

Spin-orbital locked magnetic excitations in a half-metallic double perovskite $\text{Ba}_2\text{FeReO}_6$

K. W. Plumb,¹ A. M. Cook,¹ J. P. Clancy,¹ A. I. Kolesnikov,²
B. C. Jeon,³ T. W. Noh,³ A. Paramekanti,^{1,4} and Young-June Kim¹

¹*Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7*

²*Neutron Scattering Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

³*Center for Functional Interfaces of Correlated Electron Systems,
Institute for Basic Science, and Department of Physics & Astronomy,
Seoul National University, Seoul 151-747, Korea*

⁴*Canadian Institute for Advanced Research, Toronto, Ontario, M5G 1Z8, Canada*

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We present a powder inelastic neutron scattering study of magnetic excitations in $\text{Ba}_2\text{FeReO}_6$, a member of the double perovskite family of materials which exhibit half-metallic behavior and high Curie temperatures. We find clear evidence of two well-defined dispersing magnetic modes in its low temperature ferrimagnetic state. We develop a local moment model, which incorporates the interaction of Fe spins with spin-orbit locked magnetic moments on Re, and show that this captures our experimental observations. Our study further opens up double perovskites as model systems to explore the interplay of strong correlations and spin-orbit coupling in 5d transition metal oxides.

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Strong electronic correlations in the 3d and 4d transition metal oxides (TMOs) lead to such remarkable phenomena as high temperature superconductivity in the cuprates [1], colossal magnetoresistance in the manganites [2], and possible chiral superconductivity in the ruthenates [3]. In 5d-TMOs, the traditional viewpoint suggests that the larger spread of atomic wavefunctions leads to a smaller local Hubbard repulsion and a larger overlap between neighboring atomic orbitals, which cooperate to suppress strong correlation effects. Indeed, simple oxides like ReO_3 are good metals [4]. This traditional picture has been challenged by recent work on iridium-based complex oxides, which shows that the large spin-orbit (SO) coupling on Ir can split the t_{2g} crystal field levels, yielding a reduced bandwidth for effective $j=1/2$ electrons and the re-emergence of strong correlations [5]. Iridates like Na_2IrO_3 , $\text{Na}_4\text{Ir}_3\text{O}_8$, $\text{Eu}_2\text{Ir}_2\text{O}_7$ and $\text{Y}_2\text{Ir}_2\text{O}_7$, are of great interest since they may support correlated SO coupled magnetism or topological phases [6–14].

A distinct route to strong correlations in 5d-TMOs may be realized in *ordered* double perovskites (DPs), with chemical formula $\text{A}_2\text{BB}'\text{O}_6$, obtained by stacking alternating ABO_3 and $\text{AB}'\text{O}_3$ perovskite units. In this structure, neighboring $\text{B}(\text{B}')$ site ions are further apart by $\sqrt{2}$ (see Fig. 1). With 5d metal ions on the B' sites, the larger $\text{B}'\text{-B}'$ distance suppresses direct 5d orbital overlap, enhancing strong correlations. There is a growing interest in DPs such as A_2FeReO_6 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$) [15–21] and $\text{Sr}_2\text{CrOsO}_6$ [22, 23], with a 3d magnetic B -ion and a 5d B' -ion, since they exhibit high Curie temperatures. In addition, the half-metallic character and significant polarization of many DPs makes them ideal candidates for spintronic applications such as spin injection [24, 25]. Despite this great fundamental and technological interest

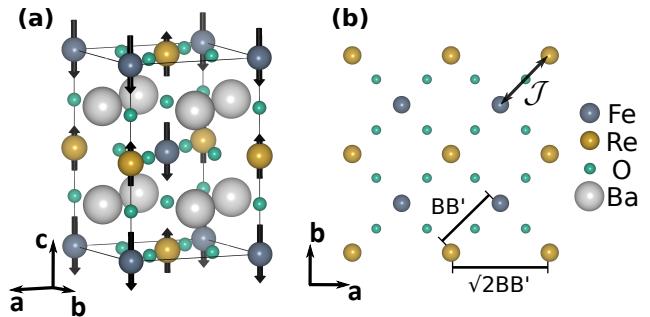


FIG. 1. Crystal structure of $\text{Ba}_2\text{FeReO}_6$. (a) Schematic of the crystallographic unit cell showing the relative orientation of Fe and Re moments. (b) Projection into ab -plane illustrating the separation between $\text{B}(\text{B}')$ site ions, and the exchange pathway J between neighboring Fe and Re sites.

in the DP materials [26–29], there is a significant lack of experimental work on their magnetic excitations.

In this Letter, we address this issue by using inelastic neutron scattering (INS) on polycrystalline $\text{Ba}_2\text{FeReO}_6$ to study the magnetic excitations in its ferrimagnetic state, complemented by a theoretical modelling of the observed spectrum. Our main results, which are summarized in Fig. 2, are as follows. (i) We provide experimental evidence of *two* dispersive magnetic modes in the magnetic excitation spectrum, showing that Fe and Re electrons both exhibit strong correlations and contribute to the magnetization dynamics. (ii) We find evidence of nearly gapless magnetic excitations in the inelastic spectrum, indicating a weak locking of Re-moments to the lattice in the ferrimagnetic state. (iii) We discuss a minimal local moment model of strongly coupled spin and orbital degrees of freedom on Re interacting with spins on Fe,

which captures our experimental observations. (iv) We combine our results with published magnetization and X-ray magnetic circular dichroism (XMCD) data to obtain estimates of the Re and Fe moments and the effective Re-Fe exchange interaction. Our work further opens up 5d-based DPs as model systems to study the interplay of spin orbit coupling and strong electronic correlations.

Experiments: Total 8.6g of polycrystalline $\text{Ba}_2\text{FeReO}_6$ sample was synthesized using the standard solid-state method reported previously [20, 30]. In some DPs, anti-site disorder (mixing of B and B' site atoms) is significant, and suppresses saturated magnetic moments. However, for $\text{Ba}_2\text{FeReO}_6$, a large difference ($\sim 8\%$) in the ionic radii of Fe^{3+} and Re^{5+} seems to mitigate this problem. From the structural refinement of x-ray powder diffraction data, we infer an anti-site disorder of $\lesssim 1\%$, consistent with that reported by Winkler et al. [31].

Neutron scattering measurements were carried out on the fine resolution Fermi-chopper spectrometer SEQUOIA at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Measurements were performed with Fermi chopper 1 rotating at a frequency of 300 Hz and phased for incident energies of 27 and 120 meV. A T0 chopper rotating at 180 Hz was used to eliminate a fast neutron background. The sample was sealed in an Al can and mounted on a closed cycle cryostat. Data were also collected for an empty Al sample can at $T = 34$ K, with an identical instrumental configuration. The absorption corrected empty can intensities were subtracted from the raw data at $T = 34$ K to remove scattering from the sample environment.

Throughout this article we use pseudo-cubic notation $a = b = c \approx 4.01 \text{ \AA}$ and index the momentum transfer \mathbf{Q} in units of $1/a$ to aid comparison with theoretical calculations. In our magnetic model ferrimagnetism arises from G-type antiferromagnetic arrangement of inequivalent Fe and Re moments so that magnetic Bragg peaks occur at the antiferromagnetic wavevector $\mathbf{Q}_{\text{AF}} = (\pi, \pi, \pi)$ and the ferromagnetic wavevector $\mathbf{Q}_{\text{FM}} = (2\pi, 0, 0)$.

Maps of the inelastic neutron scattering intensity for 27 meV and 120 meV incident neutron energies are shown in Fig. 2 (a) and (b) respectively. An inelastic feature emanating from $Q = 1.35 \text{ \AA}^{-1}$ corresponding to \mathbf{Q}_{AF} is clearly resolved. The inelastic feature extends into two-bands of excitations with maximum intensities near 25 meV and 39 meV. The scattering is strongest at low-Q and decays rapidly for increasing Q as is expected generally from the form factor dependence for magnetic scattering. Results from our theoretical model are shown in Fig. 2 (c)-(d) with the best-fit parameters.

The temperature and energy dependence of putative magnetic scattering in $\text{Ba}_2\text{FeReO}_6$ is presented in Fig. 3. Bragg peaks at $Q = 1.35 \text{ \AA}^{-1}$ corresponding to \mathbf{Q}_{AF} , and $Q = 1.56 \text{ \AA}^{-1}$ corresponding to \mathbf{Q}_{FM} are shown in Fig. 3 (a). The elastic magnetic intensity decreases upon warming and the antiferromagnetic Bragg

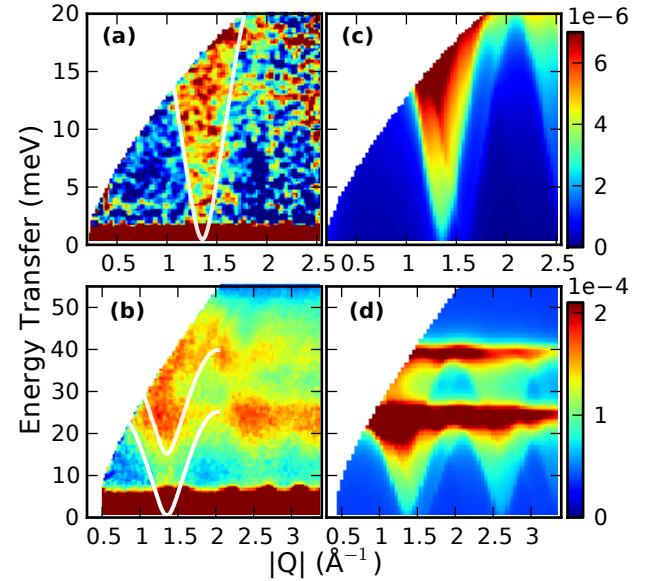


FIG. 2. Comparison of spin wave model and measured powder averaged magnetic scattering intensity for $T = 34$ K. An empty Al-Can background signal has been subtracted from the data. (a) and (b) are neutron scattering data for incident energies of 27 and 120 meV respectively. (c)-(d) Powder averaged dynamic structure factor calculated from the spin wave model with $6\mathcal{J}_{\text{eff}}\mathcal{F} = 39$ meV, and $6\mathcal{J}_{\text{eff}}\mathcal{R} = 25$ meV. Solid white lines in (a) and (b) show the dispersion relation from the spin wave model along $(0, 0, 0) - (\pi, \pi, \pi) - (3\pi/2, 3\pi/2, 3\pi/2)$.

peak vanishes above 300 K, consistent with the reported $T_c \approx 304$ K for $\text{Ba}_2\text{FeReO}_6$ [19]. Constant momentum transfer cuts detailing the inelastic scattering emerging from the magnetic zone center are shown in Fig. 3 (b). The fluctuation-dissipation theorem $S(Q, E) = (n(E, T) + 1)\chi''(Q, E)$ relates the imaginary component of the dynamic susceptibility $\chi''(Q, E)$ to the dynamic structure factor measured directly by neutron scattering where $n(E, T)$ is the Bose thermal occupation factor. Correcting the INS intensity by the Bose factor allows for comparison of the inelastic scattering across the entire 400 K temperature range on a single intensity scale. Two strong inelastic features are visible near 25 meV and 39 meV which decrease in intensity upon increasing temperature. The temperature, momentum, and energy dependence of the low-Q inelastic scattering is entirely consistent with expectations for scattering from powder averaged spin-waves. Broader examination of the data reveals two bands of phonon scattering which partially obscures the magnetic signal above 3 \AA^{-1} ; however, the phonon and magnetic scattering are well resolved since the magnetic form factor rapidly attenuates the magnetic intensity with increasing Q while the phonon scattering intensity increases with Q (see Supplemental Material). Constant energy cuts across the low energy magnetic scattering are shown in Fig. 3 (c). An inelastic fea-

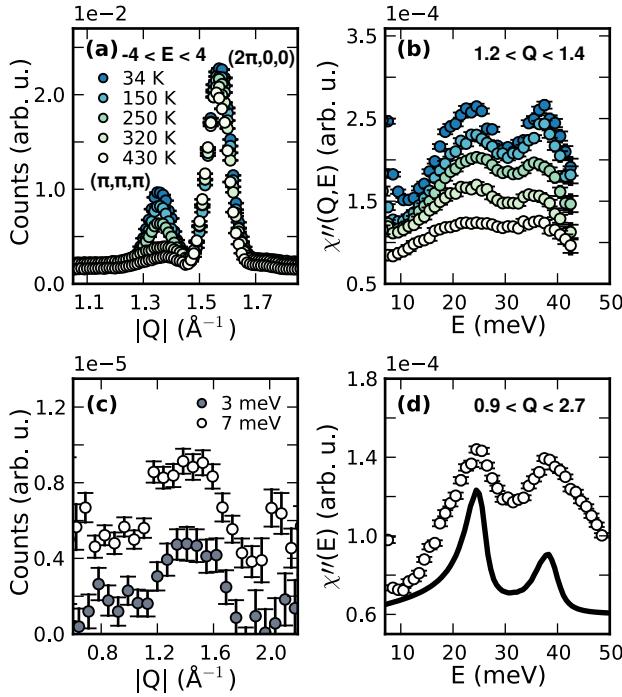


FIG. 3. Representative cuts through $S(Q,E)$. (a) Temperature dependence of magnetic Bragg peaks at $\{\pi, \pi, \pi\}$ and $\{2\pi, 0, 0\}$ determined by integrating the $E_i = 120$ meV data over the elastic line resolution $[-4 < E < 4$ meV]. (b) Temperature dependence of Bose factor corrected inelastic scattering near the magnetic zone center. (c) Constant energy cuts from the $E_i = 27$ meV data at 34 K, each energy cut was integrated over ± 1 meV, the 7 meV cut is offset for clarity. (d) Bose factor corrected inelastic scattering at 34 K integrated over a magnetic Brillouin zone representing the magnetic density of states, the solid line is an equivalent cut from the spin wave model calculation. An empty can background has been subtracted from data in (c) and (d).

ture emerging from the antiferromagnetic zone center is clearly resolved within our experimental resolution down to at least 3 meV. The scattering intensity is strongest near the antiferromagnetic wavevector at $Q=1.35$ Å⁻¹ — where the structure factor for magnetic scattering is maximized — and is small near the nuclear Bragg peak. This Q-dependence identifies the low energy inelastic scattering as magnetic in origin and places an upper bound of 3 meV for any gap in the spin wave dispersion. The Q-integrated inelastic intensity is peaked at the magnon zone boundary energy where the density of states for spin waves is maximized, enabling a precise determination of the zone-boundary energies from the powder averaged spectrum. The dynamic susceptibility integrated over the magnetic Brillouin zone is shown in Fig. 3 (d); scattering is strongly peaked at 25 meV and 39 meV. An equivalent cut from the powder averaged spin wave theory using the same parameters as in Fig. 2 (c) and (d) is also shown in the figure.

Local moment model: The well-defined magnetic modes in Fig. 2, and the fact that the closely related material Ca₂FeReO₆ is an insulator, suggests that strong electronic correlations are important in Ba₂FeReO₆. A local moment model thus provides a useful vantage point to describe its magnetic excitations. The simplest such Hamiltonian is $H=\mathcal{J}\sum_{\langle rr'\rangle}\vec{S}_r\vec{\mathcal{F}}_{r'}-\lambda\sum_{r\in Re}\vec{L}_r\vec{S}_r$, with a nearest neighbor antiferromagnetic exchange interaction between the Fe spin $\vec{\mathcal{F}}$ and the Re spin \vec{S} induced by intersite tunneling. In addition, we include SOC between orbital (\vec{L}) and spin (\vec{S}) angular momentum on Re. We ignore SOC on Fe. This model should be broadly applicable to many DPs with an orbitally nondegenerate magnetic B-site (e.g., Fe), and a magnetic B'-site with active t_{2g} orbitals (e.g., Re).

On the Fe sites, a nominal valence assignment of Fe³⁺ together with a strong Hund's coupling leads to a spin $\mathcal{F}=5/2$. On the Re sites, a nominal valence assignment of Re⁵⁺ ($5d^2$) leads to two electrons in the t_{2g} orbital. Thus, in contrast to the iridates, not only SOC but also Hund's coupling (J_H) is important in determining the magnetic state on Re [32]. The interaction Hamiltonian together with the SOC, when projected to the t_{2g} orbital [33], takes the form

$$H_{\text{Re}}=-2J_H\vec{S}^2-\frac{J_H}{2}\vec{L}^2-\lambda(\vec{l}_1\cdot\vec{s}_1+\vec{l}_2\cdot\vec{s}_2), \quad (1)$$

where $\vec{S}=\vec{s}_1+\vec{s}_2$ and $\vec{L}=\vec{l}_1+\vec{l}_2$. As seen in Fig. 4(a), H_{Re} supports a 5-fold degenerate ground state over a wide range of J_H/λ (see Supplemental Material). For $J_H/\lambda \gtrsim 1$, Fig. 4(b) shows that this ground state manifold may be viewed as made up of $L=1$ and $S=1$ moments locked into a state with total angular momentum $\vec{\mathcal{R}}=\vec{L}+\vec{S}$, with $\mathcal{R}=2$.

For Ba₂FeReO₆, where $\lambda \gg \mathcal{J}$, the local moment Hamiltonian simplifies to $H_{\text{eff}}=\mathcal{J}_{\text{eff}}\sum_{\langle rr'\rangle}\vec{\mathcal{R}}_r\cdot\vec{\mathcal{F}}_{r'}$, yielding an effective Heisenberg model with moments \mathcal{R}, \mathcal{F} on the Re and Fe sites, respectively. We find that $\mathcal{J}_{\text{eff}}=\mathcal{J}\frac{\mathcal{R}(\mathcal{R}+1)+S(S+1)-L(L+1)}{2\mathcal{R}(\mathcal{R}+1)}$; for $L=S=1$, and $\mathcal{R}=2$, we obtain $\mathcal{J}_{\text{eff}}=\mathcal{J}/2$. We expect that the metallic nature of Ba₂FeReO₆, and the concomitant carrier delocalization, will lead to a smaller effective value of \mathcal{F}, \mathcal{R} compared to this highly localized viewpoint.

Spin wave dispersion: The model H_{eff} has a ferrimagnetic ground state, with antiferromagnetic order of $\vec{\mathcal{F}}$ and $\vec{\mathcal{R}}$ leading to a net ordered moment. A spin wave calculation [34] around this ground state yields two modes, with energies $\Omega_{\pm}(\mathbf{q})=\sqrt{\mathcal{S}_{\pm}^2\gamma_0^2-\mathcal{F}\mathcal{R}\gamma_{\mathbf{q}}^2}\pm\mathcal{S}_{-}\gamma_0$ where $\mathcal{S}_{\pm}=(\mathcal{F}\pm\mathcal{R})/2$, and $\gamma_{\mathbf{q}}=2\mathcal{J}_{\text{eff}}(\cos q_x+\cos q_y+\cos q_z)$, with $\gamma_0=6\mathcal{J}_{\text{eff}}$. At the ordering wavevector, Ω_- has a gapless quadratic dispersion, while Ω_+ has a gap $2\mathcal{S}_{-}\gamma_0$. At $T=0$, we find the dynamic structure factor for transverse spin fluctuations

$$S_{\perp}(\mathbf{q},\omega)=2\pi\sum_{\sigma=\pm}(G_{\mathbf{q}}-\sigma\mathcal{S}_{-})\delta(\omega-\Omega_{\sigma}(\mathbf{q})) \quad (2)$$

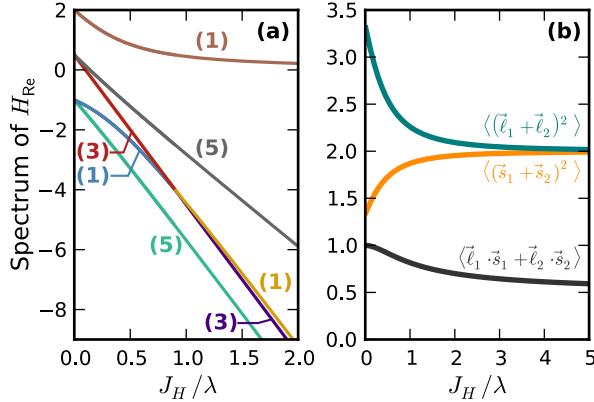


FIG. 4. (a) Spectrum of H_{Re} (in units of λ) versus J_H/λ , with degeneracies indicated in brackets. For $J_H=0$, the eigenstates at three distinct energies correspond to different ways of filling two electrons into SO coupled single-particle states with angular momentum $j = 3/2$ and $j = 1/2$. When $\lambda = 0$, we find two-particle angular momentum eigenstates 3P , 1D , and 1S in increasing order of energy. A weak SO coupling, with $J_H/\lambda \gg 1$, splits the lowest 3P manifold into 3P_2 , 3P_1 , 3P_0 . (b) Interaction dependence of total orbital and spin angular momentum, and magnitude of SO energy. For $J_H \gtrsim \lambda$, the ground state is composed of $L=1, S=1$ moments which lock to yield a total angular momentum $\vec{\mathcal{R}} = \vec{L} + \vec{S}$, with $\mathcal{R}=2$.

where $G_{\mathbf{q}} = (\gamma_0 S_+^2 - \gamma_{\mathbf{q}} \mathcal{F} \mathcal{R}) / \sqrt{S_+^2 \gamma_0^2 - \mathcal{F} \mathcal{R} \gamma_{\mathbf{q}}^2}$. As shown in Fig. 2(a-d) and Fig. 3(d), setting $\gamma_0 \mathcal{F} = 39$ meV and $\gamma_0 \mathcal{R} = 25$ meV in the theoretical plots leads to a broad agreement between the experimental data and the powder averaged theoretical result for $S(\mathbf{q}, \omega)$, both in the existence and dispersion of the two magnetic modes, and in the (near) gaplessness of the lower energy mode.

Spin-orbital locking on Re: For momenta with $\gamma_{\mathbf{q}}=0$, the spin wave dispersion yields $\Omega_+/\Omega_- = \mathcal{F}/\mathcal{R}$. Since these momenta dominate the magnon density of states, we can use the ratio of the observed peak positions in Fig. 3 (39 meV, 25 meV), to deduce that $\mathcal{F}/\mathcal{R} \approx 1.6$. If we assume that the Re moments have a pure spin origin, we have to set $\mathcal{R} \lesssim 1$. This assumption, however, yields a Fe spin $\mathcal{F} \lesssim 1.6$, which is anomalously low — first principles calculations [20, 35], a naïve valence assignment of Fe^{3+} , and the measured large saturation magnetization [30], all point to a much larger Fe moment. Our observations thus strongly suggest that we must have $\mathcal{R} > 1$, indicating a nonzero orbital contribution to the Re moment, in qualitative agreement with XMCD measurements.

In order to obtain estimates of the moment sizes and the exchange coupling, we combine our INS results with previous XMCD and magnetization data. XMCD measurements indicate a significant static orbital contribution to the magnetization on Re, with $\mu_{\text{Re}}^{\text{orb}}/\mu_{\text{Re}}^{\text{spin}} \approx -0.3$. This allows us to set $L \approx 0.6S$, which yields $S \approx 0.63\mathcal{R}$ and $L \approx 0.37\mathcal{R}$. High field magnetization measurements on $\text{Ba}_2\text{FeReO}_6$ indicate a saturation magnetization $m_{\text{sat}} \approx$

$3\mu_B$. Together with our neutron data, this constrains the moment sizes to be $\mathcal{R} \approx 1.3$ and $\mathcal{F} \approx 2.1$, yielding an estimated exchange coupling $\mathcal{J}_{\text{eff}} \approx 3.1$ meV. We have checked that including a small direct Re-Re Heisenberg exchange $\sim 0.1\mathcal{J}_{\text{eff}}$ slightly modifies the spin wave dispersion but does not significantly affect our estimate of \mathcal{R} . (A large Re-Re exchange coupling leads to a dispersion which is not consistent with our data.) Thus, while previous XMCD measurements on $\text{Ba}_2\text{FeReO}_6$ have shown that there is a static orbital contribution to the ordered magnetic moment on Re in the ferrimagnetic state, our work shows that such SO locked moments on Re also play a role in the low energy magnetic excitations.

Magnetic transition temperature: We use the above values of the moment sizes and exchange couplings to estimate the magnetic T_c . The nearest neighbor classical Heisenberg model on a three-dimensional cubic lattice, with moments \mathcal{F}, \mathcal{R} on the two sublattices, has a mean field transition temperature $2\mathcal{J}_{\text{eff}}\mathcal{F}\mathcal{R}$. Assuming a quantum renormalized $T_c \approx 2\mathcal{J}_{\text{eff}}\sqrt{\mathcal{F}\mathcal{R}}(\sqrt{\mathcal{F}\mathcal{R}} + 1)$, we estimate $T_c \approx 315$ K, in rough agreement with the measured $T_c^{\text{expt}} \approx 304$ K. If one takes the limit of fully localized moments, setting $\mathcal{F} = 2.5$ and $\mathcal{R} = 2$, one obtains $T_c \approx 520$ K, remarkably close to that of the insulating compound $\text{Ca}_2\text{FeReO}_6$. T_c calculations retaining the itinerant Re electrons will be reported elsewhere.

Structural transition and absence of spin gap: $\text{Ba}_2\text{FeReO}_6$ has a weak tetragonal distortion, with $c/a < 1$, which onsets at the magnetic T_c [19]. Since a Jahn-Teller distortion would lead to $c/a > 1$, not necessarily coincident with T_c , we ascribe this distortion to SOC. Going beyond H_{eff} , we expect a term $-\epsilon \sum_{\mathbf{r}} (\mathcal{R}_{\mathbf{r},x}^4 + \mathcal{R}_{\mathbf{r},y}^4 + \mathcal{R}_{\mathbf{r},z}^4)$, arising from the cubic anisotropy, which locks the Re moment (and thus also the Fe spins) to the crystal axes. Such a magnetostructural locking term with $\epsilon > 0$ explains the observed tetragonal distortion at T_c as arising from weak orbital order, and would lead to a spin gap of order ϵ . This locking is expected to be small; on experimental grounds since we find no clear evidence of a spin gap, and on theoretical grounds since it arises from a spin-orbit induced weak mixing of well-separated t_{2g} and e_g crystal field levels [32]. A small magnetostructural locking term is consistent with the measured weak coercive field ~ 0.2 Tesla.

Summary: We have used inelastic neutron scattering and theoretical modelling to study the magnetic excitations in $\text{Ba}_2\text{FeReO}_6$, inferring the presence of strong correlations and spin orbit coupled moments on Re, and obtaining a broad understanding of the phenomenology in its ferrimagnetic state. Further efforts are necessary to synthesize single crystals or good quality thin films of $\text{Ba}_2\text{FeReO}_6$ and other DPs. In future work, we will extend our experiments to other DP materials, and incorporate the itinerant character of Re electrons in our theoretical modelling, both of which would lead to a better understanding of novel 5d-based TMOs.

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INTERACTION EFFECTS: ATOMIC LIMIT

For the $d^{(2)}, d^{(3)}, d^{(4)}$ configuration of electrons in the t_{2g} orbital, we have to consider matrix elements of the Coulomb interaction on the same footing as the spin orbit coupling. The interaction Hamiltonian projected to the t_{2g} orbitals is given by[36]

$$\begin{aligned} H_{\text{int}} = & U \sum_{\alpha} n_{\alpha\uparrow} n_{\alpha\downarrow} + (U - 5 \frac{J_H}{2}) \sum_{\alpha<\beta} n_{\alpha} n_{\beta} \\ & - 2J_H \sum_{\alpha<\beta} \vec{S}_{\alpha} \cdot \vec{S}_{\beta} + J_H \sum_{\alpha \neq \beta} d_{\alpha\uparrow}^{\dagger} d_{\alpha\downarrow}^{\dagger} d_{\beta\downarrow} d_{\beta\uparrow}. \end{aligned} \quad (3)$$

After some algebra, this can be reexpressed in terms of rotationally invariant operators as

$$H_{\text{int}} = \frac{U - 3J_H}{2} n_{\text{tot}}^2 - 2J_H \vec{S}_{\text{tot}}^2 - \frac{J_H}{2} \vec{L}_{\text{tot}}^2 \quad (4)$$

where we assume the normal ordered form of these operators. For a $d^{(2)}$ configuration, $n_{\text{tot}} = 2$. Including the spin orbit coupling term leads to the effective atomic Hamiltonian for Re

$$H_{\text{Re}} = -2J_H \vec{S}^2 - \frac{J_H}{2} \vec{L}^2 - \lambda(\vec{\ell}_1 \cdot \vec{s}_1 + \vec{\ell}_2 \cdot \vec{s}_2) \quad (5)$$

where $\vec{L} = \vec{\ell}_1 + \vec{\ell}_2$ and $\vec{S} = \vec{s}_1 + \vec{s}_2$. To diagonalize this Hamiltonian for a $d^{(2)}$ configuration, we write the full Hamiltonian in the basis $|L, m_{\ell}, S, m_s\rangle$ corresponding to total orbital and total spin angular momentum. Since the individual orbital angular momenta $\ell_1 = \ell_2 = 1$ and individual spin angular momenta are $s_1 = s_2 = 1/2$, we use a shorthand for the Clebsch-Gordan coefficients, defining them via

$$|L, m_{\ell}, S, m_s\rangle = |L, m_{\ell}\rangle \otimes |S, m_s\rangle \quad (6)$$

$$|L, m_{\ell}\rangle = \sum_{m_1, m_2} C_{m_1, m_2}^{L, m_{\ell}} |m_1, m_2\rangle \quad (7)$$

$$|S, m_s\rangle = \sum_{s_1, s_2} C_{s_1, s_2}^{S, m_s} |s_1, s_2\rangle \quad (8)$$

in terms of which the full Hamiltonian becomes

$$\langle L', m'_{\ell}, S', m'_s | H_{\text{at}}^{(2)} | L, m_{\ell}, S, m_s \rangle \equiv H_{L, m_{\ell}, S, m_s}^{L', m'_{\ell}, S', m'_s} \quad (9)$$

where

$$\begin{aligned} H_{L, m_{\ell}, S, m_s}^{L', m'_{\ell}, S', m'_s} = & \delta_{L, L'} \delta_{S, S'} \delta_{m'_{\ell}, m_{\ell}} \delta_{m'_s, m_s} E_{L, S} \\ & - \lambda \sum_{m_1, m_2, s_1, s_2} C_{m_1, m_2}^{L, m_{\ell}} C_{s_1, s_2}^{S, m_s} (2m_1 s_1 \bar{C}_{m_1, m_2}^{L', m'_{\ell}} \bar{C}_{s_1, s_2}^{S', m'_s} \\ & + \sqrt{2} \bar{C}_{m_1+1, m_2}^{L', m'_{\ell}} \bar{C}_{s_1-1, s_2}^{S', m'_s} + \sqrt{2} \bar{C}_{m_1-1, m_2}^{L', m'_{\ell}} \bar{C}_{s_1+1, s_2}^{S', m'_s}) \end{aligned} \quad (10)$$

and

$$E_{L, S} = \left[-2J_H S(S+1) - \frac{J_H}{2} L(L+1) \right] \quad (11)$$

Here, we must restrict ourselves to totally antisymmetric electronic states; $(L, S) = (0, 0), (1, 1), (2, 0)$ yield the allowed 15 basis states.

When $J_H = 0$, we find eigenstates at three distinct energies corresponding to filling two electrons into single-particle states corresponding to a low energy $j = 3/2$ manifold or a higher energy $j = 1/2$ doublet. On the other hand, when $\lambda = 0$, we find H_{Re} has, in increasing order of energy, total angular momentum eigenstates 3P , 1D , and 1S .

The numerically computed spectrum of H_{Re} is shown in Fig. 4 of the paper. Over a wide range of J_H/λ , we find a 5-fold degenerate ground state when spin-orbit coupling competes with J_H . For $J_H/\lambda \gg 1$, we can show that the 3P ground states at $\lambda = 0$ split into spin-orbit coupled states which may be labelled by total angular momentum $L + S = 2, 1, 0$ in increasing order of energy. (corresponding to ${}^3P_2, {}^3P_1, {}^3P_0$ states with degeneracies 5, 3, 1). This shows that a local $-\lambda \vec{L} \cdot \vec{S}$, with $L = S = 1$, is a good description of the lowest energy manifold of states when $J_H/\lambda \gtrsim 1$. However, when $J_H \lesssim \lambda$, this sequence changes to 5, 1, 3 (in ascending order) suggesting that such a simple description fails.

PHONON BACKGROUND

The measured scattering intensity consists of a number of components including coherent nuclear and magnetic scattering, as well as incoherent processes. Additional background scattering originating from the sample environment, and detector dark current is eliminated by subtracting the signal measured for an empty Al sample can using identical instrumental configuration. The signal of interest is coherent scattering from magnons, which has a momentum dependent intensity dominated by the magnetic form factor. In general, the magnetic form-factor rapidly decays as a function of Q , thus the magnetic INS intensity will decrease with increasing Q . In contrast, both coherent scattering from phonons and incoherent nuclear scattering intensities increase quadratically with Q in a powder averaged measurement [37]. Any periodic modulations of the coherent phonon scattering arising from the structure factor should also increase in intensity with Q .

A map of the inelastic neutron scattering at 34 K, for 120 meV incident energy is shown in Fig. 5 (a). There are three bands of inelastic scattering, around 25, 40, and 70 meV which increase in intensity with increasing Q . We associate each of these with three phonon bands. The magnetic signal emerges from the antiferromagnetic zone center at $Q = 1.35 \text{ \AA}^{-1}$ and extends into two bands with maximum intensities at 25 meV and 39 meV.

To highlight the momentum dependence of the scattering intensities constant energy cuts through each band of inelastic scattering are shown in Fig. 5 (b) – (d). Around 70 meV, [Fig. 5 (b)], the scattering is dominated by phonons, here the momentum dependence of scattering intensity is entirely described by the quadratic form

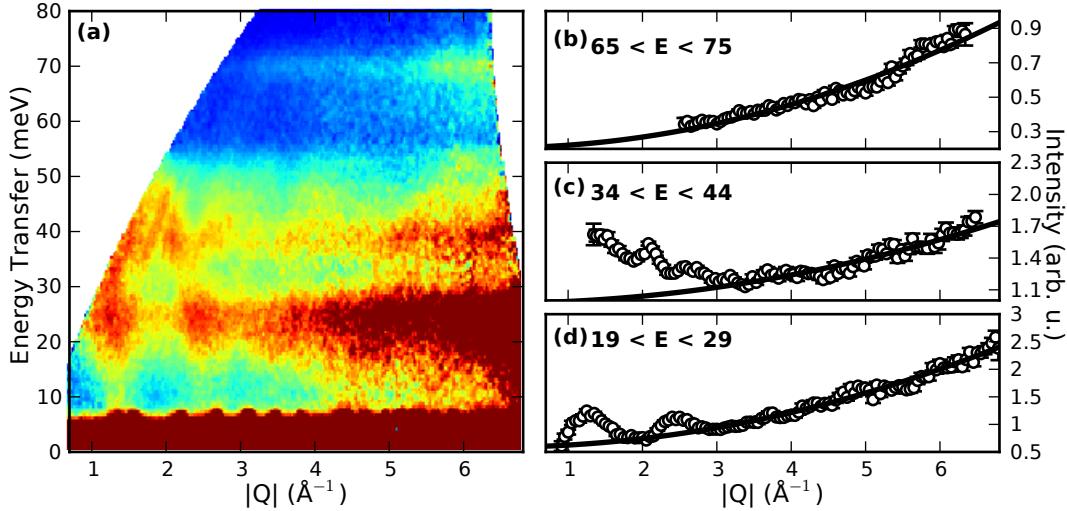


FIG. 5. (a) Neutron scattering intensity at 34 K for and incident energy of 120 meV. An empty Al can background has been subtracted from the data. (b)—(d) Constant energy cuts across bands of inelastic scattering at 70, 40 and 25 meV respectively. Solid black lines are a fit to $I(Q) = A(E) + BQ^2$ delimiting the Q-dependent contribution of phonon scattering at each energy.

$I(Q) = A(E) + BQ^2$, where A is a constant function of Q parameterizing background originating from the small multiple scattering contributions to the inelastic scattering. On average A is a decaying function of energy. In Fig. 5 (c) and (d) the overall intensity increases with increasing Q at high Q , and above $Q = 3 \text{ \AA}^{-1}$ the scattering is dominated by phonons, as can be seen from the fits to $I(Q)$ (solid black lines). However, below $Q = 3 \text{ \AA}^{-1}$ the INS intensity clearly increases above the phonon background with decreasing Q . Furthermore in Fig. 5 (d) the low Q scattering intensity modulation is consistent with

the magnetic Brillouin zone. Thus, the magnetic scattering is well separated in Q from the phonon scattering, and the magnetic scattering is clearly identified through momentum, and temperature dependencies (see Fig. 3 of the main text). We note that the two lower phonon modes, which are common to many perovskite materials, are at energies which are not far from the zone-boundary magnon mode energies. Further single crystal inelastic neutron scattering measurements are required to determine whether this is a mere coincidence, or a result of magnon-phonon coupling in this material.