Spin-gap opening accompanied by a strong magnetoelastic response in the $S = 1$ magnetic dimer system Ba$_3$BiRu$_2$O$_9$

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(Dated: February 19, 2022)

Neutron diffraction, magnetization, resistivity, and heat capacity measurements on the 6H-perovskite Ba$_3$BiRu$_2$O$_9$ reveal simultaneous magnetic and structural dimmerization driven by strong magnetoelastic coupling. An isostructural but strongly displacive first-order transition on cooling through $T^* = 176$ K is associated with a change in the nature of direct Ru–Ru bonds within Ru$_2$O$_9$ face-sharing octahedra. Above $T^*$, Ba$_3$BiRu$_2$O$_9$ is an $S = 1$ magnetic dimer system with intradimer exchange interactions $J_0/k_B = 320$ K and interdimer exchange interactions $J'/k_B = -160$ K. Below $T^*$, a spin-gapped state emerges with $\Delta \approx 220$ K. Ab initio calculations confirm antiferromagnetic exchange within dimers, but the transition is not accompanied by long-range magnetic order.

PACS numbers: 61.05.fm, 75.10.Pq, 75.30.Et, 75.30.Kz, 75.40.-s, 75.47.Lx

Quantum cooperative phenomena involving charge, spin, orbital, and lattice order parameters are among the most explored areas of modern solid-state physics. A particularly rich vein of quantum cooperative phenomena are low-dimensional magnetic systems featuring motifs such as dimers, chains, ladders, and plaquettes, where coupling between spin and lattice degrees of freedom can give rise to magnetoelastic effects such as the spin-Peierls transition in $S = 1/2$ Ising-chain antiferromagnets.

The most thoroughly studied are based on $S = 1/2$ 3d transition metal cations such as Cu$^{2+}$, V$^{4+}$ and Ti$^{3+}$. The less common $S = 1$ systems remain relatively neglected, although $S = 1$ ruthenates (low-spin Ru$^{4+}$), in particular, show fascinating properties including superconductivity (Sr$_2$RuO$_4$), non-Fermi liquid behaviour (La$_4$Ru$_5$O$_{19}$) and low-dimensional character (the famous spin-gapped Haldane phase Ti$_2$Ru$_2$O$_7$).

This report concerns Ba$_3$BiRu$_2$O$_9$, first reported by Darriet et al. as a 6H-perovskite with a small monoclinic ($C2/c$) distortion. It contains Bi$_6$O$_9$ octahedral-sharing vertices with Ru$_2$O$_9$ face-sharing octahedral dimers, and Ba$^{2+}$ ions occupying high-coordinate $A$ sites (Fig. 1). It forms part of the Ba$_3$R$_2$O$_9$ series, where $R$ is a rare-earth or 3d transition metal (Bi, Y) or zirconium. The rare-earth $R$ cations usually have a 3+ oxidation state, giving Ru$^{5+}$ dimers; but Tb, Pr, and Ce have 4+ oxidation states, giving Ru$^{8+}$ dimers, and shrinking the unit cell due to the reduced ionic radius of $R$ (Fig. 1). Our experimental lattice parameters for Ba$_3$BiRu$_2$O$_9$ strongly suggest that it belongs in this Ru$^{8+}$ category.

Polycrystalline Ba$_3$BiRu$_2$O$_9$ was synthesized by solid-state reaction. Neutron powder diffraction (NPD) data were collected on the instrument Wombat at OPAL, ANSTO, from 2 to 300 K using 2.9609 A neutrons; and at 2 K on the HRPD diffractometer at ISIS. Structure refinements via the Rietveld method were carried out using GSAS with the EXPGUI front-end. Magnetic susceptibility, electrical resistivity and heat capacity were measured in a Quantum Design PPMS. Ab initio calculations were performed in the generalized gradient approximation (GGA) using the Vienna ab initio Simulations Package (VASP 5.2). A supercell containing two primitive cells (60 atoms) was used with standard PAW potentials, a $k$-mesh of 162 points in the irreducible Brillouin zone wedge and a cutoff energy of 450 eV. Total energy converged to within $10^{-5}$ eV.

FIG. 1. (Color online) Ionic radii of $R^{3+}$ ($R = \text{Bi, Y, rare-earth}$) in 6-fold coordination vs. unit cell lengths $a$, $b/\sqrt{3}$ (filled circles) and $c$ (open squares) for Ba$_3$R$_2$O$_9$ at 298 K. Error bars are smaller than symbols. Adapted from Doi et al. and references therein, with $R = \text{Bi}$ from the present work. The refined (HRPD@ISIS) 2 K structure of Ba$_3$BiRu$_2$O$_9$ is shown with BiO$_6$ octahedra (violet), Ru$_2$O$_9$ dimers (grey), Ba$^{2+}$ (green), and O$^{2-}$ ions (red). Polyhedral units are expanded and drawn with 90% probability thermal ellipsoids.
The apparent 4+ oxidation state for the single crystal is very unusual (it would have an unstable 5d^{10}6s^{1} valence configuration), leading us to consider whether the structural transition is driven by disproportionation (2Bi^{4+} → Bi^{3+} + Bi^{5+}) or charge transfer (Bi^{4+} + 2Ru^{4+} → Bi^{3+} + 2Ru^{4.5+}). Either process should be obvious in bond valence sums (BVS) calculated from experimentally refined structure parameters. BVS (Fig. 2d) show no anomaly for Ru on cooling, ruling out charge transfer.

For Bi they shows a small anomaly; however, our NPD data show no evidence for symmetry lowering (additional or split peaks below the transition) due to long-range Bi^{3+}-Bi^{5+} order. Moreover, Bi^{4+} oxides generally disproportionate at much higher temperatures than the transition of interest here (e.g., two distinct Bi sites can be distinguished by BVS in BaBiO_{6} even at 900 K [16]). The 6s electron on Bi^{4+} probably localises at similarly high temperatures in Ba_{3}BiRu_{2}O_{9}, but long-range Bi^{3+}-Bi^{5+} order is frustrated by the triangular disposition of Bi sites, with the only evidence being slightly anisotropic oxygen atomic displacement parameters (ADPs) (Fig. 1). Most importantly, ADPs and diffraction peak widths show no discontinuities at the structural transition to indicate a significant change in local disorder or lattice strain.

It does seem likely that “Bi^{4+}” plays an important role in the transition at T’, considering that no such transition is observed for any R^{4+} (R = rare earth) cation. Unfortunately, the evidence at this stage is insufficient to identify the precise nature of that role. One possibility is that Bi^{4+} may be acting as a transient charge reservoir, communicating changes in the electronic state between isolated Ru_{2}O_{9} dimers as they switch from the high- and low-temperature forms, thereby facilitating a first-order transition that never takes place where more stable R^{4+} cations are involved.

Molar magnetic susceptibility χ is shown in Fig. 3. The structure consists of effectively isolated Ru_{2}O_{9} units, so the expression for isolated S = 1 dimers:

$$\chi_{iso} = \frac{2N_{A}g^{2}\mu_{B}^{2}(1 + 5 \exp(-2J_{0}/k_{B}T))}{k_{B}(3 + \exp(J_{0}/k_{B}T) + 5 \exp(-2J_{0}/k_{B}T))}$$

should be appropriate, where N_{A} is Avogadro’s number, μ_{B} is a Bohr magneton, k_{B} is the Boltzmann constant, g is the standard electron g = 2 factor and J_{0} is the intradimer magnetic coupling. However, a much bet-
inter quality of fit is obtained if interdimer interactions \(J'\) are included in the calculations in the mean-field approximation, so susceptibility \(\chi_{\text{dim}}\) can be written as:

\[
\chi_{\text{dim}} = \frac{\chi_{\text{iso}}}{1 + \lambda \chi_{\text{iso}}} \tag{2}
\]

where \(\lambda = J' / N a g^2 \mu_B^2\). A fit above 180 K \(\chi(T) = (1 - x) \chi_{\text{dim}} + x \chi_{\text{iso}} + c / (T - \Theta)\), which combines dimer, temperature independent and Curie-Weiss contributions \((C = 1 \text{emu K mole}^{-1} \text{for } S = 1 \text{ impurities})\) respectively, is shown. The best fit is to \(J_0/k_B = 320(20) \text{ K}, J'/k_B = -160(10) \text{ K}, x = 0.02, \Theta = 0 \text{ K and } \chi_0 = 0.0011 \text{ emu mole}^{-1}\). This is comparable to Ba₃PrRu₂O₉[6], where \(J_0/k_B = 280 \text{ K}\). A comment should be made here concerning next-nearest neighbor interactions. While nearest neighbors are obviously those within Ru₂O₉ planes, higher-order neighbors are less obvious. Each Ru⁴⁺ is surrounded by 6 others in the pseudo-hexagonal ab plane and 3 from the neighboring plane, connected via Ru-O-Bi-O-Ru superexchange paths of approximately equal length. In the C2/c space group, these 9 sites comprise 5 inequivalent positions, leading to 5 different exchange constants \(J_i, i = 1...5\) (inset in Fig. 3). As \(J' = \sum_{i=1}^{N} n_i J_i\), where \(n_i\) is the multiplicity of next-nearest neighbors interacting via \(J_i\), the average interdimer exchange parameter is \(J / k_B = -17.7 \text{ K}\). The intradimer coupling \(J_0\) is about double the absolute value of this interdimer \(J'\). Susceptibility results thus show that above \(T^* = 176 \text{ K}\), Ba₃BiRu₂O₉ is an antiferromagnetic (AFM) dimer system with weak ferromagnetic (FM) next-nearest neighbours interactions.

A drastic drop in magnetic susceptibility below \(T^*\) is highlighted by a maximum in the temperature derivative of \(\chi(T)\) (inset in Fig. 4). As \(T^*\) coincides with the discontinuities in cell volume and \(d\rho_{Ru-Ru}\), Ba₃BiRu₂O₉ appears to undergo coincident structural/magnetic dimerization. We tentatively ascribe this to the opening of a gap in the spin-excitation spectrum between non-magnetic singlet ground state and excited triplet spin configurations within dimers. The magnetic susceptibility of such a system should follow \(\chi_{\text{sg}}\):

\[
\chi_{\text{sg}} = a T^{\alpha} \exp(-\Delta_{\chi} / k_B T) \tag{3}
\]

where \(a\) is a constant and \(\Delta_{\chi}\) is the value of the spin gap. A least-square fit performed in 2-150 K temperature range to the equation: \(\chi(T) = \chi_{\text{sg}} + \chi_0 + c / (T - \Theta)\) (shown in Fig. 3 blue line) yields \(a = 0.00021 \text{ emu mol}^{-1} \text{K}^{-0.5}, \Delta_{\chi} / k_B = 247(2) \text{ K}, \chi_0 = 0.0006 \text{ emu mol}^{-1}, c = 0.013 \text{ emu mol}^{-1} \text{K}^{-1}, \text{and } \Theta = -5.5 \text{ K}\).

Fig. 4 shows the temperature dependence of electrical resistivity \(\rho\). Ba₃BiRu₂O₉ is nonmetallic - it exhibits increasing resistance with decreasing temperature - like other Ru 6H-type perovskites [6, 17]. We tested various models for insulators, but the best fit was obtained with the variable-range hopping expression [18]:

\[
\log \rho = a + b T^{-1/4} \tag{4}
\]

where \(n\) is the dimensionality of hopping and \(a\) and \(b\) are constants. This transport mechanism is expected for an insulating sample with strong inhomogeneity, where charge carriers are localised into states with various energies within a band gap. Transport between such states is realized with the help of a phonon, so that conduction occurs at a finite temperature. A least-square fit yields \(a = -5.2 \Omega \text{cm}, b = 99 \text{K}^{0.5} \Omega \text{cm} \text{ and } n = 0.97 \text{ (i.e. } \sim 1\), pointing to 1D hopping. Below \(T^*\), \(\rho\) increases rapidly, seen as a drastic change in its temperature derivative (inset in Fig. 4), and Eq. 4 is no longer valid. This is reminiscent of superconducting cuprates, where out-of-plane resistivity increases due to the opening of a spin-gap [19].

Fig. 5 shows the temperature dependence of the heat capacity \(C_p / T\) ratio. The main feature is a sharp anomaly at \(T^*\), suggesting a large release of magnetic and/or structural entropy. The total heat capacity of a solid consists of lattice, magnetic, and electronic contributions, but without a suitable phononic reference material (isostuctural but with no unpaired \(d\) electrons) the deconvolution of \(C_p\) is nontrivial. Initial attempts using a lattice term in the Debye approximation with a single characteristic frequency failed to produce a satisfactory fit. We have therefore used the approach of Junod et al. [20, 21], which has been successfully applied to a number of oxide and intermetallic systems [22, 24], where the lattice contribution to the heat capacity is described by a sum of independent Debye and Einstein terms assigned to different groups of atoms. After testing all combinations of Debye and/or Einstein modes assigned to different sublattices, the best \(\alpha^2\) coefficient was obtained by fitting \(C_p\) below 150 K to a combination of 3 Debye modes assigned...
to the Ba, Bi, and O sublattices, one Einstein mode from the Ru sublattice, and an additional term describing local magnetic excitations across the gap $\Delta_{\text{C}}$:

$$C_{\text{sg}} = nR\frac{(\Delta_{\text{C}}/k_BT)^2 \exp(-\Delta_{\text{C}}/k_BT)}{1 + n \exp(-\Delta_{\text{C}}/k_BT)}$$

(5)

where $n = 3$ for singlet-triplet excitations and $R$ is the gas constant. We neglected the electronic contribution because the sample was found to be semiconducting. The best fit yielded $\Theta^{\text{Bi}} = 101(1)$, $\Theta^{\text{Ba}} = 296(4)$, $\Theta^{\text{O}} = 630(4)$, $\Theta^{\text{Ru}} = 111(1)$, and $\Delta_{\text{C}}/k_B = 193(6)$ K. Note that $\Delta_{\text{C}}$, estimated using this methodology, is of the same order as $\Delta_{\chi}$. These contributions are shown in Fig. 5. The inset shows the $C_p/T^3$ ratio, where the maximum at 16 K is an apparent hallmark of Einstein modes $[20; 21]$. Neither a Debye model nor the spin-gap formula were able to reproduce this feature. The mean spin-gap from susceptibility and heat capacity $\overline{\Delta} = (\Delta_{\chi} + \Delta_{\text{C}})/2k_B \approx 220$ K is equal to 0.7$J_0/k_B$. This is in perfect agreement with the $\Delta_{\chi}$ ratio calculated for $\text{Ba}_3\text{Mn}_2\text{O}_8$ ($\Delta/k_B = 12.2$ K and $J_0/k_B = 17.4$ K $[23]$), which has a similar structure consisting of hexagonal layers of $S = 1$ Mn$^{5+}$ dimers.

The transition at $T^*$ must be related to these changes in inter- and intradimer exchange interactions. We therefore performed ab initio calculations on supercells for the structures refined at 300 and 2 K. As differences between total energies of different spin orientations appear due to the spin degrees of freedom, one can map total energies onto the Heisenberg Hamiltonian:

$$\hat{H} = - \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

(6)

with one intradimer exchange parameter $J_0$ and two interdimer ones, $J_{ab} = (4J_1 + 2J_2)/6$ (in-plane) and $J_c = (J_3 + J_4 + J_5)/3$ (along c) - please refer to the inset in Fig. 5. At 300 K, intradimer coupling was estimated as $J^{\text{HT}}_{\text{ab}}/k_B = 259$ K in the presence of interdimer couplings $J^{\text{HT}}_{\text{ab}}/k_B = -2.4$ K and $J^{\text{HT}}_{\text{c}}/k_B = 5.4$ K, pointing to the domination of exchange within $\text{Ru}_2\text{O}_9$ units and its AFM character. At 2 K, the parameters are $J^{\text{HT}}_{\text{ab}}/k_B = 216$ K, $J^{\text{HT}}_{\text{ab}}/k_B = 5.7$ K and $J^{\text{HT}}_{\text{c}}/k_B = 9.2$ K. These values of $J_0$ are somewhat smaller than obtained from susceptibility ($J_0/k_B = 320$ K), but significant contributions from next-nearest neighbors ($J_{ab}$ and $J_c$) justify use of the interacting dimer model. It is worth noting that both AFM exchange integrals $J_{ab}$ and $J_c$ at 2 K suggest magnetic frustration, which was proposed as the origin of the spin-gap opening in $\text{Mo}_3\text{Sb}_7$ $[20; 21]$.

In conclusion, we observe a spin-gap opening in the $S = 1$ system $\text{Ba}_3\text{BiRu}_2\text{O}_9$ below $T^* = 176$ K, with a spin-gap value of $\approx 220$ K. A magnetoelastic effect is observed as a decrease in the Ru–Ru distance within $\text{Ru}_2\text{O}_9$ dimers below $T^*$, as well as in the magnetic, thermodynamic and electronic properties. An increase of unit cell volume is tentatively associated with a relaxation of the structure at $T^*$, although we cannot exclude other possibilities such as orbital ordering. Ab initio calculations confirm strong AFM coupling within $\text{Ru}_2\text{O}_9$ dimers. Calculations to investigate the strong correlation effects typical of low-dimensional systems, using +Hubbard $U$ methods, are now required, as well as direct confirmation of the spin-gapped state by inelastic neutron scattering.

This work was supported by the ARC (DP0984585, DP0877695), AINSE, and the AMRFP. Dr Kevin Knight of ISIS assisted in HRPD data collection.

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