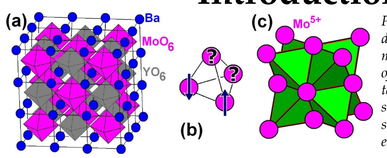



*Fig. (1) (a) The rock-salt-ordered double perovskite $A_2BB'O_6$, with magnetic B' ions. (b) Frustration of AF-correlated moments on a tetrahedron. (c) Magnetic sublattice of the double perovskite structure, comprising a network of edge-sharing tetrahedra.*

Polycrystalline specimens of $Ba_2YRuO_6$, $Ba_2YReO_6$ and $Ba_2CaOsO_6$ were prepared by solid state methods, and characterized using x-ray diffraction and magnetic susceptibility. B-site disorder was assessed using magic-angle spinning (MAS) NMR, and generally found to be small (<3%).

Geometric frustration is highly sensitive to subtle structural distortions, and the perovskite structure is capable of accommodating most elements of the periodic table with or without a variety of structural distortions. All three samples were indexed to the ideal cubic double perovskite structure at room temperature and low temperature, with no evidence for tetragonal or monoclinic distortions down to 2-3K. The lattice parameters at room temperature were 8.33559(9) Å (Ru), 8.3627(2) Å (Re), and 8.3619(6) Å (Os).

Recent theoretical work [1,2] has indicated the significance of spin-orbit coupling (SOC) in frustrated systems. SOC splits the degeneracy of the $t_{2g}$ manifold, potentially resulting in ground states distinct from the orbitally quenched L-S coupling picture for $d^1$ ($j_{eff} = 3/2$ vs. $s = 1/2$), $d^2$ ($j_{eff} = 2$ vs. $s = 1$) and $d^3$ ($j_{eff} = 3/2$ in a partially filled quartet vs. a $s = 3/2$ orbital singlet) configurations.

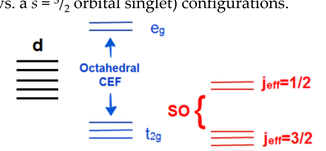



*Fig. (2) Splitting of d orbitals by an octahedral crystal electric field (blue), and by spin-orbit coupling (red). SOC splits the $t_{2g}$ manifold into a $j_{eff}$=3/2 quadruplet and a jeff=1/2 doublet, giving rise to distinct electronic ground states as compared to the CEF-only case.*

Chen et al. have modeled $d^1$ and $d^2$ double perovskites at the mean field theory level, predicting rich phase diagrams exhibiting ground states including commensurate ferromagnetism and antiferromagnetism, two- and four-sublattice states, a quadrupolar ordered state, and a spin-nematic state.

## $Ba_2YRuO_6$: neutron scattering [3]

$Ba_2YRuO_6$, based on the $4d^3$ $Ru^{5+}$ ion, was previously found [7] to exhibit commensurate AF order below $T_N$ = 36K, with purported short-range order up to T* = 47K. The Weiss temperature is a large and negative −522K, implying $f$ ~ 11-15.

Neutron scattering measurements were carried out using the *SEQUOIA* time-of-flight spectrometer at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory, using $E_i$ = 11 meV and 120 meV, in a closed cycle refrigerator between 6K and 290K. The ~10g polycrystalline specimen was contained in a 5 x 5 cm BN-masked planar aluminum can with He exchange gas. Measurements of an identical empty can were used for background subtraction, and data were normalized to a white-beam vanadium run.

Our measurements find long-range AF order up to 47K, with elastic and inelastic scattering extending from the [100] and [110] magnetic Bragg peaks, consistent with Type I AF fcc order. In addition, we detect the development of a 5 meV gap below 36K. The magnetic bandwidth extends up to 14 meV.

*Fig. (3) (below) Magnetic susceptibility of $Ba_2YRuO_6$ demonstrating onset of irreversibility near 47K. (inset) Inverse susceptibility, demonstrating Curie-Weiss high-T behavior; $\mu_{eff}$ = 3.65 $\mu_B$ ($s = 3/2$ spin-only value 3.87 $\mu_B$).*

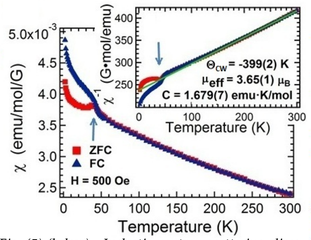



*Fig. (4) (below) (a) T=100K subtracted elastic neutron scattering data with $E_i$ = 11 meV, exhibiting [100] and [110] magnetic Bragg peaks up to T = 45K. (b) Inelastic data over [1,2] meV. Low-energy inelastic scattering is suppressed by the development of a 5 meV gap, seen in Figs. 5 and 6.*

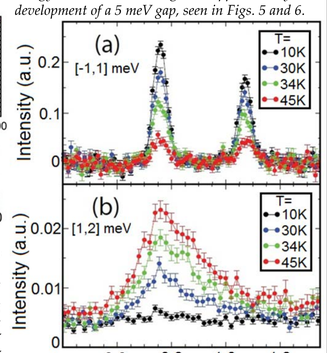



*Fig. (5) (below) Inelastic neutron scattering slices for $Ba_2YRuO_6$ over T ranging from 10K to 75K. Note inelastic scattering centered about |Q| = 0.7 Å$^{-1}$ ([100] magnetic Bragg peak); this scattering condenses down toward the elastic channel above $T_N$, and is associated with the formation of a 5 meV gap below 36K. The horizontal feature near 2 meV is spurious and is present in empty-can data.*

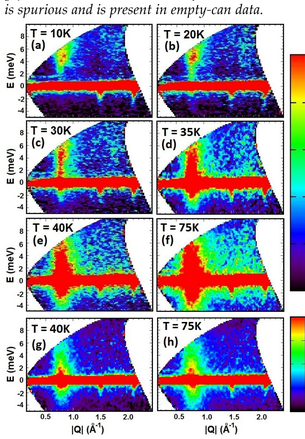
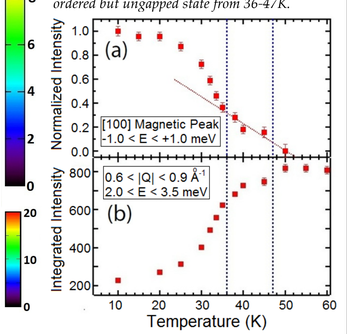



*Fig. (6) (below) |Q|-integrated elastic (a) and inelastic (b) scattering intensity, indicating the existence of two distinct temperature regimes: (i) the gapped state below 36K, and (ii) the ordered but ungapped state from 36-47K.*




Such a gap is unexpected for a $d^3$ ion, which is an orbital singlet in the L-S coupling picture. It is suggestive of anisotropy, perhaps due to an increased tendency toward J-J coupling. SOC is generally weak relative to typical orbital splitting energy scales in 3*d* systems, but progressively stronger in 4*d* and 5*d* systems.

This system appears to possess several energy scales – the ~400K Weiss temperature, the ~150K magnetic scattering bandwidth, and both the ordering temperature and magnetic scattering gap are about ~50K. Several systems [4] appear to exhibit scaling of the gap with respect to $T_N$ and/or the spin-orbit coupling constant λ, though the significance of this finding remains uncertain.

## $Ba_2CaOsO_6$: muon spin relaxation [5]

$Ba_2CaOsO_6$, ($5d^2$ Os6+), was studied using magnetic susceptibility, heat capacity, powder neutron diffraction, and muon spin relaxation (μSR). ZFC/FC irreversibility sets in below 47K, with $\Theta_{CW}$ -156K, indicating AF correlations, and $\mu_{eff}$ = 1.640 $\mu_B$, much less than the $s = 1$ spin-only value 2.83 $\mu_B$, indicating significant SOC effects.

Heat capacity [6] and Fisher heat capacity d(χT)/dT peaks exist near the susceptibility irreversibility temperature, but no magnetic neutron Bragg peaks were detected down to 3.5K, yielding an estimated upper limit of 0.7 $\mu_B$/Os.

To resolve the nature of the ground state, μSR measurements were performed at TRIUMF, on a ~1g powder sample. We find long-lived muon spin precession, consistent with long-range order, although muons are a local probe so no definitive conclusions regarding the long-range nature of the state can be made.

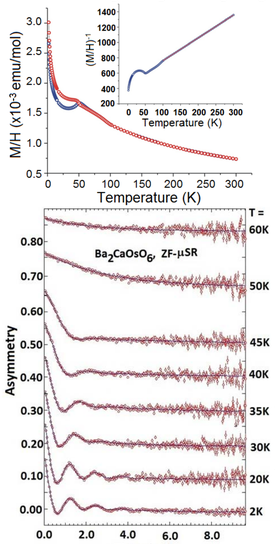
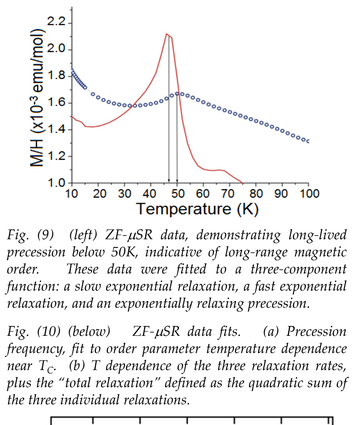



*Fig. (7) (left) Susceptibility of $Ba_2CaOsO_6$ with feature near 50K. (inset) Inverse susceptibility, demonstrating high-temperature AF Curie-Weiss behavior.*

*Fig. (8) (below) Low-T ZFC susceptibility (blue), and Fisher heat capacity d(χT)/dt (red).*



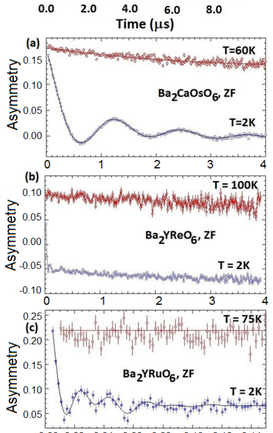




*Fig. (9) (left) ZF-μSR data, demonstrating long-lived precession below 50K, indicative of long-range magnetic order. These data were fitted to a three-component function: a slow exponential relaxation, a fast exponential relaxation, and an exponentially relaxing precession.*

*Fig. (10) (below) ZF-μSR data fits. (a) Precession frequency, fit to order parameter temperature dependence near $T_C$. (b) T dependence of the three relaxation rates, plus the "total relaxation" defined as the quadratic sum of the three individual relaxations.*

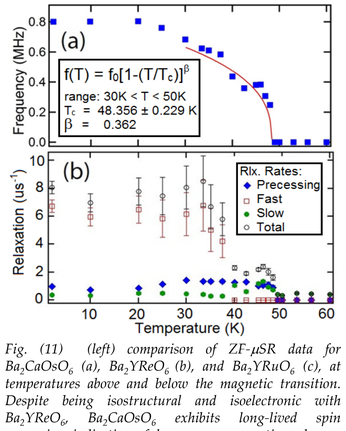






*Fig. (11) (left) comparison of ZF-μSR data for $Ba_2CaOsO_6$ (a), $Ba_2YReO_6$ (b), and $Ba_2YRuO_6$ (c), at temperatures above and below the magnetic transition. Despite being isostructural and isoelectronic with $Ba_2YReO_6$, $Ba_2CaOsO_6$ exhibits long-lived spin precession indicative of long-range magnetic order, as seen in $Ba_2YRuO_6$, and unlike the spin glass $Ba_2YReO_6$.*

This contrasts starkly with the glassy behavior in the isoelectronic and isostructural $Ba_2YReO_6$ [7], which should have a similar spin-orbit coupling parameter. The lineshape is similar to that of $Ba_2YRuO_6$ ($\mu_{eff}$ = 2.2 $\mu_B$/Ru [9]); comparison of precession and relaxation rates yields an estimated ordered moment size of 0.2 $\mu_B$ in $Ba_2CaOsO_6$. Recent theory [1] suggests a variety of ordered ground states for $d^2$ double perovskites with significant SOC; while the exact nature of the order in $Ba_2CaOsO_6$ remains undetermined, it appears to be consistent with theory. The origin of the glassy behavior of $Ba_2YReO_6$ in the absence of obvious structural disorder is less clear.

## Results and Conclusions

Neutron scattering and μSR have been used to study powder samples of structurally undistorted double perovskites, which exhibit geometric frustration due to tetrahedral coordination of magnetic B′ ions.

These techniques provide unique and complementary information relevant to studies of frustration.

Commensurate AF, consistent with Type I fcc order, up to 47K in $Ba_2YRuO6$ ($4d^3$ $Ru^{5+}$), and a 5 meV gap below 36K was detected with inelastic neutron scattering.

This gap is unexpected, and spin-orbit coupling is suggested as the origin.

Apparent LRO in $Ba_2CaOsO_6$ ($5d^2$ $Os^{6+}$) was detected with μSR, in contrast to spin glass behavior in isostructural and isoelectronic $Ba_2YReO_6$ ($5d^2$ $Re^{5+}$).

The precession/relaxation rates in $Ba_2CaOsO_6$ can be compared with the known 2.2 $\mu_B$/Ru moment in $Ba_2YRuO_6$ to derive an estimated ordered moment of 0.2 $\mu_B$/Os. This is very difficult to detect in a neutron scattering experiment, but easily accessible to μSR.

Chen et al. propose a phase diagram for $d^2$ systems with sizable SOC, suggesting several candidate AF ordered states for both $Ba_2YReO_6$ and $Ba_2CaOsO_6$.

$Ba_2CaOsO_6$ appears to be consistent with this prediction, although we cannot determine the spatial nature of the ordered state using μSR.

However, the lack of LRO in $Ba_2YReO_6$ despite evidence for structural disorder remains mysterious.

Double perovskites, which can be made from most elements in the periodic table due to the chemical versatility of the perovskite structure, are a valuable platform for systematic studies of frustration physics.

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