**Extended Abstract**

(For Ph.D. Open Seminar)

# INVESTIGATION OF STRONGLY CORRELATED RUTHNATES THROUGH NEUTRON SCATTERING

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**Abstract**

The study of strongly correlated electron systems has gained huge attention in the field of condensed matter physics, in particular, 4d/5d-transition-metal oxides, where strong spin–orbit coupling (SOC), electron-electron coulomb interactions, and large crystal-electric-field (CEF) effects compete with each other and exhibit a versatile exotic ground state in different crystallographic ambience. Among them, the Ruthenates represent a unique platform to explore emergent phenomena such as spin frustration, charge ordering, superconductivity, metal-insulator transition, magnetoelectric coupling. While the intrinsic physics of ruthenates alone is remarkably rich, the incorporation of rare-earth elements introduces additional 4*f* moments that couple with Ru(4*d*) electrons. This *d-f* coupling can further tune the magnetic ground state, controlling the functional properties of the systems. However, the research on Ruthenates (4d- systems) and especially 4*d*-4*f* systems is limited.

This thesis focuses on unraveling the interplay between crystal and magnetic structure, spin dynamics, and electronic correlations in Ru-based oxides, namely, a trimer system $Ba_5Ru_3O_{12}$, and 4*d*-4*f* coupled $Ba_3RRu_2O_9$ (R=Ho, Tb, Sm) series. The high-level synchrotron X-ray diffraction (XRD), time-of-flight neutron diffraction (ND) and inelastic neutron scattering (INS) experiments, complemented with spin-wave simulations and theoretical calculations, have been employed to understand the spin-structure, magnetic exchange interactions, spin-excitations, and unconventional ground states.

Here, we have experimentally demonstrated the mechanism of spin-driven ferroelectricity, which arises due to inverse Dzyaloshinskii–Moriya (D-M) between Ru(4*d*) and Ho(4*f*) spins due to strong 4d-4f coupling, a unique mechanism not addressed yet. The compound $Ba_3TbRu_2O_9$ exhibits an unconventional $Tb^{+4}$ valence state and intriguing spin-structure, unlike all other rare-earth members ($R^{+3}$) in this family. While our systematic temperature-dependent synchrotron XRD and ND documents a structural transition and possible charge-ordering of the isostructural $Ba_3SmRu_2O_9$ compound, in sharp contrast to heavy rare-earth (Ho/Tb) members in this series.

Our microscopic investigation on a fascinating barium ruthenate, $Ba_5Ru_3O_{12}$, containing isolated $Ru_3O_{12}$-trimers, evident a unique ground state. The combined results of INS spectra, spinW modelling, and AIML technique attribute to complex magnetic exchange interactions, exchange anisotropy, strong electronic correlation, and possible spin-phonon coupling in this system.

Our investigation sheds light on how ruthenium-based systems host diverse emergent phenomena and explains how their ground state (and thus physical properties) can be tuned by structural motifs.

**Publications related to thesis work**

1. **E. Kushwaha**, S. Ghosh, J. Sannigrahi, G. Roy, M. Kumar, S. Cottrell , M. B. Stone , Y. Fang , D. T. Adroja, X Ke and T. Basu*, Interplay between trimer structure and magnetic ground state in Ba5Ru3O12 probed by Neutron and muSR techniques, **Phys. Rev. B (accepted)**, **2025**, DOI: **https://doi.org/10.1103/c5s4-4hxw.**
2. **E. Kushwaha**, G. Roy, A. M. dos Santos, M. Kumar, S.Ghosh, T. Heitmann and T. Basu*, Unconventional s-orbital state of Tb and cooperative Ru(4d)-Tb(4f) spin-ordering in strongly correlated 4d-4f system, Ba3TbRu2O9, **J. Mater. Chem. C,** 13, 15384-15389**, 2025**. **DOI: https://doi.org/10.1039/D5TC01652E**
3. **E. Kushwaha**, G. Roy, M. Kumar, A. M. dos Santos, S. Ghosh, D. T. Adroja, V. Caignaert, O. Perez, A. Pautrat, and T. Basu*, Origin of spin-driven ferroelectricity and effect of external pressure on the complex magnetism of the 6H perovskite Ba3HoRu2O9, **Phys. Rev. B** 109,224418, **2024. DOI: https://doi.org/10.1103/PhysRevB.109.224418**

4. **E. Kushwaha et. al.,** Investigation of Charge Ordering and Structural Transitions in 4d-4f systems, $Ba_3SmRu_2O_9$, **(Manuscript under preparation)**

***The thesis is structured as follows:***

**Chapter 1: Introduction**

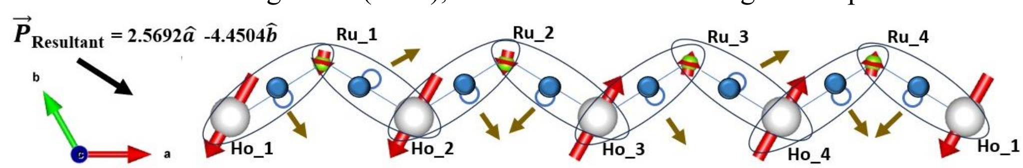
Provides the theoretical background on strongly correlated systems, focusing on the role of 4d orbitals, spin–orbit coupling, hybridization, and d–f interactions in ruthenates and other strongly correlated electron systems.

**Chapter 2: Experimental Techniques**

This chapter describes the synthesis of polycrystalline samples using the solid-state reaction method and their structural characterization through powder X-ray diffraction using Rietveld refinement. Neutron diffraction measurements were performed to probe structural and magnetic properties, while inelastic neutron scattering experiments, complemented by SpinW simulations, were employed to investigate spin dynamics and excitations.

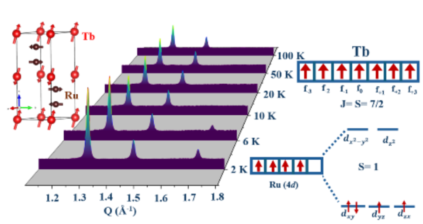
**Chapter 3: Origin of spin-driven ferroelectricity and effect of external pressure on the complex magnetism of the 6H perovskite $Ba_3HoRu_2O_9$**

This chapter presents the mechanism of spin-driven ferroelectricity in the $Ba_3HoRu_2O_9$ system. Time-of-flight neutron diffraction, dielectric spectroscopy, and theoretical analysis reveal that inverse Dzyaloshinskii–Moriya interactions between Ru(4*d*) and Ho(4*f*) spins induce oxygen displacements, giving rise to a macroscopic polarization. The results demonstrate, for the first time, that 4*d*-4*f* cross-coupling can break inversion symmetry and stabilize ferroelectricity below the magnetic ordering temperature. Complementary studies show that while magnetic fields suppress the ferroelectric state, external pressure enhances it, underlining the tunability of this phenomenon. Synchrotron XRD further supports a non-centrosymmetric structural assignment ($P\bar{6}2c$), consistent with the emergence of polarization.




**Chapter 4: Unconventional S-orbital state of Tb and cooperative Ru(4*d*)-Tb(4*f*) spin-ordering in the strongly correlated 4*d*-4*f* system $Ba_3TbRu_2O_9$**

This chapter focuses on $Ba_3TbRu_2O_9$ system, which belongs to the $Ba_3RRu_2O_9$ family. Our combined bulk and microscopic analyses revealed that the $Tb^{4+}$ ($4f^7$) electronic configuration results in an s-like state with an orbital moment ($L$) of zero and spin-only value ($S$) of 7/2, and $Ru^{4+}$ exhibits $S = 1$ despite the presence of strong spin-lattice coupling in this compound, representing a sharp contrast to other reported members of this family. Cooperative 4*d*-4*f* spin ordering was observed below the Néel temperature ($T_N \approx 9.5$ K), indicating strong Ru(4*d*)-Tb(4*f*) correlations in the system. Tb moments order antiferromagnetically in the bc-plane, whereas Ru moments align antiferromagnetically along the b-axis. Furthermore, a collinear

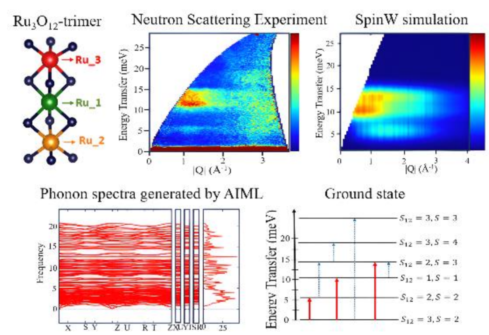


antiferromagnetic arrangement of spins was observed within the $Ru_2O_9$ dimers throughout the structure, unlike other reported members of this series (*e.g.*, Ho and Nd).

**Chapter 5: Investigation of Charge Ordering and Structural Transitions in $Ba_3SmRu_2O_9$**

In this chapter, the structural and magnetic properties of $Ba_3SmRu_2O_9$ are examined using temperature-dependent synchrotrons XRD and ND. Temperature-dependent synchrotron XRD data of $Ba_3SmRu_2O_9$ suggest lowering symmetry from a hexagonal structure (P63/mmc) to a monoclinic structure (C2/c space group, which further reduced to P2/c space group) below 80 K, which can be due to charge ordering or a Jahn-Teller distortion that influences the Ru-O-Ru bond angles. ND performed on this system suggests a very small magnetic moment of Sm.

**Chapter 6: Interplay between trimer structure and magnetic ground state in $Ba_5Ru_3O_{12}$ probed by neutron and $\mu$SR techniques**




This chapter focuses on the investigation of $Ba_5Ru_3O_{12}$ system, where inelastic neutron scattering revealed spin-wave excitations and magnon-phonon coupling, indicative of competing exchange interactions, spin frustration, and magnetic anisotropy. The detailed nearest and next-nearest magnetic exchange interactions are estimated through SpinW (MATLAB) simulation on experimental INS spectra, maintaining the non-colinear spin structure consistent with the experiment. Our combined theoretical calculations and experimental spectra have interpreted the spin-excitation and depicted the ground state of the Ru-trimer.

**Chapter 7: Conclusions and Outlook**

Summarizes the findings across different ruthenate systems, emphasizing the role of *d*-*f* coupling, spin-orbit interactions in stabilizing exotic magnetic and multiferroic states. Future directions include tuning these properties via chemical substitution, external pressure, and high-field neutron scattering.