Complex magnetic structure in Ba$_5$Ru$_3$O$_{12}$ with isolated Ru$_3$O$_{12}$-trimer

T. Basu$^1$, F. Y. Wei$^2$, Q. Zhang$^3$, Y. Fang$^2$, and X. Ke$^1$

$^1$Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, USA

$^2$Jiangsu Laboratory of Advanced Functional Materials, Department of Physics, Changshu Institute of Technology, Changshu 215500, China

$^3$Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Abstract

We report detailed magnetic, transport, heat-capacity, and neutron diffraction measurements of Ba$_5$Ru$_3$O$_{12}$, a compound consisting of isolated Ru$_3$O$_{12}$ trimers. We show that this system develops long-range antiferromagnetic ordering at $T_N \sim 60$ K without structural distortion and metal-insulator-type transition, which is in sharp contrast to other Barium Ruthenate trimer systems such as 9R-BaRuO$_3$ and Ba$_4$Ru$_3$O$_{10}$. A complex magnetic structure is revealed which is attributable to the magnetic frustration due to competing exchange interactions between Ru ions on different crystallographic sites within the Ru$_3$O$_{12}$ trimer.
I. Introduction

The interplay between electronic correlation of extended 4$d$-orbital, crystal-field effect and strong spin-orbit coupling in Ruthenates yields a rich variety of physical properties, such as superconductivity, Mott-insulator, orbital ordering, quantum spin-liquid, metal-insulator transition, etc.\textsuperscript{1–6} Because of the ground state instability due to such competing effects, a small external perturbation, e.g., doping, pressure, magnetic field, can readily modify the electronic and magnetic correlations and thus the ground state properties of systems even in the same family.\textsuperscript{3,7–9} For example, among the $\text{ARuO}_3$ (A= Ca, Sr, Ba) Ruthenate family, $\text{SrRuO}_3$ with orthorhombic perovskite structure is an itinerant ferromagnet below 165 K,\textsuperscript{10} whereas the iso-structural compound $\text{CaRuO}_3$ is a paramagnetic non-Fermi-liquid metal.\textsuperscript{11} On the other hand, the iso-chemical compound $\text{BaRuO}_3$, where the Ba-cation has larger ionic radius compared to Sr/Ca, crystallizes in hexagonal or rhombohedral perovskite structure (four(4H)-, six(6H), or nine(9R)-layered structures) that depends on the synthesis condition, and thus exhibits various physical properties.\textsuperscript{12}

In particular, 9R-$\text{BaRuO}_3$ (space group $\text{R-3m}$), which consists of corner-sharing $\text{Ru}_3\text{O}_{12}$-trimers, shows a metal-insulator-type (semiconductor-insulator) transition around 110 K which is accompanied by a structural change, a feature distinct from hexagonal $\text{BaRuO}_3$.\textsuperscript{13} No long-range magnetic ordering is observed for all $\text{BaRuO}_3$ compounds (Ru$^{4+}$, $S = 1$ in low-spin state).\textsuperscript{13} In contrast, $\text{Ba}_4\text{Ru}_3\text{O}_{10}$, which crystallizes in orthorhombic structure (space group $\text{Cmca}$) and consists of chains of $\text{Ru}_3\text{O}_{10}$-trimers running along $c$-axis in a zig-zag manner \textsuperscript{14–17}, exhibits a metal-insulator-type (semiconductor-insulator) transition around 105 K that is accompanied by antiferromagnetic (AFM) ordering but no structural transition. In addition, $\text{Ba}_4\text{LnRu}_3\text{O}_{12}$ (Ln= La, Rare-earth), which has an average valance state of +4.33/Ru (when Ln=Ln$^{+3}$), is iso-structural to
9R-BaRuO₃ (Space group R-3m) and consists of similar Ru₃O₁₂-trimers, though the trimers connected through LnO₆-octahedra. Nevertheless, different from 9R-BaRuO₃, Ba₄LnRu₃O₁₂ does not exhibit any structural or metal-insulator-type transition and undergoes long-range magnetic ordering at low temperature. The long-range-ordering (LRO) in semiconducting Ba₄LnRu₃O₁₂ with Ln being magnetic rare-earth atom is understood to be triggered by the rare-earth magnetic ordering. Intriguingly, Ba₄LaRu₃O₁₂, where Ru₃O₁₂-trimers are connected via non-magnetic La-atom, also exhibits long-range magnetic ordering at ~ 6 K, which is in sharp contrast to 9R-BaRuO₃. Similarly, iso-structural compound Ba₄NbRu₃O₁₂ with a different valance state of Ru (+3.67/Ru for Ru₃O₁₂-trimers) behaves as a Mott-insulator and magnetically orders around 4 K with a strong geometrical frustration. Therefore, both valance state and local crystal environment of Ru-ion play an important role on the physical properties of Ruthenates even in the similar family. The small structural change/distortion can significantly modify magnetic correlation and spin-lattice coupling, which leads to vastly different ground states and intriguing physical properties.

The title compound, Ba₅Ru₃O₁₂ (an average valance state of +4.67/Ru), which has nearly similar crystal structure to the aforementioned 9R-BaRuO₃, Ba₄Ru₃O₁₀ or Ba₄Ln(Nb)Ru₃O₁₂, crystalizes in Pnma space group and consists of Ru₃O₁₂-trimers (Fig. 1). Each trimer is composed of face-sharing RuO₆-octahedra, similar to other Ruthenates mentioned above. Nevertheless, in contrast to other Barium Ruthenates, the Ru₃O₁₂-trimers of Ba₅Ru₃O₁₂ are not connected to each-other¹⁴. Interestingly, despite the isolated trimer structure, a previous report of magnetic susceptibility suggests that Ba₅Ru₃O₁₂ exhibits an AFM ordering below 60 K.¹⁴ Despite that there are some studies of trimer Ruthenates where trimers are connected, thus far only a brief report exists on this isolated trimer system.¹⁴ Therefore, it is highly desirable to investigate Ba₅Ru₃O₁₂ in
detail to study the nature of its magnetic ground state and to better understand the electronic and magnetic correlation in this new trimer system.

In this paper we have reported comprehensive magnetic, transport, heat-capacity and neutron diffraction measurements on Ba$_5$Ru$_3$O$_{12}$. We have revealed a complex antiferromagnetic spin structure below $T_N \approx 60$ K which is presumably ascribed to competing magnetic exchange interactions between Ru ions on different crystallographic sites. Neither structural phase transition nor a change in electronic properties is observed to accompany with the onset of magnetic ordering.

II. Experimental Details

The polycrystalline Ba$_5$Ru$_3$O$_{12}$ sample was synthesized using solid state chemistry method by mixing high quality (>99.9%) chemical of BaCO$_3$ and RuO$_2$, as described in earlier report. The stoichiometric mixture of raw materials was pressed into pellets and sintered in air at 600 °C for 24 h and then taken out to regrind. After repeating three cycles of this process, the powder was pressed into pellets and then sintered at 1200 °C for 24 h. Magnetic susceptibility measurements as a function of temperature and magnetic field were performed using a commercial SQUID-VSM magnetometer. The resistivity and heat capacity measurements were conducted using Physical Properties Measurements System (PPMS). Neutron powder diffraction measurements were carried out using a high-resolution time-of-flight neutron powder diffractometer (POWGEN) with a bandwidth with central wavelengths of 2.665 Å in Oak Ridge National Laboratory. An POWGEN automatic changer (PAC) was used to cover the temperature region of 10-300 K. The magnetic structure was resolved using Fullprof package and SARAh program.
III. Results

A. Magnetic properties

The DC magnetic susceptibility ($\chi = M/H$) as a function of temperature in the presence of 1 kOe magnetic field is shown in Fig.2(a). The paramagnetic Curie-Weiss (C-W) behavior deviates below 120 K, implying the development of short-range correlation. With further lowering the temperature $\chi$ starts to decrease sharply below $\sim 60$ K ($T_N$), manifesting a well-defined long-range AFM ordering. The C-W fit ($\chi = \chi_0 + c/(T-\Theta_{CW})$) between 200-350 K yields Curie temperature ($\Theta_{CW}$) of -118 K and an effective magnetic moment ($\mu_{eff}$) of 4.42 $\mu_B$ per formula unit, with negligible $\chi_0 = -0.00013$. The negative value of $\Theta_{CW}$ indicates dominant AFM interactions in this system. The $\Theta_{CW}$ is much larger than $T_N$, suggesting moderate magnetic frustration with a frustration parameter ($|\Theta_{CW} / T_N|$) $\sim 2$. The isothermal magnetization ($M(H)$) below $T_N$ (as shown in Fig.2(b) for $T = 3$ and 40 K) exhibit a linear behavior as a function of magnetic field, supporting the AFM nature of this compound.

B. Heat-capacity and Resistivity

The temperature dependent heat-capacity ($C$) measured at $H = 0$ and 5 T are plotted in Fig.2(c). The typical $\lambda$-shape peak below $T_N$ confirms the long-range magnetic ordering of this compound. We do not observe any appreciable change at $H = 5$ T, suggesting that the associate Zeeman energy is much smaller than the dominant magnetic exchange interaction. We have also measured DC resistivity for the titled compound. The resistivity increases exponentially with lowering the temperature down to 10 K (see inset of Fig. 2(a)), which indicates insulating behavior (with an activation energy of 0.05 eV) of this compound. An insulating behavior is also reported in $\text{Ba}_4\text{Ln(Nb)Ru}_3\text{O}_{12}$.\textsuperscript{4} No metal-insulator transition is observed, unlike $\text{BaRuO}_3$ or $\text{Ba}_4\text{Ru}_3\text{O}_{10}$.\textsuperscript{13,16}
C. Neutron Powder Diffraction

We have performed neutron power diffraction measurements to resolve the magnetic structure of \( \text{Ba}_5\text{Ru}_3\text{O}_{12} \). The neutron diffraction profile measured at 100 K (above \( T_N \)) is well fitted with the reported space group \( \text{Pnma} \), as shown in Fig.3(a), which affirms single-phase of the material. For \( \text{Ba}_5\text{Ru}_3\text{O}_{12} \) there are three distinct inequivalent Ru-sites in \( \text{Ru}_3\text{O}_{12} \)-trimer (i.e., Ru1, Ru2, Ru3 (Fig.1)) but with same Wyckoff position 4c (x, 1/4, z). This is distinct from other trimer systems discussed above which have only two inequivalent Ru-sites with different Wyckoff positions. The atomic position of Ru1 (the middle Ru atom of the trimer), Ru2 and Ru3 in \( \text{Ba}_5\text{Ru}_3\text{O}_{12} \) are (0.7859, 0.25, 0.5575), (0.8806, 0.25, 0.6735), (0.6935, 0.25, 0.4309), respectively (Fig.1). It is worth noting that the bond-length between Ru1 and Ru2 is \( \sim2.51 \) Å, whereas it is \( \sim2.69 \) Å between Ru1 and Ru3. \( \text{RuO}_6 \) octahedra are slightly distorted and the distortion is different for different Ru-sites. The bond angles of O-Ru-O are tabulated in Table-SI in Supplemental Material.\(^{20}\)

The neutron diffraction pattern as a function of the momentum transfer (Q) measured at \( T = 10 \) and 100 K is plotted in Fig. 3(b), which shows the change of Bragg peak intensity below and above \( T_N \). At \( T = 10 \) K, besides the enhanced intensity of some of Bragg reflections compared to the 100 K data, an additional Bragg peak is observed at \( Q \sim 1.07 \) Å\(^{-1}\) that corresponds to (0 1 0). Furthermore, no structural change is observed at 10 K compared to that of 100K, which excludes any structural phase transition accompanying with the magnetic transition.

The propagation vector is found to be \( \mathbf{k} = (0\ 0\ 0) \). The irreducible representations (I.R.) and basis vectors (B.V.) of the Ru1 spins for \( \text{Pnma} \) space group associated with the propagation vector, obtained from SARAh program, are shown in Table I. Because of the same Wyckoff site of three Ru-atoms, obviously, Ru2 and Ru3-atoms have exactly the same I.R. and B.V as Ru1-atom. There
are eight irreducible representations for each Ru-atom, as represented by $\Gamma_{\text{mag}}(\text{Ru})= 1\Gamma_1^1 + 2\Gamma_2^1 + 2\Gamma_3^1 + 1\Gamma_4^1 + 1\Gamma_5^1 + 2\Gamma_6^1 + 2\Gamma_7^1 + 1\Gamma_8^1$. The magnetic moments along crystallographic $a$, $b$ and $c$-axis are described by $\Psi_2(\Gamma_2)$, $\Psi_3(\Gamma_3)$, $\Psi_8(\Gamma_6)$, $\Psi_{10}(\Gamma_7)$ B.V., $\Psi_1(\Gamma_1)$, $\Psi_6(\Gamma_4)$, $\Psi_7(\Gamma_5)$, $\Psi_{12}(\Gamma_8)$ B.V., and $\Psi_3(\Gamma_2)$, $\Psi_5(\Gamma_3)$, $\Psi_9(\Gamma_6)$, $\Psi_{11}(\Gamma_7)$ B.V., respectively. Since neutrons couple to the magnetic moment component perpendicular to $Q$, the absence of noticeable difference in the $(002)$ Bragg peak intensity measured at 10 K and 100 K, suggests that the magnetic moment is oriented along $c$, or at least the $c$-component of magnetic moment ($M_c$) is dominant. First, we consider the basis functions which only have $M_c$ component, that is, $\Psi_3(\Gamma_2)$, $\Psi_5(\Gamma_3)$, $\Psi_9(\Gamma_6)$, and $\Psi_{11}(\Gamma_7)$. Among these basis functions, $\Psi_9(\Gamma_6)$ yields best profile matching in Rietveld refinement, as shown in Fig.4(a). The obtained magnetic structure is illustrated in Fig.5(a) where magnetic moments are collinearly aligned along the $c$-axis. Ru1 and Ru2 spins are parallel aligned, while Ru1 and Ru3 spins are antiparallel aligned. This is reasonable considering FM direct exchange interaction between Ru1 and Ru2 due to metallic bond length (less than Ru-Ru bond ~2.65 Å in Ru-metal) and the antiferromagnetic super-exchange interaction of Ru1-O-Ru3 bond. The FM direct exchange interaction between Ru1 and Ru2 is expected to compete with the Ru1-O-Ru2 AFM super-exchange interaction, giving rise to magnetic frustration. We notice that although the refinement using $\Psi_9(\Gamma_6)$ basis function nearly captures the extra magnetic Bragg peak $(010)$ and the enhanced Bragg peak intensity of most of nuclear reflections, there is a mismatch in experimentally and theoretically obtained intensity of the $(114)$ reflection (see Inset of Fig 4(a)). In addition, the negligible change in the intensity of $(200)$ Bragg peak between 10 K and 100 K suggests the possibility of $a$-component of magnetic moment ($M_a$). Thus, we have tried a combination of basis functions which can give magnetic moment in $ac$-plane. We find that the low temperature neutron scattering data is best fitted using a combination of $\Psi_2(\Gamma_2)$ and $\Psi_9(\Gamma_6)$, as
shown in Fig.4(b). For instance, as shown in the inset of Fig. 4(b), both (0 1 0) and (1 1 4) Bragg peaks are much better fitted using this model compared to those using the other earlier one (see the inset of Fig 4(a)). The obtained magnetic structure based from this refinement is depicted in Fig.5(b). The magnetic moments are non-collinear and confined in the \(ac\)-plane. The moment of Ru1 (middle of trimer) are oriented along \(c\)-axis, and the moments of Ru2 and Ru3 are oriented in \(ac\)-plane with a canting angle of \(74.4^\circ\) and \(62^\circ\) relative to the \(c\)-axis. The moment size of Ru1, Ru2, Ru3 is \(\sim1.52, 1.36,\) and \(0.91 \mu_B\), respectively. This yields a total moment of \(3.79 \mu_B\) per \(Ru_3O_{12}\)-trimer.

Such a canted magnetic structure possibly arises from different competing nearest neighbor and next-nearest neighbor interactions between different inequivalent Ru-sites. Based on Goodenough-Anderson-Kanamori rules, the nearest-neighbor exchange interactions \((J_{nn})\) includes i) Ru1-Ru2 ferromagnetic direct exchange interaction, ii) Ru1-O-Ru2 AFM super-exchange interaction, and iii) Ru1-O-Ru3 AFM super-exchange interaction. However, the next-nearest-neighbor super-super-exchange interactions \((J_{nnn})\) between Ru1 and Ru3 in the trimer may not be negligible. The competition among \(J_{nn}\) and \(J_{nnn}\), where \(J_{nn} < J_{nnn}\), introduces exchange frustration and therefore may stabilize the system with a canted spin structure. The neighboring trimers are antiferromagnetically coupled via the super-super-exchange interaction (i.e. Ru1-O-O-Ru1), which yields 3D long-range AFM ordering.

A temperature- and \(d\)-dependent neutron scattering intensity map is shown in Fig.6. One can see that the \((0 1 0)\) reflection emerges and the intensity of \((1 0 2)\) becomes enhanced below 60 K, which further confirms the magnetic ordering.

We have also performed the neutron scattering measurements on another trimer Ruthenate \(Ba_4Ru_3O_{10}\) for comparison, which is documented in the Supplemental Material. The good fitting
of Rietveld refinement at 140 K, (Fig.S2a in the Supplemental Material) confirms the desired structure with Cmca space group as reported earlier. The Rietveld refinement at 10 K is depicted in Fig.S2b in the Supplemental Material. A preliminary neutron diffraction study by Klein, et al. documented an enhancement on (002)-peak below magnetic ordering and proposed a magnetic structure. In addition to (002) Bragg peak, we have observed an enhancement of the neutron diffraction intensity of some other additional Bragg peaks compared to the data taken at 140 K. Some of those magnetic Bragg peaks are depicted in Insets of Fig. S2a in the Supplemental Material. All these peaks are well-modeled with propagation vector $k = (0 0 0)$ (see Fig. S2b and Insets in the Supplemental Material). The magnetic structure obtained from the refinement confirms the prediction of earlier report by Klein, et al. There is no magnetic moment on Ru1, thereby the trimer essentially behaves like a dimer, which is distinct from Ba$_5$Ru$_3$O$_{12}$. The moment on Ru2 is 1.05 $\mu_B$ and points to the $b$-direction. The spins on Ru2 are antiferromagnetically coupled within a trimer. The spins in two adjacent trimers are ferromagnetically coupled along the $a$-direction and antiferromagnetically coupled along the $c$-direction (See Fig. S3 in Supplemental Material).

IV. Discussion and Conclusion

As discussed previously, the obtained magnetic moment of Ba$_5$Ru$_3$O$_{12}$ based on Rietveld refinement to the neutron diffraction data is about 3.79 $\mu_B$ per Ru$_3$O$_{12}$-trimer. For the RuO$_6$ octahedron, the $d$-orbital splits into lower energy $t_{2g}$ and higher energy $e_g$ orbitals due to crystal field effect in octahedral symmetry. Thus, considering discrete Ru-atom, naively one would expect that Ru$^{4+}$ ($d^4$) has four electrons in $t_{2g}$-orbital which would yield $S = 1$ effective quantum number and that Ru$^{4+}$ ($d^3$) yields $S = 3/2$ effective quantum number. This would give a total moment of 8 $\mu_B$ (considering Lande-$g$ factor of 2) for three Ru-atom, i.e. per Ru$_3$O$_{12}$-trimer, which
is much higher than the experimentally obtained moment of Ru$_3$O$_{12}$-trimer. Therefore, other mechanisms need to be considered to account for the reduced magnetic moment in this system.

First, we consider molecular orbital of Ru$_3$O$_{12}$ trimer with D$_{3d}$ symmetry due to Ru-Ru metallic bonding, as proposed for some of other trimer systems. The 9R-BaRuO$_3$ compound does not exhibit any magnetic ordering. The Ru-Ru distance is ~2.53 Å which is shorter than Ru-metal, yielding a hybridization between $d$-orbitals. Because of this strong metal-metal bonding of Ru atoms within a trimer, the whole trimer may behave as a single molecular-orbital-like state instead of three discrete Ru-orbitals, if the kinetic energy gain due to metallicity is larger than coulomb interaction (Hund’s coupling). The total valence electron count of Ru$_3$O$_{12}$ trimer is 12 (Ru$^{4+}$ $\rightarrow$ d$^4$). Considering the metal-metal bonding, the electronic configuration of a Ru$_3$O$_{12}$-trimer with D$_{3d}$ symmetry is $(a_{1g})^2(e_g)^4(a_{2u})^2(e_u)^4$, which yields $S = 0$, and thus the compound behaves as a non-magnet. Similarly, metal-metal bonding with single molecular-like-orbital state has been predicted in another trimer compound Ba$_4$NbRu$_3$O$_{12}$, which consist of 13-electron in effective $d$-orbital of Ru$_3$O$_{12}$ trimer and thus yields an effective $S = 1/2$ in the trimer. However, the same picture cannot be applied to Ba$_4$Ru$_3$O$_{10}$ (Ru$^{4+}$ $\rightarrow$ d$^4$) which exhibits magnetic ordering at 105 K with non-zero spin-moment at Ru2-site of the trimer. And for Ba$_5$Ru$_3$O$_{12}$, it contains 10 valance electrons in total for each Ru$_3$O$_{12}$ trimer. As a result, considering D$_{3d}$ symmetry of Ru$_3$O$_{12}$-trimer, that is, $(a_{1g})^2(e_g)^4(a_{2u})^2(e_u)^2$, one would anticipate $S = 1$ in its ground state. The magnetic moment obtained based on this model is smaller than the experimental value of this compound.

Second, we consider the effects of spin-orbit coupling. It is known that, in octahedral symmetry, the spin-orbit coupling ($\lambda$) may split the Ru orbital triplet $^3T_{1g}$ into three sublevels with energies $E = -2\lambda (J = 0)$, $E = -\lambda (J = 1)$, and $E = \lambda (J = 2)$. In this case, Ru$^{4+}$ cations adopt $J = 0$ in its ground state and therefore the system would not order magnetically. However, if the RuO$_6$
octahedra in trimers are not symmetrically connected in all direction, it may lift the degeneracy of the $t_{2g}$ orbitals and thus leads to a ground state with non-zero magnetic moment. If we consider three discrete Ru-orbital instead of a single trimer-orbital picture, this model can account for the difference in the magnetic ground states of BaRuO$_3$ and Ba$_4$Ru$_3$O$_{10}$. For BaRuO$_3$, the distortion of RuO$_6$ octahedron is small with the bond angle for O-Ru-O $\sim 180^0$, thus, the nonmagnetic $J = 0$ state can naturally apply to BaRuO$_3$. In contrast, in Ba$_4$Ru$_3$O$_{10}$ the RuO$_6$ octahedron of Ru2 atom is slightly distorted with $\sim 171^0$ bond angle for the four in-plane O-Ru2-O bonds and $\sim 180^0$ for the rest two O-Ru2-O bonds with apical oxygen atoms. It is hypothetically argued$^{16}$ that the perturbation of octahedral symmetry of Ru2 is large enough to lift the degeneracy of $t_{2g}$-orbital but not for the Ru1. This results in non-zero moment of the ground state of two Ru-atoms at edge of the trimer (Ru2) but zero moment of the center Ru atom of the trimer (Ru1). For Ba$_5$Ru$_3$O$_{12}$, considering no spin-orbit coupling for Ru$^{5+}$ (zero orbital degrees of freedom) and finite spin-orbit coupling for Ru$^{4+}$, the total moment of trimer ($S=3/2$ for two Ru and $J=0$ for one Ru) will be 6 $\mu_B$, which is higher than the experimentally obtained value. Also, for Ba$_5$Ru$_3$O$_{12}$, as tabulated in in Table-SI, there is large deviation of the O-Ru-O bond angles from $180^0$, as observed in Ru2-atom for Ba$_4$Ru$_3$O$_{10}$, which also indicates that probably, this model (spin-orbit coupling) alone is not valid for our title compound.

Thus, the above two mechanisms that have been proposed for other trimers systems could not be applied to account for the experimentally obtained effective moment in Ba$_5$Ru$_3$O$_{12}$. This suggests the complex magnetism of this compound, on which geometrical frustration and hybridization both plays significant role.

In summary, our detailed investigation on Ba$_5$Ru$_3$O$_{12}$ trimer system reveals a long-range antiferromagnetic ordering below 60 K. A complex magnetism with canted spin-structure is
observed, distinct from other trimer systems such as BaRuO$_3$, Ba$_4$Ru$_3$O$_{10}$, or, Ba$_4$LnRu$_3$O$_{12}$, which is attributable to magnetic frustration due to competing exchange interactions between nearest-neighbor and next-nearest-neighbor Ru-atom on different sites within Ru$_3$O$_{12}$-trimer. Such a complex behavior arises as a result of different level of hybridization (localization) on different Ru sites and strong spin-frustration in this trimer system. The system exhibits insulating behavior throughout the temperature range measured. No metal-insulator-like transition is observed, unlike BaRuO$_3$ and Ba$_4$Ru$_3$O$_{10}$. This study demonstrates that the valance state and hybridization of Ru-atom, together with the RuO$_6$ octahedral distortion, play an important role on electronic and magnetic correlations in Ruthenates.

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Figure Captions:

**Fig.1.** Crystal structure of Ba$_5$Ru$_3$O$_{12}$. The Ru-trimers are shown in (b-c).

**Fig.2.** (a) The temperature depended $DC$ magnetic susceptibility measured with 1 kOe magnetic field. The red curve is the Curie-Weiss fit in paramagnetic region from 200 to 350 K. The inset shows the resistivity as a function of temperature measured at zero magnetic field. (b) Isothermal magnetization as a function of magnetic field at $T = 3$ and 40 K. (c) Heat Capacity as a function of temperature measured at $H = 0$ and 5 T.
Fig. 3. (a) Rietveld refinement to the neutron powder diffraction pattern measured at $T = 100$ K. The open black circle represents the experimental data, while the red solid line shows the Rietveld fitting. The vertical bars display the Bragg peak positions of crystal structure. The continuous blue line at the bottom shows the difference between the experimental and calculated intensity. (b) Comparison of neutron powder diffraction pattern collected at $T = 10$ and $100$ K. The inset shows an expanded view at higher Q. The $(H K L)$ values are indexed for most of reflections.

Fig. 4. Rietveld refinement to the neutron powder diffraction pattern measured at $T = 10$ K modeled with (a) $\Psi_9(\Gamma_6)$ only and (b) a combination of $\Psi_2(\Gamma_2)$ and $\Psi_9(\Gamma_6)$. The open black circles represent the experimental data, while the red solid curve shows the Rietveld fitting. The vertical bars display the Bragg peak positions of crystal structure, the next lower vertical lines represent magnetic Bragg peaks associated with the propagation vector $k = (0 0 0)$. The continuous blue line at the bottom of the figure shows the difference between the experimental and calculated intensity. The insets show an expanded view of some Bragg reflections.

Fig. 5. Magnetic structure of Ba$_5$Ru$_3$O$_{12}$ modeled with (a) $\Psi_9(\Gamma_6)$ only and (b) a combination of $\Psi_2(\Gamma_2)$ and $\Psi_9(\Gamma_6)$.

Fig. 6. Temperature- and $d$-dependent neutron scattering intensity map. The red arrows point to the onset of magnetic transition.
Table I: The irreducible representations and basis vectors for each Ru-site (4c) for space group \( Pnma \) and the propagation vector \( k = (0 0 0) \).

| I.R. | B.V. | x, y, z | x+1/2, -y+1/2, -z+1/2 | -x,y+1/2,-z | -x+1/2, -y, z+1/2 |
|------|------|---------|------------------------|-------------|------------------|
| Γ₁   | \( \Psi_1 \) | 0 2 0 | 0 -2 0 | 0 2 0 | 0 -2 0 |
| Γ₂   | \( \Psi_2 \) | 2 0 0 | 2 0 0 | -2 0 0 | -2 0 0 |
|      | \( \Psi_3 \) | 0 0 2 | 0 0 -2 | 0 0 -2 | 0 0 2 |
| Γ₃   | \( \Psi_4 \) | 2 0 0 | 2 0 0 | 2 0 0 | 2 0 0 |
|      | \( \Psi_5 \) | 0 0 2 | 0 0 -2 | 0 0 2 | 0 0 -2 |
| Γ₄   | \( \Psi_6 \) | 0 2 0 | 0 -2 0 | 0 -2 0 | 0 2 0 |
| Γ₅   | \( \Psi_7 \) | 0 2 0 | 0 2 0 | 0 2 0 | 0 2 0 |
| Γ₆   | \( \Psi_8 \) | 2 0 0 | -2 0 0 | -2 0 0 | 2 0 0 |
|      | \( \Psi_9 \) | 0 0 2 | 0 0 2 | 0 0 -2 | 0 0 -2 |
| Γ₇   | \( \Psi_{10} \) | 2 0 0 | -2 0 0 | 2 0 0 | -2 0 0 |
|      | \( \Psi_{11} \) | 0 0 2 | 0 0 2 | 0 0 2 | 0 0 2 |
| Γ₈   | \( \Psi_{12} \) | 0 2 0 | 0 2 0 | 0 -2 0 | 0 -2 0 |
Figure 1.

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Supplemental Material

Table-I: The O-Ru-O bond of RuO6 octahedron angle for different Ru and Oxygen sites for Ba₅Ru₃O₁₂.

| <O-Ru1-O | <O-Ru2-O | <O-Ru3-O |
|----------|----------|----------|
| < O8-Ru1-O1 | 82.9° | < O7-Ru2-O4 | 84.0° | < O8-Ru3-O1 | 79.4° |
| < O1-Ru1-O4 | 93.7° | < O4-Ru2-O2 | 92.8° | < O1-Ru3-O3 | 98.4° |
| < O4-Ru1-O7 | 88.7° | < O2-Ru2-O5 | 94.5° | < O3-Ru3-O6 | 95.8° |
| < O7-Ru1-O8 | 173.4° | < O5-Ru2-O7 | 172.7° | < O6-Ru3-O8 | 164.9° |
| < O1-Ru1-O4 | 178.3° | < O2-Ru2-O4 | 173.8° | < O1-Ru3-O3 | 171.1° |

The Ru1-O distances are 1.98-2.0 Å, whereas, the Ru2-O and Ru3-O distances are 1.88-2.07 Å and 1.86-2.1 Å.

Neutron Powder Diffraction of Ba₄Ru₃O₁₀

Fig. S1. Crystal structure of Ba₄Ru₃O₁₀.
Fig. S2. Rietveld fitting of t.o.f powder neutron diffraction pattern collected at (a) 140 K and (b) 10 K for the compound Ba₄Ru₃O₁₀. The open black circle represents the experimental data, while the red solid line shows the Rietveld fitting. The vertical bars display the Bragg peak positions of crystal structure of Ba₅Ru₃O₁₂, the next lower vertical lines represent magnetic Bragg peaks associated with \( k = (0 \ 0 \ 0) \). The continuous blue line at the bottom of the figure shows the difference between the experimental and calculated intensity. Insets shows the magnified picture of some (H K L) peaks.
Fig. S3. Magnetic structure of Ba$_4$Ru$_3$O$_{10}$.

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