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Van Vleck Excitonic Magnetism in Ruthenium Pyrochlores

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Abstract

Strong spin-orbit coupling in d^4 systems is expected to stabilize a nonmagnetic $J = 0$ singlet ground state, yet many ruthenium pyrochlores exhibit robust long-range magnetic order. Motivated by this apparent contradiction, we develop a microscopic theory of Van Vleck excitonic magnetism on the pyrochlore lattice. Starting from a multi-orbital Hubbard model with spin-orbit coupling, we derive the effective superexchange interactions within the low-energy singlet-triplet manifold of Ru^{4+} ions. We analyze the resulting excitonic Hamiltonian using both the spectrum of triplon excitations and a variational treatment of the condensed phase. We identify the instability of the nonmagnetic singlet state toward triplon condensation and determine the resulting magnetic phase diagram as a function of the microscopic hopping parameters. The phase diagram reproduces the magnetic orders known from conventional pyrochlore models while also predicting an additional magnetic phase unique to the singlet-triplet description. Finally, we apply the theory to the pyrochlore ruthenates, with particular emphasis on $\text{Nd}_2\text{Ru}_2\text{O}_7$, and show that it lies in close proximity to the excitonic quantum critical point. Our results establish a microscopic framework for understanding excitonic magnetism in pyrochlore ruthenates and their magnetic excitation spectrum, providing direct connections to spectroscopic probes, including Raman scattering.

Introduction

The interplay of orbital, spin, and lattice degrees of freedom has long been recognized as a central organizing principle of transition-metal oxides. A cornerstone of this field is the Kugel-Khomskii theory, which established how superexchange couples spin and orbital degrees of freedom, giving rise to a rich variety of collective phases in transition-metal oxides [1]. In the presence of strong spin-orbit coupling, however, spin and orbital degrees of freedom become further entangled, leading to unconventional forms of magnetism that go beyond the standard paradigm of localized moments. A representative example is provided by d^4 systems, where spin-orbit coupling favors a nonmagnetic $J = 0$ ground state. At first sight, such systems appear incompatible with magnetic order, since well-defined local moments are absent. Remarkably, however, exchange interactions can drive the coherent condensation of low-energy singlet-triplet excitations. This mechanism, proposed by Khaliullin [2], established the concept of Van Vleck *excitonic* magnetism, in which magnetic order arises from the condensation of spin-orbit excitons rather than from preformed local moments.

The excitonic scenario has stimulated extensive theoretical and experimental studies of $4d^4$ ruthenates [3, 4, 5, 6, 7, 8, 9], particularly Ca_2RuO_4 [3, 4, 5, 6, 10], where excitonic magnetism and its collective excitations have been investigated in considerable detail. It has also inspired extensive work on $5d^4$ iridates [11, 12, 13, 14, 15, 16, 17, 18, 19], particularly the double perovskites Sr_2YIrO_6 [11, 12] and Ba_2YIrO_6 [13, 14, 15], where the realization of a $J = 0$ ground state and the extent to which excitonic magnetism is realized remain subjects of active debate. Together, these studies have established excitonic magnetism as a realistic mechanism of magnetic order and identified a growing family of candidate materials.

An important open question is how excitonic magnetism is modified by lattice geometry, particularly in frustrated three-dimensional systems. Pyrochlore ruthenates $A_2\text{Ru}_2\text{O}_7$, where A is a rare-earth ion, provide an ideal platform to address this question [20, 21, 22, 23, 24, 25, 26, 27]. In these materials, Ru ($4d^4$) ions form a network of corner-sharing tetrahedra that combines strong spin-orbit coupling, geometric frustration, and bond-dependent hopping processes. Moreover, the rare-earth series provides a natural

route for tuning structural distortions and exchange interactions, enabling a systematic exploration of the excitonic regime. These characteristics make pyrochlore ruthenates a unique setting in which to investigate Van Vleck excitonic magnetism beyond the layered and perovskite compounds studied so far.

Although the local electronic structure of Ru ions suggests a nonmagnetic $J = 0$ singlet ground state, many pyrochlore ruthenates develop long-range magnetic order of the Ru sublattice at temperatures of order 100 K [20, 23, 28, 29, 30, 31, 32, 33]. This coexistence of a nominally nonmagnetic ion with robust magnetic order presents a central puzzle for the entire family of compounds. One possible interpretation is that crystal-field effects compete with spin-orbit coupling, driving the system away from the ideal $J = 0$ limit toward a more conventional $S = 1$ local-moment description, as assumed in previous studies of spin-1 pyrochlore antiferromagnets [34]. An alternative explanation is provided by the excitonic scenario, in which intersite exchange interactions overcome the singlet-triplet gap and drive the condensation of spin-orbit excitons. Establishing whether this mechanism is realized in pyrochlore ruthenates requires a microscopic theory that connects the multi-orbital electronic structure of Ru^{4+} ions to the magnetic ground state and its collective excitation spectrum.

In this work, we develop a microscopic theory of Van Vleck excitonic magnetism on the pyrochlore lattice. Starting from a multi-orbital Hubbard model with spin-orbit coupling, we derive the effective superexchange interactions within the local singlet-triplet manifold of Ru^{4+} ions. We determine the conditions under which the nonmagnetic $J = 0$ state becomes unstable toward triplon condensation and construct the resulting magnetic phase diagram. Besides reproducing the magnetic orders familiar from conventional spin-1 pyrochlore models, the excitonic framework predicts an additional magnetic phase that is unique to the singlet-triplet description.

Among the pyrochlore ruthenates, $\text{Nd}_2\text{Ru}_2\text{O}_7$ provides an ideal testing ground for this theory. Its Ru magnetic order has been characterized by neutron diffraction and magnetization measurements [21, 23], while recent Raman scattering experiments have revealed well-defined low-energy magnetic excitations associated with the Ru sublattice [25, 26]. These complementary experimental results provide strong constraints for a microscopic theory of excitonic magnetism. We therefore apply our microscopic framework to this material and show that it lies in close proximity to the excitonic quantum critical point, providing a unified description of its magnetic ground state and excitation spectrum.

Results

Lattice and single-ion physics

In pyrochlore ruthenates $\text{A}_2\text{Ru}_2\text{O}_7$, the Ru ions form a network of corner-sharing tetrahedra [see Fig. 1(a)], which provides the lattice geometry for the excitonic degrees of freedom considered below. The rare-earth A -site ions may also carry magnetic moments [20, 21]. However, their ordering typically occurs at much lower energy scales and can often be treated separately from the Ru-sublattice magnetism. For example, in $\text{Nd}_2\text{Ru}_2\text{O}_7$, the Nd moments order into an AIAO configuration only below ~ 1.8 K [23].

On the pyrochlore lattice of Ru ions, each primitive unit cell contains four sublattice sites forming a tetrahedron. Nearest-neighbor bonds are classified by their orientation with respect to the global cubic axes: bonds perpendicular to the X , Y , and Z directions are referred to as $X(X')$ -, $Y(Y')$ -, and $Z(Z')$ -bonds, respectively. Each Ru ion is surrounded by an oxygen octahedron, and neighboring octahedra share corners, giving rise to bond-dependent local environments. The four sublattice sites thus have distinct local coordinate frames, as illustrated for sites 1 and 4 on the Z -bond in Fig. 1(a).

The corner-sharing geometry can be understood by starting from two edge-sharing oxygen octahedra aligned with the global coordinate frame and counter-rotating them about the global $[1\bar{1}0]$ axis until one pair of oxygen ions coincides, thereby forming a corner-sharing configuration [see Fig. 1(a)]. For ideal octahedra, this rotation angle is $\arctan(2\sqrt{2})$, resulting in a bond angle $\angle\text{Ru-O-Ru} = 2\arctan(2\sqrt{2}) \approx 141.058^\circ$ at the bridging oxygen. As a result, each Ru site acquires its own local Cartesian frame, e.g., $(\hat{x}_1, \hat{y}_1, \hat{z}_1)$ and $(\hat{x}_4, \hat{y}_4, \hat{z}_4)$ in Fig. 1(a), in which the t_{2g} orbitals are naturally defined. The explicit local axes and the corresponding rotations to the global cubic frame are given in Methods.

At the single-ion level, the local electronic structure is governed by the combined effects of the octahedral crystal field, Hund's coupling J_H , and spin-orbit coupling (SOC) λ . The crystal field splits the five d orbitals into lower-energy t_{2g} and higher-energy e_g states. Since the e_g states lie far above the energy scales relevant here, we focus exclusively on the t_{2g} manifold. Within the t_{2g} manifold, Hund's coupling favors states with spin $S = 1$ and effective orbital angular momentum $L_{\text{eff}} = 1$. SOC further

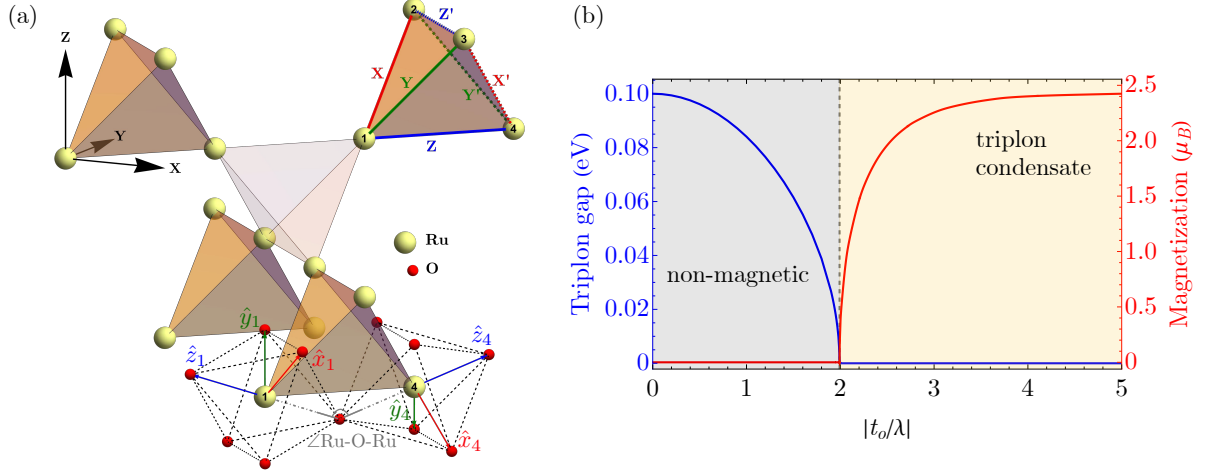


Figure 1: (a) Pyrochlore lattice of Ru ions, consisting of two types of tetrahedra (dark- and light-shaded). Black arrows (X, Y, Z) indicate the global reference frame. The local reference frames ($\hat{x}_1, \hat{y}_1, \hat{z}_1$) and ($\hat{x}_4, \hat{y}_4, \hat{z}_4$), defined by the surrounding oxygen octahedral cages, are shown for sublattice sites 1 and 4, respectively. The nearest-neighbor bonds are marked in red, blue, and green within the top-right tetrahedron. In the ideal pyrochlore structure, the bond angle at the bridging oxygen between two neighboring Ru ions is $\angle \text{Ru-O-Ru} = 2 \arctan(2\sqrt{2}) \approx 141.058^\circ$. (b) Triplon gap (blue) and the magnetization (red) as a function of oxygen-assisted hopping to spin-orbit coupling constant, $|t_o/\lambda|$, in the ideal structure of pyrochlore lattice. The dashed line marks the phase transition from a non-magnetic singlet ground state to a triplon condensation with finite magnetization, signaling magnetic ordering of the Ru moments.

lifts this degeneracy, yielding a $J = 0$ singlet ground state and excited $J = 1$ and $J = 2$ multiplets, with a singlet-triplet gap of λ and a triplet-quintet gap of 2λ [35].

To describe the relevant physics, we write the single-ion Hamiltonian on the t_{2g} manifold as

$$\mathcal{H}_{\text{ion}} = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{SOC}} + \mathcal{H}_{\Delta}, \quad (1)$$

where $\mathcal{H}_{\text{int}}$ is the multi-orbital Hubbard Hamiltonian that accounts for on-site Coulomb and Hund's interactions, $\mathcal{H}_{\text{SOC}}$ for the SOC, and $\mathcal{H}_{\Delta}$ for trigonal crystal-field distortions that vanish in the ideal octahedral limit. The SOC term is given by

$$\mathcal{H}_{\text{SOC}} = \lambda \sum_i \mathbf{S}_i \cdot \mathbf{L}_i, \quad (2)$$

where $\mathbf{S}_i$ and $\mathbf{L}_i$ are the spin and effective orbital angular momentum operators projected onto the t_{2g} manifold, with $L_{\text{eff}} = 1$. This coupling splits the local Hilbert space into multiplets of total angular momentum J . In the following, we focus on the low-energy sector spanned by the $J = 0$ singlet and $J = 1$ triplet states. The interaction term reads

$$\begin{aligned} \mathcal{H}_{\text{int}} = \sum_i \bigg(& U_1 \sum_{\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \frac{1}{2} (U_2 - J_H) \sum_{\alpha \neq \alpha', \sigma} n_{i\alpha\sigma} n_{i\alpha'\sigma} + U_2 \sum_{\alpha \neq \alpha'} n_{i\alpha\uparrow} n_{i\alpha'\downarrow} \\ & + J_H \sum_{\alpha \neq \alpha'} d_{i\alpha\uparrow}^\dagger d_{i\alpha\downarrow}^\dagger d_{i\alpha'\downarrow} d_{i\alpha'\uparrow} - J_H \sum_{\alpha \neq \alpha'} d_{i\alpha\uparrow}^\dagger d_{i\alpha\downarrow} d_{i\alpha'\downarrow}^\dagger d_{i\alpha'\uparrow} \bigg), \end{aligned} \quad (3)$$

where $d_{i\alpha\sigma}^\dagger$ ($d_{i\alpha\sigma}$) creates (annihilates) an electron at site i in orbital α with spin σ , $\alpha = yz, xz, xy$ labels the three t_{2g} orbitals, U_1 and U_2 are the intra- and inter-orbital Coulomb repulsions, J_H is Hund's coupling, and cubic symmetry enforces $U_1 = U_2 + 2J_H$.

Restricting to the $J = 0$ and $J = 1$ manifold, the singlet and triplet states can be written in terms of

$|L_z S_z\rangle$ eigenstates as

$$\begin{aligned}
|s\rangle &= |J=0, J_z=0\rangle = \frac{1}{\sqrt{3}} \left(|\bar{1}1\rangle - |00\rangle - |1\bar{1}\rangle \right), \\
|T_1\rangle &= |J=1, J_z=1\rangle = \frac{1}{\sqrt{2}} \left(|\bar{1}0\rangle - |0\bar{1}\rangle \right), \\
|T_0\rangle &= |J=1, J_z=0\rangle = \frac{1}{\sqrt{2}} \left(|1\bar{1}\rangle + |\bar{1}1\rangle \right), \\
|T_{\bar{1}}\rangle &= |J=1, J_z=-1\rangle = \frac{1}{\sqrt{2}} \left(|10\rangle + |01\rangle \right).
\end{aligned} \tag{4}$$

The triplet states $\{|T_1\rangle, |T_0\rangle, |T_{\bar{1}}\rangle\}$ are eigenstates of J_z and form the magnetic basis. However, in the absence of hopping the ground state is a $J=0$ singlet, invariant under time reversal. It is therefore more natural to work in a basis that respects this symmetry. We introduce the Cartesian “tripion” basis $\{|T^x\rangle, |T^y\rangle, |T^z\rangle\}$ [36]:

$$\begin{aligned}
|T^x\rangle &= \frac{1}{i\sqrt{2}} (|T_1\rangle - |T_{\bar{1}}\rangle), \\
|T^y\rangle &= \frac{1}{\sqrt{2}} (|T_1\rangle + |T_{\bar{1}}\rangle), \\
|T^z\rangle &= i|T_0\rangle,
\end{aligned} \tag{5}$$

which is manifestly time-reversal invariant. Together with the singlet state, these states define the local low-energy Hilbert space on each site i :

$$\{|\tau_i^\alpha\rangle\} = \{|s_i\rangle, |T_i^x\rangle, |T_i^y\rangle, |T_i^z\rangle\} \tag{6}$$

enumerated by $\alpha = 0, 1, 2, 3$, where $\alpha = 0$ labels the singlet state and $\alpha = 1, 2, 3$ label three triplet states. This construction is closely related to the excitonic representation introduced by Khaliullin [2] and further developed for tetragonal ruthenates such as Ca_2RuO_4 [3, 5], where a strong tetragonal crystal field splits the triplet manifold and effectively selects a reduced set of states, allowing one to define a pseudospin-1 basis in terms of $\{|s_i\rangle, |T_i^x\rangle, |T_i^y\rangle\}$.

In contrast, for pyrochlore ruthenates the RuO_6 octahedra are uniformly trigonally compressed. Although the trigonal distortion has the same magnitude for every octahedron, the octahedra themselves are differently oriented within the pyrochlore lattice. Consequently, the compression axis coincides with the local [111] direction of each Ru site, described by the unit vector $\mathbf{e}_{i,[111]}$ on site i . Throughout this work we adopt the convention $\Delta > 0$, corresponding to trigonal compression experimentally observed in the $\text{A}_2\text{Ru}_2\text{O}_7$ family of compounds [22, 23, 24, 33, 37, 38, 39, 40, 41, 42, 43, 44]. The resulting trigonal crystal field is described by

$$\mathcal{H}_\Delta = \sum_i \Delta (\mathbf{L}_i \cdot \mathbf{e}_{i,[111]})^2, \tag{7}$$

which splits the cubic t_{2g} manifold into a lower e'_g doublet and an upper a_{1g} singlet. In the limit of a very large trigonal splitting, the lower e'_g doublet becomes completely filled, resulting in the nonmagnetic configuration $e'_g{}^4 a_{1g}^0$ with $S = L = 0$. In pyrochlore ruthenates, however, the trigonal crystal-field splitting is smaller than the Hund’s coupling, making it energetically favorable to promote one electron into the a_{1g} orbital. The resulting high-spin configuration, $e'_g{}^3 a_{1g}^1$, has $S = 1$ and $L_{\text{eff}} = 1$, which are subsequently coupled by the spin-orbit interaction into the $J = 0$, $J = 1$, and $J = 2$ multiplets discussed above.

Effective low-energy Hamiltonian from superexchange

We next derive the superexchange interaction between the local singlet-triplet degrees of freedom. Electron hopping between neighboring Ru ions generates virtual charge fluctuations out of the $d_i^4 d_j^4$ manifold into intermediate $d_i^3 d_j^5$ ($d_i^5 d_j^3$) configurations. Integrating out these virtual states to second order in the hopping and projecting back onto the local $J = 0, 1$ manifold yields an effective superexchange Hamiltonian for the excitonic degrees of freedom. The hopping Hamiltonian is

$$\mathcal{H}_t = \sum_{i,j} \sum_{\alpha,\beta} \sum_{\sigma,\sigma'} t_{ij}^{\alpha,\beta\sigma\sigma'} d_{i\alpha\sigma}^\dagger d_{j\beta\sigma'}. \tag{8}$$

Here $d_{i\alpha\sigma}$ annihilates an electron on site i in the local t_{2g} orbital $\alpha = yz, xz, xy$ and local spin state σ . The hopping amplitudes are bond-dependent and are defined in the local orbital–spin basis. Their matrix structure reflects the geometry of the corner-sharing oxygen octahedra and the corresponding overlap of t_{2g} orbitals in the local coordinate frames.

As an example, the direct hopping matrix for the Z -bond between sites 1 and 4 is shown in Table 1. The hopping on other bonds follows from the C_3 symmetry of the cubic point group T_d . The derivation of the hopping parameters in terms of Slater–Koster parameters is given in Supplementary Information. In the ideal structure of pyrochlore considering only the oxygen-mediated hopping, we have

$$t_1 = t_o/9, \quad t_2 = -8t_o/9, \quad t_3 = 0, \quad t_4 = 0, \quad (9)$$

where the oxygen-mediated hopping amplitude is $t_o \equiv pd\pi^2/\Delta_{pd}$ determined by the overlap $pd\pi$ between t_{2g} orbital and the oxygen p orbital and the charge transfer Δ_{pd} .

	$d_{4,yz}$	$d_{4,xz}$	$d_{4,xy}$		$ \uparrow\rangle_4$	$ \downarrow\rangle_4$
$d_{1,yz}$	t_1	t_2	t_4	$ \uparrow\rangle_1$	$\frac{1}{3}$	$-\frac{2}{3} - \frac{2i}{3}$
$d_{1,xz}$	t_2	t_1	t_4	$ \downarrow\rangle_1$	$\frac{2}{3} - \frac{2i}{3}$	$\frac{1}{3}$
$d_{1,xy}$	$-t_4$	$-t_4$	t_3			

Table 1: (left) Direct hopping amplitudes from site 1 to 4 between t_{2g} orbitals expressed in their respective local basis on the Z -bond. (right) Spin states expressed in the local basis.

Formally, the superexchange Hamiltonian is obtained by second-order degenerate perturbation theory with the hopping Hamiltonian. We start from the two-site $d_i^4 d_j^4$ low-energy manifold, in which each Ru ion has $L_{\text{eff}} = 1$ and $S = 1$. Now we construct the second-order degenerate perturbation

$$\sum_{l'} \sum_I \frac{\langle l' | \mathcal{H}_t | I \rangle \langle I | \mathcal{H}_t | l \rangle}{E_0 - E_I} |l'\rangle \langle l|, \quad (10)$$

where $|l\rangle$ and $|l'\rangle$ belong to the initial $d_i^4 d_j^4$ manifold with energy E_0 , while $|I\rangle$ denotes intermediate charge-transfer states of the form $d_i^3 d_j^5$ ($d_i^5 d_j^3$).

Each contribution in Eq. (10) contains two hopping events: the first creates a virtual $d_i^3 d_j^5$ ($d_i^5 d_j^3$) charge excitation, and the second returns the system to the $d_i^4 d_j^4$ manifold. Expressing Eq. (10) in terms of spin-1 operators and $L = 1$ orbital angular momentum operators yields the Kugel–Khomskii Hamiltonian [1].

Here we are instead interested in the singlet–triplet subspace. Projecting Eq. (10) onto this subspace, we obtain a bond-dependent exchange Hamiltonian for the excitonic degrees of freedom. For convenience, we introduce hard-core bosons $\tau_{i\alpha}$ defined in Eq. (6) subject to the single-occupancy constraint $s_i^\dagger s_i + T_i^{x\dagger} T_i^x + T_i^{y\dagger} T_i^y + T_i^{z\dagger} T_i^z = 1$. In terms of these operators, the resulting nearest-neighbor interaction takes the form

$$\mathcal{H}_{\text{eff}}^{(4)} = \sum_{\langle ij \rangle} \sum_{\alpha\alpha'\beta\beta'} J_{ij}^{\alpha\alpha'\beta\beta'} \tau_{i\alpha}^\dagger \tau_{j\alpha'}^\dagger \tau_{i\beta} \tau_{j\beta'} + \text{h.c.}, \quad (11)$$

where $J_{ij}^{\alpha\alpha'\beta\beta'}$ encodes the bond-dependent exchange interactions generated by the virtual charge-transfer processes. The explicit construction of the projected bond Hamiltonians and the generation of symmetry-related bonds are described in the Methods. The projected quartic superexchange Hamiltonian (11) retains the full microscopic details of $\mathcal{H}_{\text{int}}$. Similarly, $\mathcal{H}_{\text{SOC}}$ and $\mathcal{H}_\Delta$ can be expressed in terms of the hard-core boson operators. Together with $\mathcal{H}_{\text{eff}}^{(4)}$, they constitute the full low-energy effective Hamiltonian. In the following, for simplicity, we consider the ideal octahedral structure without trigonal distortion, since the trigonal field $\mathcal{H}_\Delta$ enters in a manner analogous to the spin–orbit coupling and does not qualitatively change our results, as will be shown when we specialize to the $\text{A}_2\text{Ru}_2\text{O}_7$ family of compounds.

Magnetic instability of the singlet ground state

The single-ion singlet ground state favored by spin–orbit coupling becomes unstable in the presence of superexchange. To demonstrate this, we assume a macroscopic singlet condensate $s \approx s^\dagger$ and replace the singlet operators s and $s^\dagger$ with $\sqrt{1 - T^{x\dagger} T^x - T^{y\dagger} T^y - T^{z\dagger} T^z}$, keeping terms up to the quadratic order in the triplon operators T^x, T^y and T^z . Stability of the singlet ground state requires a finite gap in

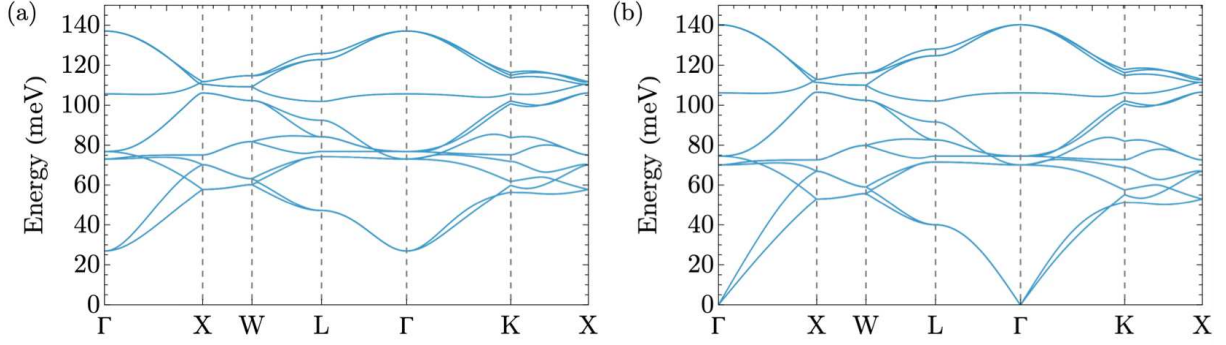


Figure 2: Dispersion of the 12 triplon bands above the singlet ground state along the high-symmetry path in momentum space, computed with $U_2 = 1.7$ eV, $J_H = 0.35$ eV, and $\lambda = 0.1$ eV: (a) below the critical hopping at $|t_o/\lambda| = 1.9$ and (b) at the critical hopping $|t_o/\lambda| = 1.9923$.

the triplon excitation spectrum. As the hopping strength, hence the superexchange, increases, this gap eventually closes, marking a quantum phase transition to a magnetically ordered ground state composed of an admixture of singlets and triplets.

As an example, we present the triplon gap closing for a typical Ru parameter set: $U_2 = 1.7$ eV, $J_H = 0.35$ eV, and $\lambda = 0.1$ eV. Fig. 1(b) shows the triplon excitation gap as a function of the dominant oxygen-mediated hopping $|t_o/\lambda|$. The gap closes rapidly near the critical hopping. The full triplon dispersion at $|t_o/\lambda| = 1.9$ [Fig. 2(a)] shows a two-fold degenerate triplon excitation gap around 27 meV at the Γ point. Upon increasing $|t_o/\lambda|$ to the critical value 1.9923, this gap closes at the Γ point [Fig. 2(b)], signaling triplon condensation and the onset of magnetic order on the Ru sublattice.

Triplon condensate

When the triplon gap closes at the Γ point, the singlet ground state becomes unstable toward triplon condensation. To determine the new ground state and the corresponding magnetic order, we construct a variational wavefunction that preserves the crystallographic unit cell, so that the magnetic unit cell consists of a single tetrahedron. On each tetrahedron, we write a product state over the four sublattices:

$$|\Psi\rangle = \prod_{\mu=1,2,3,4} \left(\cos \theta_\mu |s\rangle + \sin \theta_\mu |\mathbf{d}_\mu\rangle \right), \quad (12)$$

with variational parameters θ_μ and variational states $|\mathbf{d}_\mu\rangle$, which are normalized states within the $J = 1$ manifold, parametrized by complex unit vectors $\mathbf{d}_\mu \equiv (d_\mu^x, d_\mu^y, d_\mu^z)$ such that $|\mathbf{d}_\mu\rangle = \sum_{\alpha=x,y,z} d_\mu^{\alpha*} |T^\alpha\rangle$.

The variational parameter θ_μ controls the triplon condensate density, while $\mathbf{d}_\mu$ determines how the condensate is distributed among three triplon flavors. Within this ansatz, the singlet and triplon occupations on each sublattice μ are

$$\langle n_S \rangle_\mu = \cos^2 \theta_\mu, \quad \sum_{\alpha=x,y,z} \langle n_{T^\alpha} \rangle_\mu = \sin^2 \theta_\mu. \quad (13)$$

The distribution among the three triplon flavors also determines the direction of the ordered moment. Following Refs. [2, 7], we decompose the magnetic moment operator

$$\mathbf{M} = 2\mathbf{S} + \mathbf{L} \quad (14)$$

within the low-energy singlet–triplet manifold into two contributions,

$$\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2. \quad (15)$$

The first term is the Van Vleck excitonic magnetism arising from singlet–triplet transitions,

$$\mathbf{M}_1 = -i\sqrt{6} (s^\dagger \mathbf{T} - \mathbf{T}^\dagger s), \quad (16)$$

while the second term describes the intrinsic magnetic moment carried by the spin-1 triplons,

$$\mathbf{M}_2 = \frac{1}{2}\mathbf{J} = -\frac{i}{2}(\mathbf{T}^\dagger \times \mathbf{T}). \quad (17)$$

Evaluating these operators within the variational state gives

$$\langle \mathbf{M}_1 \rangle_\mu = 2\sqrt{6} \sin \theta_\mu \cos \theta_\mu \mathbf{v}_\mu, \quad (18)$$

$$\langle \mathbf{M}_2 \rangle_\mu = 2 \sin^2 \theta_\mu (\mathbf{u}_\mu \times \mathbf{v}_\mu), \quad (19)$$

where $\mathbf{u}_\mu$ and $\mathbf{v}_\mu$ are the real and imaginary parts of the complex unit vector $\mathbf{d}_\mu = \mathbf{u}_\mu + i\mathbf{v}_\mu$. Thus, the order parameter of the excitonic phase is not simply the triplet density, but rather a coherent hybridization amplitude between the singlet and triplet sector. In the parameter regimes discussed below, the optimized solutions are dominated by $\mathbf{v}_\mu$, which provides magnetic moment $\mathbf{M}_1$ up to $2.45\mu_B$ per Ru ion [Fig. 1(b)]. The ordered moment is therefore predominantly of Van Vleck character, with only a subleading contribution from the intrinsic triplon moment $\mathbf{M}_2$.

The new ground state is obtained by minimizing the variational energy

$$\begin{aligned} E_{\text{var}} &= \langle \Psi | \mathcal{H}_{\text{eff}}^{(4)} + \mathcal{H}_{\text{SOC}} | \Psi \rangle \\ &= \langle \Psi_{14} | \mathcal{H}_{14}^Z | \Psi_{14} \rangle + \langle \Psi_{12} | \mathcal{H}_{12}^X | \Psi_{12} \rangle + \langle \Psi_{13} | \mathcal{H}_{13}^Y | \Psi_{13} \rangle \\ &\quad + \langle \Psi_{32} | \mathcal{H}_{32}^{Z'} | \Psi_{32} \rangle + \langle \Psi_{43} | \mathcal{H}_{43}^{X'} | \Psi_{43} \rangle + \langle \Psi_{42} | \mathcal{H}_{42}^{Y'} | \Psi_{42} \rangle \end{aligned} \quad (20)$$

within a single tetrahedron with 28 real parameters. Each sublattice site contributes seven real variational parameters: one mixing angle θ_μ and the six components of $\mathbf{u}_\mu$ and $\mathbf{v}_\mu$, subject to the normalization constraint $|\mathbf{d}_\mu|^2 = 1$.

Phase diagram

The ordering of the condensed excitonic states is obtained by minimizing the variational energy, Eq. (20), with respect to θ_μ , $\mathbf{u}_\mu$, and $\mathbf{v}_\mu$. We first focus on the dominant oxygen-mediated hopping channels t_1 and t_2 , Eq. (9), which largely determine the magnetic ordering, and map out the resulting $\mathbf{q} = 0$ phase diagram in the (t_1, t_2) plane. To illustrate the richness of the excitonic condensate, we examine four representative cuts corresponding to different values of t_3 and t_4 , shown in Fig. 3, while keeping the remaining parameters fixed at $U_2 = 1.70$ eV, $J_H = 0.35$ eV, and $\lambda = 0.1$ eV. As shown below, the resulting phase diagram reproduces all of the classical $\mathbf{q} = 0$ magnetic orders of the conventional $S = 1$ pyrochlore model [34], while also stabilizing an additional tilted AFM₃ phase unique to the excitonic description.

The resulting $\mathbf{q} = 0$ phase diagrams are shown in Fig. 3. The different regions correspond to distinct magnetic orderings of the triplon condensate, each specified by four unit vectors, one on each sublattice of a tetrahedron:

$$\begin{aligned} \text{(i) all-in-all-out (AIAO):} \quad \mathbf{e}_1 &= \frac{1}{\sqrt{3}}(1, 1, 1), \quad \mathbf{e}_2 = \frac{1}{\sqrt{3}}(1, -1, -1), \\ \mathbf{e}_3 &= \frac{1}{\sqrt{3}}(-1, 1, -1), \quad \mathbf{e}_4 = \frac{1}{\sqrt{3}}(-1, -1, 1), \end{aligned} \quad (21)$$

$$\begin{aligned} \text{(ii) splayed ferromagnet (splayed FM):} \quad \mathbf{e}_1 &= \left(\frac{\sin \alpha}{\sqrt{2}}, \frac{\sin \alpha}{\sqrt{2}}, \cos \alpha \right), \quad \mathbf{e}_2 = \left(-\frac{\sin \alpha}{\sqrt{2}}, \frac{\sin \alpha}{\sqrt{2}}, \cos \alpha \right), \\ \mathbf{e}_3 &= \left(\frac{\sin \alpha}{\sqrt{2}}, -\frac{\sin \alpha}{\sqrt{2}}, \cos \alpha \right), \quad \mathbf{e}_4 = \left(-\frac{\sin \alpha}{\sqrt{2}}, -\frac{\sin \alpha}{\sqrt{2}}, \cos \alpha \right), \end{aligned} \quad (22)$$

$$\begin{aligned} \text{(iii) coplanar XY antiferromagnet (AFM}_1\text{):} \quad \mathbf{e}_1 &= \frac{1}{\sqrt{2}}(1, -1, 0), \quad \mathbf{e}_2 = \frac{1}{\sqrt{2}}(1, 1, 0), \\ \mathbf{e}_3 &= \frac{1}{\sqrt{2}}(-1, -1, 0), \quad \mathbf{e}_4 = \frac{1}{\sqrt{2}}(-1, 1, 0), \end{aligned} \quad (23)$$

$$\begin{aligned} \text{(iv) coplanar XY antiferromagnet (AFM}_2\text{):} \quad \mathbf{e}_1 &= \frac{1}{\sqrt{2}}(1, -1, 0), \quad \mathbf{e}_2 = \frac{1}{\sqrt{2}}(-1, -1, 0), \\ \mathbf{e}_3 &= \frac{1}{\sqrt{2}}(1, 1, 0), \quad \mathbf{e}_4 = \frac{1}{\sqrt{2}}(-1, 1, 0), \end{aligned} \quad (24)$$

$$\begin{aligned} \text{(v) noncoplanar XY antiferromagnet (AFM}_3\text{):} \quad \mathbf{e}_1 &= \frac{1}{\sqrt{6}}(-1, -1, 2), \quad \mathbf{e}_2 = \frac{1}{\sqrt{6}}(-1, 1, -2), \\ \mathbf{e}_3 &= \frac{1}{\sqrt{6}}(1, -1, -2), \quad \mathbf{e}_4 = \frac{1}{\sqrt{6}}(1, 1, 2), \end{aligned} \quad (25)$$

where α denotes the splay angle measured from the Z-axis. These classical $\mathbf{q} = 0$ orderings can also be classified by the irreducible representations of the O_h point group (see Ref. [45] for details). The AFM₁

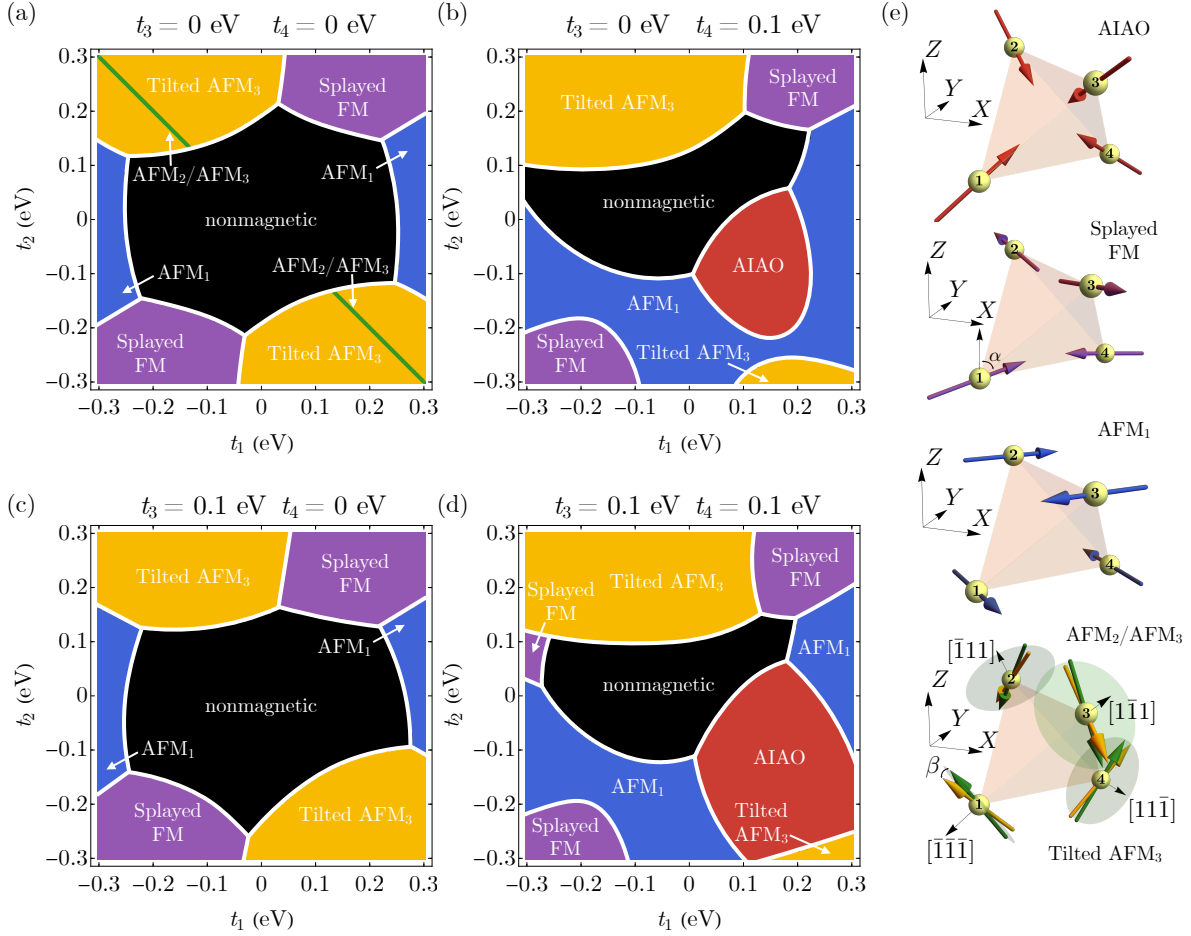


Figure 3: $\mathbf{q} = 0$ phase diagram of the microscopic model as a function of the dominant hoppings t_1 and t_2 obtained by minimizing the variational ground-state energy at (a) $t_3 = t_4 = 0$ eV, (b) $t_3 = 0$ eV and $t_4 = 0.1$ eV, (c) $t_3 = 0.1$ eV and $t_4 = 0$ eV, (d) $t_3 = 0.1$ eV and $t_4 = 0.1$ eV. Along the green line in (a), where $t_1 = -t_2$ and $t_3 = t_4 = 0$, an accidental $U(1)$ symmetry emerges that allows all four spins to rotate by a common angle within their respective local planes perpendicular to the axis pointing toward the center of the tetrahedron. The spin configuration of each phase is depicted in (e): the splayed FM is parametrized by the splay angle α measured from the z -axis, and the tilted AFM₃ state by the tilt angle β measured out of these local planes.

and AFM₂ orderings are related by reversing the spins on sublattices 2 and 3 and therefore represent distinct magnetic phases. The AFM₂ and AFM₃ orderings, by contrast, form a degenerate manifold of states connected by an accidental $U(1)$ symmetry that rotates each spin simultaneously within the local plane perpendicular to axes defined by AIAO states (21).

An extended region of the phase diagram shown in Fig. 3 is occupied by a tilted noncoplanar XY antiferromagnetic state. We refer to this state as tilted AFM₃ and parametrize it as

$$\begin{aligned} \mathbf{e}_1 &= \left(-\frac{\sin \alpha}{\sqrt{2}}, -\frac{\sin \alpha}{\sqrt{2}}, \cos \alpha \right), \quad \mathbf{e}_2 = \left(-\frac{\sin \alpha}{\sqrt{2}}, \frac{\sin \alpha}{\sqrt{2}}, -\cos \alpha \right), \\ \mathbf{e}_3 &= \left(\frac{\sin \alpha}{\sqrt{2}}, -\frac{\sin \alpha}{\sqrt{2}}, -\cos \alpha \right), \quad \mathbf{e}_4 = \left(\frac{\sin \alpha}{\sqrt{2}}, \frac{\sin \alpha}{\sqrt{2}}, \cos \alpha \right), \end{aligned} \quad (26)$$

where α again denotes the splay angle measured from the global Z -axis and setting $\alpha = \arctan(1/\sqrt{2})$ recovers the AFM₃ state. We can define the tilting angle $\beta \equiv \alpha - \arctan(1/\sqrt{2})$ to quantify the deviation from the degenerate AFM₂/AFM₃ manifold. Different from the conventional $S = 1$ model, the AFM₂/AFM₃ degeneracy survives only along the line $t_1 = -t_2$ with $t_3 = t_4 = 0$.

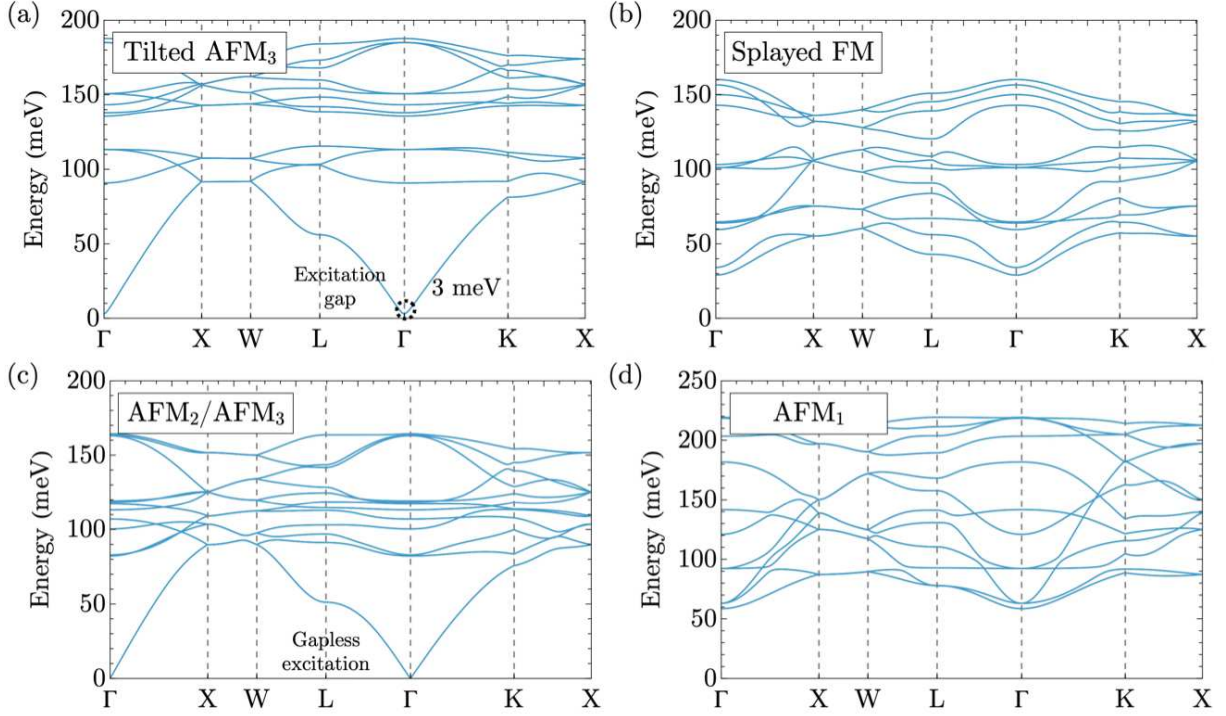


Figure 4: Excitation of triplon condensate with four magnetic structure shown in Fig. 3(a), fixing $t_3 = t_4 = 0$. (a) Tilted AFM_3 ($t_1 = -0.1$ eV, $t_2 = 0.2$ eV), (b) Splayed FM ($t_1 = 0.1$ eV, $t_2 = 0.2$ eV), (c) $\text{AFM}_2/\text{AFM}_3$ ($t_1 = -0.15$ eV, $t_2 = 0.15$ eV), and (d) AFM_1 ($t_1 = 0.3$ eV, $t_2 = 0.0$ eV).

Excitation spectrum of triplon condensate

Over most of the phase diagram, the ground state develops long-range order through triplon condensation and is described by the variational wavefunction of Eq. (12). To compute excitations above the ground state with triplon condensate, we introduce a unitary transformation

$$\begin{pmatrix} |s\rangle \\ |T^x\rangle \\ |T^y\rangle \\ |T^z\rangle \end{pmatrix} = \begin{pmatrix} \cos \theta & 0 & 0 & i \sin \theta \\ (u_x + iv_x) \sin \theta & -\frac{u_y - iv_y}{\sqrt{u_x^2 + u_y^2 + v_x^2 + v_y^2}} & -\frac{v_x v_x}{\sqrt{u_x^2 + u_y^2 + v_x^2 + v_y^2}} & (-iu_x + v_x) \cos \theta \\ (u_y + iv_y) \sin \theta & \frac{u_x - iv_x}{\sqrt{u_x^2 + u_y^2 + v_x^2 + v_y^2}} & -\frac{v_y v_z}{\sqrt{u_x^2 + u_y^2 + v_x^2 + v_y^2}} & (-iu_y + v_y) \cos \theta \\ (u_z + iv_z) \sin \theta & 0 & \sqrt{u_x^2 + u_y^2 + v_x^2 + v_y^2} & (-iu_z + v_z) \cos \theta \end{pmatrix} \begin{pmatrix} |\Psi\rangle \\ |\Phi_1\rangle \\ |\Phi_2\rangle \\ |\Phi_3\rangle \end{pmatrix} \quad (27)$$

that rotates the original basis $\{|s\rangle, |T^x\rangle, |T^y\rangle, |T^z\rangle\}$ into a new orthonormal basis $\{|\Psi\rangle, |\Phi_1\rangle, |\Phi_2\rangle, |\Phi_3\rangle\}$, where $|\Psi\rangle$ is the variational ground state corresponding to triplon condensate and $|\Phi_1\rangle, |\Phi_2\rangle, |\Phi_3\rangle$ are new excited states. Equation (11) can then be rewritten in terms of the corresponding hard-core bosons $\{\Psi, \Phi_1, \Phi_2, \Phi_3\}$, subject to the single-occupancy constraint $\Psi^\dagger \Psi + \Phi_1^\dagger \Phi_1 + \Phi_2^\dagger \Phi_2 + \Phi_3^\dagger \Phi_3 = 1$. Assuming that the Ψ bosons condense, we approximate $\Psi \approx \Psi^\dagger$ and replace them with $\sqrt{1 - \Phi_1^\dagger \Phi_1 - \Phi_2^\dagger \Phi_2 - \Phi_3^\dagger \Phi_3}$. Expanding Eq. (11) to quadratic order in Φ_1, Φ_2 , and Φ_3 . The resulting quadratic Hamiltonian yields the excitation spectrum of the triplon-condensed phase.

We compute the excitation spectrum for the four ordered ground states shown in Fig. 3(a). The results are presented in Fig. 4. The tilted AFM_3 state, obtained by a small tilting angle β away from the $\text{AFM}_2/\text{AFM}_3$ manifold, exhibits a pseudo-Goldstone mode of approximately 3 meV at the Γ point, in contrast to the true Goldstone mode that develops in the $\text{AFM}_2/\text{AFM}_3$ state [Fig. 4(a) and (c)]. This low-energy pseudo-Goldstone mode provides a clear experimental signature of the tilted AFM_3 state, whereas the remaining ordered phases exhibit a sizable excitation gap at the Γ point [Fig. 4(b) and (d)].

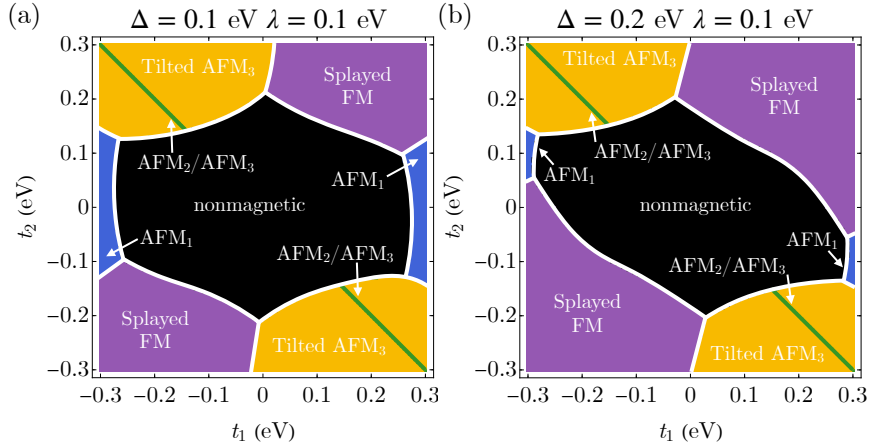


Figure 5: Phase diagram of the microscopic model with trigonal distortion: (a) The trigonal field Δ is comparable to spin-orbit coupling, (b) The trigonal field Δ is twice to spin-orbit coupling. All the other parameters are kept the same as in Fig. 3(a).

Application to $\text{A}_2\text{Ru}_2\text{O}_7$

We now apply the Van Vleck magnetism framework to ruthenate pyrochlores $\text{A}_2\text{Ru}_2\text{O}_7$. The experimentally reported properties of the Ru subsystem in $\text{A}_2\text{Ru}_2\text{O}_7$ are summarized in Table 2. Across this family of compounds, the Ru moments order at temperatures between 80 K and 150 K. Structurally, the family of $\text{A}_2\text{Ru}_2\text{O}_7$ compounds all deviate from the ideal pyrochlore geometry, with the bond angle $\angle\text{Ru-O-Ru}$ differing significantly from 141.058° . Therefore, we also include the trigonal distortion in our calculation to properly account for magnetic properties in real materials.

In the parameter regime dominated by oxygen-mediated hopping ($t_3 = 0$ and $t_4 = 0$), we find that a trigonal distortion of strength comparable to, or even larger than, the spin-orbit coupling does not qualitatively change the phase diagram from Fig. 3(a) (see Fig. 5). Using the DFT parameters from Ref. [27] (listed in Table 3), we find that the $\text{A}_2\text{Ru}_2\text{O}_7$ compounds lie predominantly in the upper-left region of the phase diagram in Fig. 5, corresponding to experimentally measured $\text{AFM}_2/\text{AFM}_3$ or tilted AFM_3 states (listed in Table 2). While this comparison correctly captures the overall magnetic tendencies across the family, quantitative discrepancies remain. The calculated critical spin-orbit couplings (see Table 3), above which the triplon condensate can no longer be stabilized and the $J = 0$ singlet remains the ground state, are generally smaller than the expected atomic value for Ru ions. Also the predicted magnetic ground states (last column of Table 3) disagree with experiment for several compounds. This suggests that the DFT-derived microscopic parameters require further refinement for a fully quantitative description.

$\text{Nd}_2\text{Ru}_2\text{O}_7$ and Raman responses

We now turn to $\text{Nd}_2\text{Ru}_2\text{O}_7$, for which inelastic Raman scattering measurements have revealed low-energy magnetic excitations [25]. This compound provides an opportunity to test the microscopic Van Vleck framework against both the magnetic ground state and the excitation spectrum, including its Raman signatures.

Starting from the hopping parameters obtained from DFT (Table 3 Ref. [27]), we find that the parameter set for $\text{Nd}_2\text{Ru}_2\text{O}_7$ lies very close to the excitonic quantum critical point, but remains slightly on the nonmagnetic side of the instability. Equivalently, the critical spin-orbit coupling required to stabilize the triplon-condensed phase is somewhat smaller than the realistic atomic value for Ru ion, $\lambda \simeq 0.1$ eV. Since the spin-orbit coupling is an essentially atomic property of the Ru ion and is expected to vary only weakly among insulating ruthenates, we attribute this discrepancy to the microscopic parameters inferred from DFT, whose values depend sensitively on structural details and electronic correlations. We therefore keep the physically realistic value $\lambda = 0.1$ eV fixed and instead make only small adjustments to the hopping and interaction parameters. Specifically, we increase t_4 from 0.034 eV to 0.08 eV while keeping all other parameters unchanged from the $\text{Nd}_2\text{Ru}_2\text{O}_7$ values listed in Table 3. As shown in Table 1, the antisymmetric hopping t_4 originates from the absence of inversion symmetry on the Ru-Ru bond,

	T_N	$\angle\text{Ru-O-Ru}$	μ_{Ru}	Ru magnetic structure
$\text{Y}_2\text{Ru}_2\text{O}_7$	76(2) K [28]	$128.45(2)^\circ$ [22]	$1.36\mu_B$ [21]	AFM ₂ /AFM ₃ [28]
$\text{Pr}_2\text{Ru}_2\text{O}_7$	163 K [29]	131.69° [24]	$1.48\mu_B$ [48]	AFM ₂ /AFM ₃ [48]
$\text{Nd}_2\text{Ru}_2\text{O}_7$	146 K [23]	130.8° [23]	$1.18\mu_B$ [21]	AFM ₂ /AFM ₃ [21]
$\text{Sm}_2\text{Ru}_2\text{O}_7$	135 K [20]	128.85° [37, 38]	/	/
$\text{Eu}_2\text{Ru}_2\text{O}_7$	118 K [30]	125.52° [39]	$2.79\mu_B$ [49]	/
$\text{Gd}_2\text{Ru}_2\text{O}_7$	114(1) K [31]	$130.23(1)^\circ$ [40]	$2.83\mu_B$ [31]	tilted AFM ₃ [31]
$\text{Tb}_2\text{Ru}_2\text{O}_7$	110 K [32]	128.48° [41]	$0.9(1)\mu_B$ [32]	tilted AFM ₃ [32]
$\text{Dy}_2\text{Ru}_2\text{O}_7$	~ 100 K [50]	130.23° [42]	/	tilted AFM ₃ [50]
$\text{Ho}_2\text{Ru}_2\text{O}_7$	95 K [51]	128.64° [43]	$1.2\mu_B$ [43]	AFM ₂ /AFM ₃ [43]
$\text{Er}_2\text{Ru}_2\text{O}_7$	95 K [44]	$128.24(9)^\circ$ [44]	$\sim 2.0\mu_B$ [44]	tilted AFM ₃ [44]
$\text{Yb}_2\text{Ru}_2\text{O}_7$	85 K [33]	126.9° [33]	$1.41\mu_B$ [33]	AFM ₂ /AFM ₃ [33]

Table 2: Experimentally reported properties of the Ru subsystem in the $\text{A}_2\text{Ru}_2\text{O}_7$ family of compounds. The Ru-O-Ru bond angle is computed from the reported position of the O ion sitting at Wyckoff position $48f : (x, 1/8, 1/8)$ as $\arccos(1 - 2/(3 + 16x(2x - 1)))$. A slash indicates that no experimental data have been reported in that entry.

making a moderate increase in t_4 reasonable in the pyrochlore lattice.

The resulting parameter set yields a tilted AFM₃ ground state with magnetic moment $1.49 \mu_B$ and a small tilting angle $\beta \approx 0.5^\circ$, in which the Ru moments lie nearly within the degenerate AFM₂/AFM₃ manifold [Fig. 6(b)]. The corresponding low-energy excitation spectrum is shown in Fig. 6(a), and the lowest magnetic excitation occurs at approximately 2.96 meV, in agreement with the lowest-energy magnetic mode observed in Raman scattering [25], whose microscopic origin has remained unresolved.

To establish that this excitation indeed corresponds to the experimentally observed Raman mode, we compute its Raman intensity and polarization dependence. Our aim here is not to describe the full Raman response of $\text{Nd}_2\text{Ru}_2\text{O}_7$, which has already been analyzed in Ref. [25], but rather to identify the microscopic origin of this previously unexplained low-energy magnetic mode. Although the higher-energy excitations may hybridize with the $J = 2$ manifold (neglected in the singlet-triplet picture of Van Vleck magnetism) when hopping becomes sufficiently strong, the ground state and lowest-energy excitation are energetically well separated from the $J = 2$ manifold and should remain largely unaffected. To this end, we evaluate the angle-resolved Raman intensity of the lowest excitation within the Loudon-Fleury formalism [46] in the xy plane for both parallel and crossed polarization channels [Fig. 6(c)] (see the Methods section for details). The calculated polarization dependence agrees well with experiment [25], confirming that the observed low-energy Raman feature originates from the pseudo-Goldstone mode of the tilted AFM₃ state. The only noticeable discrepancy is the broken fourfold symmetry observed in the crossed polarization channel. This is likely a limitation of the Loudon-Fleury approximation, which neglects the effects of oxygen-mediated hopping and the inversion-symmetry-breaking hopping t_4 . As discussed earlier, these processes can generate antisymmetric components in the Raman tensor therefore breaking the fourfold symmetry in the crossed polarization channel [47].

Discussion

In this work, we developed a microscopic theory of Van Vleck excitonic magnetism for pyrochlore ruthenates by deriving the effective singlet-triplet Hamiltonian directly from a multi-orbital Hubbard model with spin-orbit coupling. The resulting framework naturally explains how long-range magnetic order emerges from the condensation of spin-orbit excitons despite the local $J = 0$ singlet ground state.

The microscopic formulation also establishes a direct connection between the underlying electronic structure and the magnetic phase diagram. We identify the key hopping processes that govern the competition between different magnetic phases. The dominant oxygen-mediated hopping amplitudes, t_1 and t_2 , determine the overall topology of the phase diagram, whereas the symmetry-allowed hopping channels t_3 and t_4 modify the phase boundaries and lift accidental degeneracies.

The resulting phase diagram reproduces all established $\mathbf{q} = 0$ magnetic orders of the conventional spin-1 pyrochlore model [34]. At the same time, the singlet-triplet structure of the excitonic model stabilizes a distinct tilted AFM₃ phase, which has no analogue in the pure spin-1 model and occupies an extended region of the phase diagram. For $t_3 = t_4 = 0$, this phase lifts the accidental AFM₂/AFM₃ degeneracy

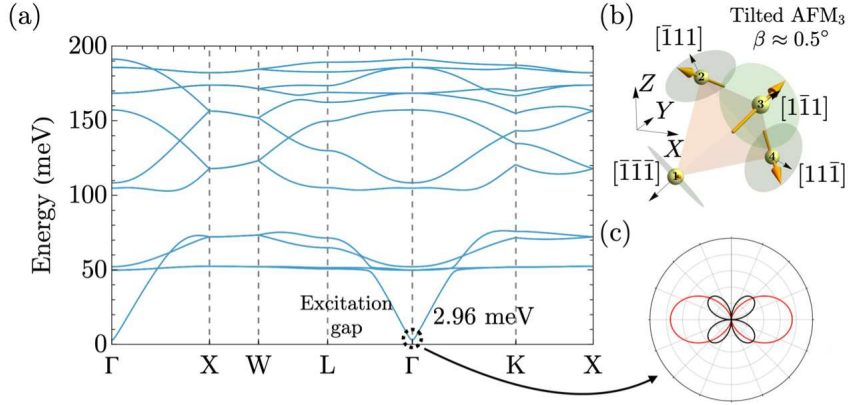


Figure 6: (a) Triplon excitation spectrum of $\text{Nd}_2\text{Ru}_2\text{O}_7$ computed using the modified set of DFT parameters ($U_2 = 1.664$ eV, $J_H = 0.344$ eV, $t_1 = -0.1059$ eV, $t_2 = 0.1501$ eV, $t_3 = 0.00157$ eV, $t_4 = 0.08$ eV, $\lambda = 0.1$ eV, and $\Delta = 0.131$ eV) along with spin-orbit coupling $\lambda = 0.1$ eV, chosen to stabilize the triplon condensate. (b) The resulting magnetic order is a tilted AFM_3 state with a tilting angle $\beta \approx 0.5^\circ$, in which the Ru moments lie nearly within the degenerate plane of $\text{AFM}_2/\text{AFM}_3$ state. (c) Angle-resolved Raman response of the low-energy pseudo-Goldstone mode at the Γ point, shown in the parallel (red) and perpendicular (black) polarization channels.

	U_2	J_H	t_1	t_2	t_3	t_4	Δ	λ_c	$ \Psi\rangle$
$\text{Pr}_2\text{Ru}_2\text{O}_7$	1.637	0.341	-0.1025	0.1543	0.0151	0.0059	0.130	0.1046	tilted AFM_3
$\text{Nd}_2\text{Ru}_2\text{O}_7$	1.664	0.344	-0.1059	0.1501	0.0157	0.0034	0.131	0.0977	tilted AFM_3
$\text{Sm}_2\text{Ru}_2\text{O}_7$	1.710	0.349	-0.1117	0.1418	0.0165	-0.0012	0.134	0.0848	tilted AFM_3
$\text{Eu}_2\text{Ru}_2\text{O}_7$	1.728	0.351	-0.1140	0.1376	0.0167	-0.0032	0.136	0.0786	tilted AFM_3
$\text{Tb}_2\text{Ru}_2\text{O}_7$	1.759	0.353	-0.1177	0.1296	0.0170	-0.0068	0.142	0.0672	tilted AFM_3
$\text{Dy}_2\text{Ru}_2\text{O}_7$	1.772	0.355	-0.1195	0.1255	0.0170	-0.0085	0.145	0.0616	AIAO
$\text{Ho}_2\text{Ru}_2\text{O}_7$	1.782	0.355	-0.1211	0.1212	0.0171	-0.0102	0.149	0.0618	AIAO
$\text{Er}_2\text{Ru}_2\text{O}_7$	1.793	0.356	-0.1225	0.1170	0.0171	-0.0119	0.152	0.0642	AIAO
$\text{Tm}_2\text{Ru}_2\text{O}_7$	1.803	0.357	-0.1240	0.1127	0.0172	-0.0135	0.156	0.0667	AIAO
$\text{Yb}_2\text{Ru}_2\text{O}_7$	1.811	0.357	-0.1247	0.1091	0.0170	-0.0145	0.158	0.0680	AIAO

Table 3: DFT parameters (in eV) for the $\text{A}_2\text{Ru}_2\text{O}_7$ family of compounds [27]. The trigonal field Δ is extracted from Fig. 3(d) of Ref. [27]. From these parameters, we compute the critical spin-orbit coupling λ_c (shown in blue) above which $J = 0$ singlet is energetically favored as the ground state. The resulting condensate order (also in blue) is listed in the last column.

everywhere except along the special line $t_1 = -t_2$. Once either t_3 or t_4 becomes finite, the tilted AFM_3 phase is stabilized also along this line. A hallmark of this phase is a low-energy pseudo-Goldstone mode, whereas the remaining ordered phases are characterized by substantially larger excitation gaps.

More importantly, the microscopic theory establishes a direct connection between the electronic structure and experimentally observable collective excitations. Applying the Van Vleck excitonic magnetism framework to $\text{Nd}_2\text{Ru}_2\text{O}_7$, we showed that modest refinements of the DFT-derived microscopic parameters are sufficient to reproduce both the magnetic ground state and the energy of the lowest magnetic excitation observed in Raman scattering. The calculated Raman polarization dependence identifies this excitation as the pseudo-Goldstone mode of the tilted AFM_3 phase, thereby providing a microscopic explanation for a low-energy Raman feature whose origin had remained unresolved.

To conclude, we have demonstrated that pyrochlore ruthenates provide a concrete realization of the Van Vleck excitonic magnetism proposed by Khaliullin [2]. More broadly, our work establishes a microscopic route from the electronic structure of spin-orbit-coupled materials to their magnetic phases and spectroscopic signatures. Because it is formulated directly in terms of the underlying multi-orbital Hamiltonian, the approach developed here can be readily applied to other candidate excitonic magnets and extended to systems in which additional low-energy multiplets become relevant.

Methods

Local frames and coordinate transformation

The complexity of studying Van Vleck magnetism inside pyrochlore compounds lies in the locally rotated octahedral environment surrounding each Ru sublattice. The local orbital basis at each Ru site is defined by the orientation of the surrounding oxygen octahedron. In the ideal structure of pyrochlore, we define these axes in terms of the global coordinate:

$$\begin{aligned}\hat{x}_1 &= \left(\frac{2}{3}, -\frac{1}{3}, \frac{2}{3}\right), & \hat{y}_1 &= \left(-\frac{1}{3}, \frac{2}{3}, \frac{2}{3}\right), & \hat{z}_1 &= \left(-\frac{2}{3}, -\frac{2}{3}, \frac{1}{3}\right), \\ \hat{x}_2 &= \left(\frac{2}{3}, \frac{1}{3}, -\frac{2}{3}\right), & \hat{y}_2 &= \left(\frac{1}{3}, \frac{2}{3}, \frac{2}{3}\right), & \hat{z}_2 &= \left(\frac{2}{3}, -\frac{2}{3}, \frac{1}{3}\right), \\ \hat{x}_3 &= \left(\frac{2}{3}, \frac{1}{3}, \frac{2}{3}\right), & \hat{y}_3 &= \left(\frac{1}{3}, \frac{2}{3}, -\frac{2}{3}\right), & \hat{z}_3 &= \left(-\frac{2}{3}, \frac{2}{3}, \frac{1}{3}\right), \\ \hat{x}_4 &= \left(\frac{2}{3}, -\frac{1}{3}, -\frac{2}{3}\right), & \hat{y}_4 &= \left(-\frac{1}{3}, \frac{2}{3}, -\frac{2}{3}\right), & \hat{z}_4 &= \left(\frac{2}{3}, \frac{2}{3}, \frac{1}{3}\right).\end{aligned}\tag{28}$$

The $J = 0$ singlet is invariant under rotation. The rotation of the $J = 1$ triplet is implemented by the Wigner matrix

$$\mathcal{D}_{m'm}^j(\alpha, \beta, \gamma) = \langle jm' | e^{-i\alpha\mathcal{J}_z} e^{-i\beta\mathcal{J}_y} e^{-i\gamma\mathcal{J}_z} | jm \rangle,\tag{29}$$

where $\mathcal{J}_x$, $\mathcal{J}_y$, and $\mathcal{J}_z$ are spin-1 matrices. The Wigner matrix acts naturally in the angular-momentum basis $\{|T_1\rangle, |T_0\rangle, |T_{-1}\rangle\}$ of the $J = 1$ triplet. We denote the corresponding rotations from the local triplet basis to the global triplet basis at sublattice μ as $\mathcal{D}_\mu^{j=1}$. In terms of Euler angles,

$$\begin{aligned}(\alpha_1, \beta_1, \gamma_1) &= \left(-\frac{3\pi}{4}, \arctan(2\sqrt{2}), \frac{3\pi}{4}\right), & (\alpha_2, \beta_2, \gamma_2) &= \left(-\frac{\pi}{4}, \arctan(2\sqrt{2}), \frac{\pi}{4}\right), \\ (\alpha_3, \beta_3, \gamma_3) &= \left(\frac{3\pi}{4}, \arctan(2\sqrt{2}), -\frac{3\pi}{4}\right), & (\alpha_4, \beta_4, \gamma_4) &= \left(\frac{\pi}{4}, \arctan(2\sqrt{2}), -\frac{\pi}{4}\right).\end{aligned}\tag{30}$$

these rotations are described by the following Wigner matrices:

$$\begin{aligned}\mathcal{D}_1^{j=1} &= \begin{pmatrix} \left(\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} & \left(-\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} & \left(-\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} \\ -\frac{i}{3} & \left(\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} & \frac{2}{3} \end{pmatrix}, \\ \mathcal{D}_2^{j=1} &= \begin{pmatrix} \left(-\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} & \left(\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} & \left(\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} \\ \frac{i}{3} & \left(-\frac{1}{3} - \frac{i}{3}\right)\sqrt{2} & \frac{2}{3} \end{pmatrix}, \\ \mathcal{D}_3^{j=1} &= \begin{pmatrix} \left(\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} & \left(-\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} & \left(-\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} \\ \frac{i}{3} & \left(\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} & \frac{2}{3} \end{pmatrix}, \\ \mathcal{D}_4^{j=1} &= \begin{pmatrix} \left(-\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} & \left(\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} & \left(\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} \\ -\frac{i}{3} & \left(-\frac{1}{3} + \frac{i}{3}\right)\sqrt{2} & \frac{2}{3} \end{pmatrix}.\end{aligned}\tag{31}$$

Construction of hopping matrices

The hopping amplitudes appearing in Eq. (8) are defined in the local t_{2g} orbital basis on each Ru site. To construct these hopping amplitudes, we first define a global five-orbital basis for each sublattice μ ,

$$|d_\mu^G\rangle = (d_{\mu,YZ}^G, d_{\mu,XZ}^G, d_{\mu,XY}^G, d_{\mu,X^2-Y^2}^G, d_{\mu,3Z^2-R^2}^G)^T,\tag{32}$$

where the superscript G indicates that the orbital shapes are expressed with respect to the global cubic axes. The corresponding local five-orbital basis at sublattice μ is denoted by

$$|d_\mu\rangle = (d_{\mu,yz}, d_{\mu,xz}, d_{\mu,xy}, d_{\mu,x^2-y^2}, d_{\mu,3z^2-r^2})^T,\tag{33}$$

where the orbital labels are defined with respect to the local axes $(\hat{x}_\mu, \hat{y}_\mu, \hat{z}_\mu)$. The transformation from the global to the local orbital basis is written as

$$|d_\mu\rangle = \mathcal{R}_{LG}^\mu |d_\mu^G\rangle. \quad (34)$$

For a nearest-neighbor bond connected by sublattice μ and ν with direction cosines (l, m, n) , we denote by $\mathcal{T}_{\mu\nu}^G(l, m, n)$ the Slater–Koster hopping matrix [52] written in the global five-orbital basis. Projecting this matrix to the local t_{2g} bases at sublattices μ and ν , respectively, gives

$$\mathcal{T}_{\mu\nu}^{t_{2g}} = \left[\mathcal{R}_{LG}^\mu \mathcal{T}_{ij}^G(l, m, n) (\mathcal{R}_{LG}^\nu)^\dagger \right]_{t_{2g}}. \quad (35)$$

Because the local spin quantization axes differ from site to site, the spin part of the hopping must also be expressed in a common convention. These spin rotations $S_{\mu\nu}$ are computed by Wigner rotation matrices $\mathcal{D}_\mu^{j=1/2}(\alpha, \beta, \gamma)$ for the spin-1/2 degree of freedom:

$$S_{\mu\nu} = \mathcal{D}_\nu^{j=1/2\dagger}(\alpha_\nu, \beta_\nu, \gamma_\nu) \mathcal{D}_\mu^{j=1/2}(\alpha_\mu, \beta_\mu, \gamma_\mu). \quad (36)$$

Combining the orbital and spin parts, the hopping amplitudes entering Eq. (8) are

$$t_{ij}^{\alpha\sigma, \beta\sigma'} = (\mathcal{T}_{\mu\nu}^{t_{2g}})_{\alpha\beta} (S_{ij})_{\sigma\sigma'}, \quad (37)$$

where μ, ν are sublattice indices of sites i and j , respectively. The explicit Slater–Koster expressions for t_1, t_2, t_3, t_4 , together with the orbital rotations are given in Supplementary Sec. ??.

Projected superexchange Hamiltonian

The effective exchange Hamiltonian is obtained by second-order perturbation theory in the hopping amplitudes $t_{ij}^{\alpha\sigma, \beta\sigma'}$. For each nearest-neighbor bond, two successive hopping processes virtually take the system from the initial $d_i^4 d_j^4$ manifold to intermediate charge-transfer configurations of the form $d_i^3 d_j^5$, and then back to the $d_i^4 d_j^4$ manifold. The single-site energy in this manifold is $E_4 = 6U_2 - J_H$, so the initial two-site energy is $E_0 = 2E_4$. The corresponding intermediate-state energy is $E_I = E_3 + E_5$. Since the d^5 configuration has energy $10U_2$, while the d^3 configuration splits into three interaction channels, the relevant intermediate energies are

$$\begin{aligned} E_{I,1} &= 10U_2 + (3U_2 - 3J_H), \\ E_{I,2} &= 10U_2 + 3U_2, \\ E_{I,3} &= 10U_2 + (3U_2 + J_H). \end{aligned} \quad (38)$$

After summing over the intermediate states, we project the resulting operator onto the local singlet-triplet manifold $\{|s\rangle, |T^x\rangle, |T^y\rangle, |T^z\rangle\}$ on each site. In practice, we first compute the projected Hamiltonian for the representative Z bond connecting sites 1 and 4. The corresponding two-site low-energy Hilbert space is spanned by

$$|\phi_{14, \alpha}\rangle \equiv |\tau_{1\mu}\rangle \otimes |\tau_{4\nu}\rangle, \quad (39)$$

where $\mu, \nu = 0, 1, 2, 3$ correspond to $|s\rangle, |T^x\rangle, |T^y\rangle, |T^z\rangle$ states, respectively. In this basis, the projected bond Hamiltonian is represented by a 16×16 matrix, denoted by $\mathcal{H}_{14}^Z$. The remaining nearest-neighbor bond Hamiltonians are generated from $\mathcal{H}_{14}^Z$ by symmetry operations of the tetrahedral point group. These operations leave the singlet component invariant and permute the Cartesian triplet components. This procedure gives the six bond Hamiltonians on a tetrahedron,

$$\{\mathcal{H}_{14}^Z, \mathcal{H}_{12}^X, \mathcal{H}_{13}^Y, \mathcal{H}_{32}^Z, \mathcal{H}_{43}^X, \mathcal{H}_{42}^Y\}. \quad (40)$$

The full nearest-neighbor exchange Hamiltonian is obtained by summing these bond Hamiltonians over all tetrahedra of the pyrochlore lattice, with the appropriate site labels. In the low-energy bosonic representation, this full interaction has the quartic form given in Eq. (11), where the sum over $\langle ij \rangle$ runs over all nearest-neighbor bonds. The explicit permutation matrices and bond-generation relations are given in Supplementary Sec. ??.

Magnetic Raman scattering

Since Van Vleck magnetism originates from virtual hopping of electrons between Ru ions, we compute the magnetic Raman response using the Loudon–Fleury formalism [46]. Within this approach, the Raman operator is generated by the same virtual hopping processes that give rise to the superexchange interaction. We define the Raman operator as

$$\mathcal{R} \equiv \sum_{\langle ij \rangle} \mathcal{R}_{\langle ij \rangle}, \quad (41)$$

where $\mathcal{R}_{\langle ij \rangle}$ acts on a pair of neighboring Ru ions connected by the bond vector $\mathbf{d}_{ij}$ and takes the form

$$\mathcal{R}_{\langle ij \rangle} \equiv -(\boldsymbol{\epsilon}_{\text{in}} \cdot \mathbf{d}_{ij})(\boldsymbol{\epsilon}_{\text{out}} \cdot \mathbf{d}_{ij})\mathcal{H}_{\text{eff}}^{(4)}. \quad (42)$$

Here $\mathcal{H}_{\text{eff}}^{(4)}$ is the superexchange Hamiltonian [Eq. (11)] obtained from second-order perturbation theory in the virtual hopping, while $\boldsymbol{\epsilon}_{\text{in(out)}}$ denote the polarization vectors of the incoming (outgoing) photons. We assume the incoming light frequency to be off-resonance, so that the Raman operator is approximately frequency independent.

The Raman intensity is given by the dynamical correlation function of the Raman operator,

$$I(\Omega) \propto \int dt e^{i\Omega t} \langle \mathcal{R}(t) \mathcal{R}(0) \rangle. \quad (43)$$

To compute the angle-resolved Raman response, we consider the parallel channel $\boldsymbol{\epsilon}_{\text{in}}^{\parallel} = \boldsymbol{\epsilon}_{\text{out}}^{\parallel} = (\cos \theta, \sin \theta, 0)$ and the crossed channel $\boldsymbol{\epsilon}_{\text{in}}^{\perp} = (\cos \theta, \sin \theta, 0)$, $\boldsymbol{\epsilon}_{\text{out}}^{\perp} = (-\sin \theta, \cos \theta, 0)$, where the polarization vectors lie in the global XY -plane. In the triplon-condensed phase, the elementary excitations are no longer the original triplons $\{|T^x\rangle, |T^y\rangle, |T^z\rangle\}$ but the normal modes $\{|\Phi_1\rangle, |\Phi_2\rangle, |\Phi_3\rangle\}$ obtained after the unitary transformation of Eq. (27). Accordingly, the superexchange Hamiltonian, and hence the Raman operator, is rewritten in this basis and expanded to quadratic order in the excitation operators. The Raman spectra are then obtained from the corresponding quadratic Hamiltonian.

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Author Contributions

S.S. and Y.Y. contributed equally to this work and share first authorship. Y.Y. and N.B.P. devised the project. S.S., Y.Y. and N.B.P. performed calculations. Y.Y. performed the analysis of the Raman response in $\text{Nd}_2\text{Ru}_2\text{O}_7$. S.S., Y.Y. and N.B.P. contributed to the interpretation of the results and the writing of the paper.

Competing interests

The authors declare no competing interests.

Data availability

Most of the calculations presented in this work are analytical and are described in the Methods and Supplementary Information. The theoretical data generated and analyzed during this study are not publicly available because they primarily consist of intermediate analytical calculations and numerical checks that are not required to reproduce the main results. They are, however, available from the corresponding author.

Code availability

The mathematica codes used during the current study are not publicly available because they contain preliminary and intermediate calculations that are not directly essential for reproducing or interpreting the main results, but are available from the corresponding author upon reasonable request.

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