Emergence of highly bond-dependent anisotropic magnetic interactions in Sr₄RhO₆: a theoretical study

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The quantum spin liquid states as a natural ground state of the Kitaev model have led to a quest for new materials candidates hosting Kitaev physics. Yet, there are very few materials hosting Kitaev physics. Using a combination of \textit{ab initio} and model Hamiltonian methods, we propose that Sr₄RhO₆ belongs to this category. With a tight-binding model and exact diagonalization approach, we show that despite substantial trigonal-like distortion, the electronic and magnetic properties of Sr₄RhO₆ can be well described in terms of pseudo-spin = 1/2 states. Magnetic interactions among this pseudo-spins, estimated using the second-order perturbation method are highly bond-dependent anisotropic in nature with two particularly noticeable features, antiferromagnetic Kitaev and Dzyaloshinskii-Moriya interactions. The gaped spin-wave spectra of Sr₄RhO₆ obtained with linear spin-wave theory are consistent with the underlying magnetic frustration. Further spectra analysis reveals a crucial role of these interactions in Sr₄RhO₆. In the end, we briefly discuss the enhanced magnetic interactions in a similar material Ca₄RhO₆ and propose it be another magnetic candidate belonging to the 4d class.

I. Introduction

Orbital and spin angular momentum of an electron are coupled through a relativistic effect called spin-orbit coupling (SOC). Many interesting phenomena such as the anomalous Hall effect, manipulation of spin currents, the emergence of topological properties in weakly correlated systems has been extensively studied [1–3]. However, the strongly correlated materials provide host even richer physics because of the presence of additional interactions such as crystal field splitting (Δ\textsubscript{CF}) and on-site Hubbard (U), often competing with SOC [4, 5]. This competition gives rise to exotic phenomenon like realization of unconventional superconductivity [6–8], emergence of topological phases [9] and Kitaev physics [10]. Among these examples, Kitaev physics [11] particularly has recently got a lot of attention as a driving mechanism in realization of quantum spin liquid states [12, 13].

The work of Jackeli and Khaliullin [10] accelerated the progress towards the realization of Kitaev physics in real materials. Their proposal was based on magnetic interactions between pseudo-spins on a honeycomb lattice of transition metal ions originating from the interplay of strong electrostatic crystal field (CF) of anions and SOC at transition metal sites. The five degenerate \textit{d} orbitals of transition metal ion split into triply degenerate \textit{t}\textsubscript{2g} and doubly degenerate \textit{e}\textsubscript{g} orbitals due to Δ\textsubscript{CF} (see Fig. 1(a)). Energetically lower \textit{t}\textsubscript{2g} manifold further splits in the presence of SOC to form the half-filled pseudo-spin \( J_{\text{eff}} = \frac{1}{2} \) states dominating low energy space of materials. Magnetic interactions between these \( J_{\text{eff}} = \frac{1}{2} \) pseudo-spin states was proposed to be dominantly Kitaev-type.

Cobaltates [14–23], iridates [24–31] and \( \alpha \)-RuCl\(_3\) [32–36] are some of the examples falling in this category. Recent studies on Ir-based double perovskite compounds have further widen the horizon of Kitaev physics on frustrated fcc lattice formed by magnetic ions with spatially separated octahedral environment [37–41].

These pseudo-spin \( J_{\text{eff}} = \frac{1}{2} \) behave as Kramers’s doublet (i.e. \( J_{\text{eff}}^\gamma \), where \( \gamma = x, y, z \) operators follow the fermionic anti-commutation relation) only in the limits, \( \Delta_{\text{CF}} \to \infty \) and when the splitting among the \textit{t}\textsubscript{2g} manifold due to additional trigonal(tetragonal) distortions \( \Delta_{\text{CF}}^{\text{t}}(\Delta_{\text{CF}}^{\text{tet}}) \to 0 \). However, the real materials mentioned above are far from these ideal limits making the situation even more complex. Such complexities are inevitable when a minor change in details of these interactions may have dramatic effects on the macroscopic behavior of the material. For example, in iridates despite the presence of additional \( \Delta_{\text{CF}}^{\text{t}}(\Delta_{\text{CF}}^{\text{tet}}) \) distortions which are responsible for mixing between \( J_{\text{eff}} = \frac{1}{2} \) and \( \frac{3}{2} \) states [27, 31], the large SOC of Ir 5d orbitals still allow \( J_{\text{eff}} = \frac{1}{2} \) description of the magnetic properties. However, same cannot be pre-assumed for a 4d transition metal compound where SOC strength is nearly half of its 5d counterpart and \( \Delta_{\text{CF}}^{\text{t}}(\Delta_{\text{CF}}^{\text{tet}}) \) distortions of octahedra might be comparable to the SOC strength. This inhibits any generic rule for behavior prediction of such materials and hence, a case to case study is often required.

The scarcity of 4d magnetic compounds with \( J_{\text{eff}} = \frac{1}{2} \) behavior makes it even more difficult to obtain any comprehensive understanding coming from experiments. To the best of our knowledge, the only example of magnetic material in this category is \( \alpha \)-RuCl\(_3\) and has been the subject of extensive theoretical and experimental inves-
tigations [32–36]. Other 4$d$ materials such as Li$_2$RhO$_3$, Sr$_2$RhO$_4$, and some theoretically predicted Rh and Ir-based fluorides are either non-magnetic (Li$_2$RhO$_3$ shows spin-glass behavior) or paramagnetic in nature [42–44]. In the quest of new Kitaev candidates, Sr$_3$RhO$_6$ is another possible example of a 4$d$ oxide [45, 46]. Materials like Sr$_4$RhO$_6$ and some Ir-based double perovskites [37–41] with isolated metal-anion octahedra (as shown in Fig. 1(b)) may possess an advantage over materials with edge-shared geometry because the larger spatial separation between the magnetic ions in the former can minimize the direct overlap of $d$ orbitals as compared to edge shared geometry. This in turn may result in suppression of additional undesirable nearest-neighbor as well as farther neighbor Heisenberg-like isotropic coupling. Sr$_3$RhO$_6$ is believed to exhibit ideal cubic octahedral environment on Rh-sites [46] in a centrosymmetric crystal structure. Such a distinctive feature may lead to the realization of pure $J_{\text{eff}}$ = 1/2 states, a feature not realized in any of the previously mentioned Kitaev candidate materials. Despite purportedly having such lucrative features with the possibility of hosting rich physics, it is surprising to find scarcity of theoretical study dedicated to this material and hence is the focus of our study in this article.

In this study, using a combination of first-principles calculations and a tight-binding model, we first show that contrary to the earlier belief [46], the Rh-O$_6$ octahedra in Sr$_3$RhO$_6$ is not perfect and the octahedral crystal field at Rh-sites has additional trigonal-like distortions originating from the influence of the extended environment of Sr atoms. Using the exact diagonalization (ED) technique, we show that despite such a distortion, mixing between $J_{\text{eff}}$ = 1/2-3/2 states is small and description of low-energy space in terms of $J_{\text{eff}}$ = 1/2 states is still valid in this material. Magnetic interaction among these pseudospins estimated using second-order perturbation theory show highly bond-dependent anisotropic behavior with additional diagonal/off-diagonal terms appearing alongside two particularly noticeable features, antiferromagnetic Kitaev and Dzyaloshinskii-Moriya (DMI) interactions on some of the first nearest-neighbor (1NN) Rh-Rh bonds. We attribute the appearance of DMI to the local inversion symmetry breaking due to the extended environment of Sr$^{+2}$ ions. The second and third nearest-neighbor interactions are found to be negligibly small. The classically optimized magnetic ground state brings an antiferromagnetic configuration which is energetically close to the previously proposed magnetic structure. Spin wave spectra calculated using linear spin-wave theory is found to be gaped throughout the Brillouin zone, consistent with underlying frustrated magnetic interactions. The origin of various features of the spectra is analyzed separately by examining the role of various magnetic interaction terms in the spin Hamiltonian. In the end, we also show that the replacement of Sr with Ca atoms can substantially enhance the magnetic interactions and may be a better magnetic candidate in the category of 4$d$ oxides.

II. Methods

Density-functional theory calculations have been performed using projector-augmented wave method [47, 48], implemented within Vienna ab initio simulation package (VASP) [49]. The Perdew-Burke-Ernzerhof functional [50] is used for the exchange-correlation functional within the GGA formalism. We start with the experimental lattice parameters of trigonal crystal system of Sr$_3$RhO$_6$ with centrosymmetric space group space group R3c (No. 167) which are $|a|$ = $|b|$ = 9.740 Å, $|c|$ = 11.840 Å; $\alpha$ = $\beta$ = 90° and $\gamma$ = 120° [46]. Using plane wave cutoff energy 550 eV, $2 \times 2 \times 4$ Γ-centered $k$-mesh and energy convergence criteria of $10^{-5}$ eV, we optimize the lattice parameters with experimentally proposed magnetic ground (accommodated within 24 Rh atoms $2 \times 2 \times 1$ supercell) considering SOC effect at the self-consistent level. A DFT+$U$ approach employing Liechtenstein [51] scheme with on-site Coulomb interaction $U$ = 2.5 eV and exchange interaction $J_{\text{H}}$ = 0.9 eV was used. The values of $U$ and $J_{\text{H}}$ parameters are consistent with the previous study [46]. Optimized a and b lattice constants were found to be overestimated by $\sim 3.1$ % while c remains the same. Since this change in lattice constants is significant, we have used the optimized structure in further calculations.

Non-spin polarised tight-binding (TB) Hamiltonian ($H_{\text{TB}}$) was calculated by projecting onto all the five Rh-$d$ orbitals using the Wannierization procedure [52] and is shown in Fig. 2(a). Crystal field matrix on site i ($\Delta^C_{\text{i}}$) is extracted from the onsite part of $H_{\text{TB}}$. We estimated the Coulomb matrix elements $U_{ij|\omega = 0}$ within the constrained random phase approximation (cRPA) by neglecting the screening effects for all the five Rh $d$ orbitals, states corresponding to which are energetically well-separated form other states [53–55]. This provides $U$ = 2.474 eV and $J_{\text{H}}$ = 0.106 eV which was further used in our multi-band Hubbard model.

III. Results

A. Structural analysis and electronic properties

Under a large $\Delta^C_{\text{tr}}$, the low energy space Rh-$4d^5$ ions can be described by a single hole within the $t_{2g}$ manifold with effective spin moment $s$ = 1/2 and effective orbital angular moment $L'$ = 1. The spin-orbit coupling then leads to an effective total angular momentum of $J_{\text{eff}} = s - L'$ resulting in doubly degenerate pseudospin-1/2 states forming low-energy space in this material. This is schematically shown in Fig. 1(a). However, the lowering of cubic $O_h$ symmetry of octahedron due additional $\Delta^C_{\text{tr}}$ ($\Delta^C_{\text{tot}}$) terms can invalidate this picture. Hence it
and the octahedral environment. The optimization enhanced to 92.28 and 87.72°. Structural optimization also alters the O-Rh-O bond angles six Rh-O bond lengths elongated to 2.109 Å. The structural optimization with the magnetic ground state retains the $\mathbf{O}_{\text{h}}$ symmetry as was proposed earlier in Ref [46]. In this experimental crystal structure, all the six Rh-O bond lengths are $\sim 2.044$ Å while O-Rh-O bond angles are quite close to the ideal 90° with the largest deviation being 0.1°. However, full structural optimization with the magnetic ground state in our DFT calculation brings substantial changes in $a$ and $b$ lattice constants along with the changes in the local octahedral environment. The optimization enhanced $a$ and $b$ lattice constants to 10.046 Å and also all the six Rh-O bond lengths elongated to 2.109 Å. The structural optimization also alters the O-Rh-O bond angles to 92.28 and 87.72° (see Fig. 1(b)). Also, out of eight Sr neighbors in the extended environment of Rh atoms, two “apical” Sr atoms along $c$ axis are at 2.952 Å distance while other “non-apical” six are at 3.340 Å in the optimized structure. This is shown in Fig. 1(b) (short Rh-Sr distances are along A-bonds and long ones are along B/C/D-bonds). These two kinds of Rh-Sr distances were 2.960 and 3.238 Å in the starting structure. Almost similar Rh-Rh 1NN distances $\sim 5.98/6.0$ Å of all the 8 bonds before optimization has changed substantially now to $\sim 5.9$ and 6.13 Å for two A-bonds, and six B/C/D bonds respectively. Thus optimization of structure results in substantial changes in Rh-O, non-apical Rh-Sr, and overall Rh-Rh bond lengths and is consistent with enhancement of $a$ and $b$ lattice constants.

In order to understand how these changes in crystal structure affect the CF, we set up a TB model with $d$ orbital basis of $\psi^\dagger = \{d_{2z^2}, d_{x^2-y^2}, d_{xz}, d_{yz}, d_{xy}\}$ using Wannierization procedure as mentioned in methods section and the band structures obtained from both, DFT and TB are shown in Fig 2(a). The CF matrix $\Delta_{\text{CF}}$ extracted from the onsite part of $H_{\text{TB}}$ is given in Eq. 1. Entries in the matrix are in the unit of eV.

$$
\Delta_{\text{CF}} = 
\begin{bmatrix}
-2.5385 & -0.0034 & 0.0936 & -1.3124 & -0.0511 \\
-0.0034 & 2.5547 & 0.0333 & -0.0111 & -0.117 \\
0.0936 & 0.0033 & 0.1102 & 0.0504 & -0.0533 \\
-0.1324 & -0.0111 & 0.0504 & 0.1094 & 0.0567 \\
-0.0511 & -0.1170 & -0.0533 & 0.0567 & 0.1179
\end{bmatrix}
$$

By diagonalizing this matrix one can find that the $t_{2g}$- $e_g$ crystal field splitting ($\Delta t_{2g}^{\text{CF}}$) is $\sim 2.630$ eV while the triply degenerate $t_{2g}$ splits into a $a_{1g}$ singlet and $e_g$ doublet by $\Delta_{\text{CF}} \sim 160$ meV with doublet being higher in energy than the singlet. The corresponding eigenvectors are graphically represented in Fig. 2(b), where each column in the $5 \times 5$ graph represents an eigenvector with row representing absolute weight of individual orbitals. This representation clearly highlights the nature of $\Delta_{\text{CF}}$ in Sr$_2$RhO$_6$ which has been depicted in Fig. 1(a).

This particular form of $\Delta_{\text{CF}}$ can be understood as follows. The shorter “apical” Sr-Rh bond passes through the center of two triangular faces of Rh-O$_6$ octahedra as shown in Fig. 1(b)-(c). This bond is also one of the four three-fold rotational symmetry (C$_3$) axis of the Rh-O$_6$ octahedra. The electrostatic repulsion along these shorter bonds behaves as compressing strain causing changes in Rh-O bond lengths and O-Rh-O bond angles. This is analogous to the case of trigonal distortions where bond distortions take place along one of the four $C_3$ axes of the

![FIG. 1. (a) $J_{\text{eff}}$ picture for a $d^5$ system arising from octahedral crystal field ($\Delta^{\text{CF}}$) and spin-orbit coupling ($\lambda$). Additional splitting of $J_{\text{eff}}=3/2$ states due to trigonal like distortions ($\Delta^{\text{CF}}$) into two doublets $a_{1g}$ and $e_g$. (b) Side view of Sr$_2$RhO$_6$ crystal structure. Spatially separated octahedrons are evident. Local $x$, $y$, and $z$ axes on two of the octahedron are shown. $a$, $b$ and $c$ are the global crystallographic axes. Two kinds of color-coded Rh-Sr bonds along with O-Rh-O bond angles obtained after optimization of the crystal structure are shown. (c) Extended local environment (including Sr atoms) around an Rh atom in Sr$_2$RhO$_6$. Four types of Rh-Rh nearest neighbors A, B, C, and D-bonds with Rh-O Octahedra on these bonds are also shown.](image1)

![FIG. 2. (a) Band structure plot from the $ab$ initio and Wannier-based TB model calculations considering all the Rh d orbitals in the basis. (b) Graphical representation of eigenvectors of matrix in Eq. 1. In column-wise representation of eigenvectors each row represents absolute weight of individual orbitals. Labeling of eigenstates is done in accordance of Fig. 1(a).](image2)
octahedra. Thus, in Sr$_4$RhO$_6$, an extended anisotropic environment of Sr atoms produces a non-spherical crystalline potential responsible for additional $\Delta_{\text{CF}}$ of Rh-O$_6$ octahedra. The cubic $O_h$ symmetry then lowers to $D_{hd}$ in this case.

Distortions like $\Delta_{\text{CF}}$ tend to lower the energy separation between $J_{\text{eff}}=1/2$ and 3/2 states. This brings a genuine concern about whether the strength of SOC in Sr$_4$RhO$_6$ is sufficient enough to separate out these two states. To examine this point, we calculated the ab initio band structures for three cases, (i) non-magnetic, (ii) with SOC, and (iii) with SOC + $U$. SOC was included at the self-consistent level in these calculations.

In Fig. 3, we only show the bands near the Fermi level which are dominantly contributed by $t_{2g}$ orbitals, linear combinations of which form the $J_{\text{eff}}=1/2$ and 3/2 states. One can see that the inclusion of SOC leads to substantial changes in the bands structure around Fermi level in Fig. 3(b) in comparison with non-magnetic case in Fig. 3(a). In particular, SOC leads to separation of bands near -0.1 eV (red box in Fig. 3(b)) from the other bands ($J_{\text{eff}}=3/2$ bands) near -0.1 eV. Inclusion of $U$ on Re d states further contributes to this band separation as shown in Fig. 3(c). Imposition of the magnetic ground state in band structure calculation (not shown) fully opens the gap at the Fermi level making it insulating. This is similar to the case of $\alpha$-RuCl$_3$ [35] and hence $\lambda$ in Sr$_4$RhO$_6$ is expected to be similar of $\alpha$-RuCl$_3$ i.e. $\lambda \sim 140$ meV [36]. One can conclude that the electronic structure of Sr$_4$RhO$_6$ is the combined efforts of $U$, SOC, and magnetism. Having examined the role of SOC, one can further quantify the $J_{\text{eff}}=1/2$ and 3/2 states admixture due to $\Delta_{\text{CF}}$ by considering a multi-band Hubbard model for an isolated Rh$^{4+}$ ion. This is discussed in the next section.

B. Onsite Hamiltonian and the atomic features

One way to estimate the extent of mixing between the $J_{\text{eff}}=1/2$ and 3/2 states is by calculating the projection of a “pure” $J_{\text{eff}}=1/2$ and 3/2 states for the case when $\Delta_{\text{CF}}=0$ onto the “true” $J_{\text{eff}}=1/2$ obtained with Eq. 1. These states are atomic features and hence can be described in an isolated atom limit. In this limit, a multi-band Hubbard Hamiltonian at site, $i$ in the five-orbital basis reads as,

$$H_0 = H_{\text{el}} + H_{\text{soc}} + H_{\text{int}}$$

$$= \sum_{i,\sigma} \psi_{i\alpha}^\dagger \Delta_{\text{CF}} \psi_{i\sigma} + \sum_i \lambda L_i \cdot s_i$$

$$+ \frac{U}{2} \sum_{i,\alpha} n_{i\alpha\sigma} n_{i\alpha\sigma'} + \frac{U'}{2} \sum_{i,\alpha \neq \beta} n_{i\alpha} n_{i\beta}$$

$$- \frac{J_H}{2} \sum_{i,\sigma,\sigma', \alpha \neq \beta} \psi_{i\alpha\sigma}^\dagger \psi_{i\alpha\sigma'}^\dagger \psi_{i\beta\sigma'} \psi_{i\beta\sigma}$$

$$- \frac{J'}{2} \sum_{i,\alpha \neq \alpha', \alpha \neq \beta} \psi_{i\alpha\sigma}^\dagger \psi_{i\alpha'\sigma'}^\dagger \psi_{i\beta\sigma'} \psi_{i\beta\sigma}$$

(2)

In above expression, $U/U'$ are intraorbital/interorbital Hartree energies; and $J_H$ and $J'$ are Hund’s coupling and pair hopping interaction, respectively. Rotational invariance in the isolated atom limit dictates the relationships: $U' = U - 2J_H$ and $J_H = J'$. We use $U = 2.474$ eV and $J_H = 0.106$ eV which are estimated from cRPA as mentioned in the methods section. We consider $\lambda = 140$ meV which is similar to $\alpha$-RuCl$_3$ [56]. However, on a later stage we also show that $\lambda = 195$ meV does not qualitatively influence the magnetic interactions in Sr$_4$RhO$_6$. We diagonalize the above Hamiltonian considering five electrons of Rh$^{4+}$ ions which give a total of 252 eigenstates, the lowest two and the next four of which are the $J_{\text{eff}}=1/2$ states and $J_{\text{eff}}=3/2$ states, respectively.

| $\langle \phi_{\alpha} \vert \phi_{\beta} \rangle$ | $\langle \phi_{\alpha'} \vert \phi_{\beta'} \rangle$ | $\langle \phi_{\alpha} \vert \phi_{\beta} \rangle$ |
|-----------------|-----------------|-----------------|
| 1               | 0.919 0.297     | 2               |
| 3               | 0.053 0.158     | 4               |
| 5               | 0.070 0.150     | 6               |
| 6               | 0.162 0.041     |                  |

TABLE I. Projections of $J_{\text{eff}}=1/2, 3/2$ states obtained when $\Delta_{\text{CF}}=0$, onto $J_{\text{eff}}=1/2$ states with true CF from Eq. 1.

For $\Delta_{\text{CF}}=0$, $t_{2g}$-e$_g$ splitting was fixed at 2.790 eV and all the off-diagonal matrix elements were zeroed in Eq. 1. The lowest six states in this case are represented by $\{ \phi_{\alpha} \}$, $\alpha = 1, 6$ while lowest two states obtained using true CF from Eq. 1 are labelled as $\{ \phi_{\beta} \}$, $\beta = 1-2$. The projections $\langle \phi_{\alpha} \vert \phi_{\beta} \rangle$ are listed in Table I. From the table, since $\langle \phi_{\alpha'} \vert \phi_{\beta} \rangle = 0.919$ for $\alpha/\beta = 1, 2$, one can conclude that the $J_{\text{eff}}=1/2$ states retain their major weight despite a substantial $\Delta_{\text{CF}}$, validating applicability of $J_{\text{eff}}=1/2$ picture in Sr$_4$RhO$_6$. The non-zero value of projections $\langle \phi_{\alpha'} \vert \phi_{\beta} \rangle \sim 0.16$ for $\alpha = 3-6, \beta = 1-2$ indicates a small admixture of $J_{\text{eff}}=1/2$ and 3/2 states.

One of the quantities which can be measured from the resonant inelastic X-ray scattering experiments are the single-point excitations represented by sharp peaks in the scattering intensity in the relevant energy range. It can be a direct probe for cubic symmetry lowering of the Rh-O$_6$ octahedra in Sr$_4$RhO$_6$. Theoretically, such a low-lying crystal field-assisted many-body excitations bear a
close resemblance to the eigenvalues obtained from diagonalization of many-body Hamiltonian in Eq. 2. For Sr$_2$RhO$_6$, analysis of eigenvalue reveals that the $J_{\text{eff}} = 3/2$ states split into two doublets, and $J_{\text{eff}} = 1/2$ doublets, and $J_{\text{eff}} = 1/2$ doublets, with the lower $J_{\text{eff}} = 3/2$ doublet is $E_1 = 0.181$ eV. It can also be observed that $E_1$ is $\sim 30$ meV smaller than the expected value of $\frac{3}{2}\Delta_{\text{ex}}$ due to finite $\Delta_{\text{ex}}$. From the higher $J_{\text{eff}} = 3/2$ doublets, the next single ion excitation is at $\sim 1.695$ eV. This point, a broad continuum of states with energy separations of few meV in the window of $\sim 165$ meV are found in our calculations. Having investigated the electronic properties of Sr$_2$RhO$_6$, we now discuss its magnetic properties in the next section.

C. Magnetism

We start by projecting the Hamiltonian in Eq. 2 to the pseudo-spins $J_{1/2}$ subspace and introduce hoping ($H_{\text{hop}}$) as perturbation. The hopping amplitudes are extracted from $H_{TB}$ and are listed in Appendix V. In the limit $U \gg t$, the second-order perturbation term brings,

\[
\begin{align*}
H^{(2)} &= \sum_{ij} \sum_{\alpha,\alpha'} \mathcal{H}(i,j)_d |i\alpha, j\beta\rangle \langle i\alpha', j\beta'|,
\mathcal{H}(i,j)_d &= \sum_{kl} \sum_{\gamma,\lambda} \frac{1}{\Delta E} (i\alpha, j\beta)|H_{\text{hop}}|k\gamma, l\lambda \langle k\gamma, l\lambda|H_{\text{hop}}|i\alpha', j\beta'|,
\end{align*}
\]

where $1/\Delta E = \frac{1}{2}1/(E_{i\alpha} + E_{j\beta} - E_{k\lambda} - E_{l\gamma})$. Here, $|i\alpha, j\beta\rangle$ and $|i\alpha', j\beta'\rangle$ are two-site states made of $J_{1/2}$ doublets, and $|k\gamma, l\lambda\rangle$ are two-site excited states with $d^6$ and $d^4$ configurations with Hilbert space dimensions of 210 for both. $H_{\text{hop}}$ connects a two-site ground state to these excited states. The eigenstates of isolated Rh ions with 4 and 6 $d$ electrons are obtained again by exact diagonalization.

One can represent the pseudo-spins $J_{1/2}$ as $S_\mu = \langle \alpha | J_{\mu,\text{eff}} | \beta \rangle$ which are the expectation values of pseudospin $J_{\mu,\text{eff}}$ operators with $\mu = 0, x, y, z$. Here, $J_{\mu,\text{eff}}$ is the matrix representation of operator $J_{\mu,\text{eff}}$. Using it, Eq. (3) can be mapped to a spin Hamiltonian of the form,

\[
H_{\text{spin}} = S_{\mu}^\dagger \Gamma(i,j)^{\mu\nu} S_{\nu}^\dagger,
\]

In the above expression, summation over all repeated indexes is implied. The map can be achieved by solving the linear equations,

\[
-S_{\alpha\alpha'}^\mu S_{\beta\beta'}^\nu \Gamma(i,j)^{\mu\nu} = H(i,j)_{\alpha\beta\alpha'\beta'}
\]

Here, degeneracy of the Kramers doublet leads $\Gamma^{0\mu} = \Gamma^{\mu0} = 0$. Thus, the most general form of exchange interaction matrix on an Rh-Rh bond $l \in (i,j)$ is defined as,

\[
\Gamma_l = \begin{pmatrix}
J + \zeta & \eta + D' & \eta' - D'\\
\eta - D & J - \zeta & \eta'' + D'' \\
\eta' + D' & \eta'' - D'' & J + K
\end{pmatrix}
\]

In the above expression, $J$, $K$, and $\eta/\eta'$ are the Heisenberg, Kitaev and off-diagonal interaction terms between the pseudospins-1/2, while $\zeta$ is the diagonal anisotropic term. DMI is represented by $(D, D', D'')$ vector.
The Rh atoms form a body-centered cubic lattice in Sr$_4$RhO$_6$ and thus each Rh atom has eight 1NNs. Based on the nature of magnetic interactions between different 1NNs, we subdivide the Rh-Rh bonds into three distinct categories which are indicated as A/B/C/D bonds in Fig. 1(c). Values of magnetic interactions are listed in Table II. For bond A and C, the $\Gamma_1$ matrix acquire a more symmetric form since on these bonds $\zeta = \eta = \eta'$ $= \eta'' = D = D' = D'' = 0$. However, the magnetic interactions on these two bonds differ in their strengths. On B-bond, $\Gamma_B$ takes the general form of Eq. 4 and $\Gamma_D$ can be obtained by simply taking the transpose of $\Gamma_B$.

Several remarks are in order. First, one can see that the strength, as well as signs of interactions, differ for different bonds. For example, for A and C bonds $J$, $\eta$, and $\eta'$ are antiferromagnetic while for B-bond they are ferromagnetic and the antiferro Kitaev coupling is stronger on B-bond than the others. We emphasize that the antiferromagnetic Kitaev coupling in Sr$_4$RhO$_6$, although smaller, distinctly differs from the previous reports on iridates and $\alpha$-RuCl$_3$ [36, 56]. Second, quite interestingly, DMI appears on B and D bonds in the centrosymmetric structure of Sr$_4$RhO$_6$. However, $D$, $D'$, and $D''$ have opposite signs on these two bonds. We attribute this to the local inversion symmetry breaking due to anisotropic crystalline potential produced by Sr atoms in the extended environment around Rh atoms. In the bipartite bcc lattice of Rh atoms, the first neighbors of an Rh atom are all symmetry inequivalent Rh atoms and are not related by inversion. For A-bond, the apical Sr atoms situated at the center of the bonds act as inversion center (see Fig. 1(c)) and hence the hopping matrix on this bond in appendix V is symmetric, i.e. $T_{ij}^\alpha = T_{ij}$, resulting in the suppression of DMI. However, this arrangement is not available for B and D bonds leading to the form $T_{ij}^\alpha \neq T_{ij}$ of hopping matrix, resulting in the appearance of finite DMI on these bonds. Third, one may think that the Sr$^{+2}$ ions on A-bond may mediate superexchange interaction between Rh atoms through their $s$ orbitals. However, on the contrary, we find highly suppressed interactions on this bond suggesting a destructive role of the anisotropic crystalline potential of the Sr$^{+2}$ on magnetic interactions. Fourth, we found large off-diagonal terms on some of the Rh-Rh bonds. This is similar to the case of iridates and $\alpha$-RuCl$_3$ [56] resulting from substantial $\Delta''_{xy}$ distortions present in all these materials. Based on the two particularly noticeable features in the first two points, viz $-\alpha \sim \alpha$ antiferromagnetic Kitaev terms and appearance of DMI, one may consider Sr$_4$RhO$_6$ a special 4$d$ magnetic material.

| Term | Bond-type | A   | B   | C   |
|------|-----------|-----|-----|-----|
| $J$  |           | 0.291 | -1.062 | 3.260 |
| $K$  |           | 0.040 | 1.360 | 0.292 |
| $\zeta$ |         | 0.000 | 0.464 | -0.121 |
| $\eta$ |           | 0.020 | -0.867 | 0.463 |
| $\eta'$ |         | 0.000 | -1.802 | 0.354 |
| $\eta''$ |        | -0.020 | 1.047 | -0.274 |
| $D$  |           | 0.000 | 1.512 | 0.000 |
| $D'$ |           | 0.000 | 0.830 | 0.000 |
| $D''$ |          | 0.000 | -1.343 | 0.000 |

TABLE II. Estimated first neighbor (NN) Heisenberg $J$, Kitaev $K$ and diagonal $\zeta$ and off-diagonal $\eta$, $\eta'$, $\eta''$ anisotropic terms for Sr$_4$RhO$_6$ given in meV. The second nearest neighbor interactions were found to be negligibly small ($< 0.1$ meV). Parameters used are $U = 2.474$ eV, $J_H = 0.106$ eV and $\lambda = 140$ meV.

Increasing the magnitude of SOC strength $\lambda$ in our model does not change the interactions at a qualitative level. For $\lambda = 195$ meV, we find that on A-bond, the magnetic interactions remain almost similar. However, on C-bond, the magnitude of $J$ is reduced by $\sim 13\%$ while other interactions reduced to $48\%$ of their values from $\lambda = 140$ meV case. On B-bond, while $J$, $K$, and $\zeta$, remain more or less the same, the magnitude of all other terms is reduced by $24\%$ with the increase of $\lambda$. The sign of all the magnetic terms remains the same. The findings of this analysis are consistent with the previous study on $\alpha$-RuCl$_3$ [36]. Further analysis in coming sections is based on $\lambda = 140$ meV case, which is expected to be closer to the real value in Sr$_4$RhO$_6$.

Magnetic interaction of Table II are used to optimize the classical magnetic state using SpinW package [57]. The obtained magnetic ground state, represented by orthonormal vector $-(1.0 0.5 0)$, is shown in Fig. 4(b) along with the experimentally proposed one in Fig. 4(a). The antiferromagnetic state obtained in our calculations successfully captures most of the experimental features. In the experimental magnetic structure, the spin arrangement on Rh-Rh bonds (Fig. 1(c)), A and B are antiferro-
romagnetic while on C and D it is ferromagnetic. Optimized magnetic state in Fig. 4(b) from our calculations retains antiferromagnetic coupling on A and ferromagnetic coupling at D bonds. However, this configuration differs from the one shown in Fig. 4(a) on bonds B and C where the spin arrangement in the two cases are just opposite to each other i.e. on B-bond the coupling is ferro while on C-bond it is antiferromagnetic in our optimized structure. Swapping the interactions at bonds B and C does not bring the experimentally observed ground state indicating a joint meticulous effort of all the magnetic interactions to bring the ground state. We find a slight deviation of magnetic moments from the ac plane mainly due to the presence of off-diagonal terms like $\eta/\eta'/\eta''$ and DMI on some of the Rh-Rh bonds. This is consistent with the experimental finding of small tilting from c axis [46]. Our optimized magnetic configuration is energetically close to the experimentally proposed one with the former stabilized by 1.552 meV/spin. The second and third neighbor magnetic interactions are found to be negligibly small in Sr$_4$RhO$_6$ and do not bring any distinguishable change in the optimization of the magnetic ground state. Thus we ignore them in further calculations of spin-wave spectra.

Here, we would like to comment on the scale of magnetic ordering temperature of a material depends on various parameters like the strength of exchange interactions, number of neighbors, their corresponding exchange contributions, and spatial dimensions of the magnetic lattice. Although, the magnetic lattice of Rh atoms in Sr$_4$RhO$_6$ form a three-dimensional bulk structure with eight first magnetic neighbors, the strongly frustrated anisotropic nature of bond-dependent magnetic interactions might be the reason behind its experimentally observed low $T_N$ of $\sim$ 7.5 K.

## D. Spin-wave spectra

We further use the magnetic interactions listed in Table II in linear spin-wave theory to obtain the spin-wave spectra using SpinW package [57]. Obtained spectra along various reciprocal space directions is shown in Fig. 5.

Several points are to be noted about the spectra. First, one can see that the spectra have gaped along all directions in reciprocal space with a Goldstone gap of $\sim$ 2 meV. This feature of spin-wave spectra may be caused by the breakdown of SU(2) symmetry of the isotropic Heisenberg Hamiltonian. Such a symmetry breaking can be a result of additional Ising like Kitaev terms and/or diagonal/off-diagonal anisotropic terms like $\zeta$, $\eta$, $\eta'$ and $\eta''$. Second, one branch $\sim$ 8 meV in the spectra appears to be dispersion-less. It is separated from the dispersing branch by $\sim$ 0.5 meV. Such a feature has previously been observed from the inelastic neutron scattering experiments on some of the cobaltates [16], pertinent material candidates for Kitaev physics [23]. Third, it can be seen that the spin-wave spectra near $\Gamma$ point is quadratic in nature. This is in contradiction to the expected linear dispersion of spin-wave dispersion for an antiferromagnetic ground state.

![FIG. 5. Spin wave spectra of Sr$_4$RhO$_6$ obtained within linear spin wave theory considering magnetic interactions of Table II.](image)

In order to investigate the origin of previously mentioned features of spin-wave spectra of Sr$_4$RhO$_6$, we break it down to the contribution of either individual or a specific combination of magnetic interactions. The plots are shown in Fig. 6. Considering $J$ and $K$ terms together, we immediately obtain both branches with a lower branch, at $\Gamma$, showing the linear dispersion behavior of an antiferromagnet. The plot is shown in Fig. 6(a). However, the spectra are barely gaped in this case due to dominant $J$ over $K$ and which is also responsible for the dispersion width of $\sim$ 5.5 meV of the lower branch. Consideration of $K$-only term in the Hamiltonian produces a completely flat branch at $\sim$ 4 meV (not shown) consistent with the previous theoretical study on Kitev model [58]. $\zeta$-only term indeed causes the gap opening along with deviation towards a quadratic dispersion.
at \( \Gamma \) of the lower branch and as shown in Fig. 6(b). However, the energy scale, in this case, is smaller than that of the original spectra in Fig. 5. A combination of \( J + K + \zeta \) (Fig. 6(c)) reproduces some of the features in the more or less similar spectral windows as that of the original spectra. However, the dispersion width and nature of the lower branch, in this case, are inconsistent with the original one in Fig 5. Additionally, near \( \Gamma \), dispersion of the lower branch appears to be further deviating from quadratic to higher powers of \( k \). The terms \( D + D' + D'' + \eta + \eta' + \eta'' \) produces similar but relatively flatter branches than the \( \zeta \) terms and is shown Fig. 6(d). The spectral energy window, in this case, is similar to that of \( J + K + \zeta \) term. Thus one can say conclusively that the dominant off-diagonal terms are mainly responsible for the gap in spin-wave spectra of \( \text{Sr}_4\text{RhO}_6 \) while the diagonal anisotropic term decides the nature of dispersion near \( \Gamma \) point in spin-wave spectra of \( \text{Sr}_4\text{RhO}_6 \). The overall spectra which resemble a typical magnetic system with strong frustration is a joint effort of all the terms of magnetic Hamiltonian.

IV. Case of \( \text{Ca}_4\text{RhO}_6 \)

The crystal structure of \( \text{Ca}_4\text{RhO}_6 \) by replacing Sr with Ca atoms in \( \text{Sr}_4\text{RhO}_6 \) and performing a full structural optimization retains the original trigonal symmetry of crystal structure. However, \( |a|=|b| \) reduces by \( \sim 0.4\% \) while \( |c| \) reduces by \( \sim 5.1\% \). This reduction is in accordance with the smaller +2 ionic radius of Ca atoms when compared to Sr atoms. We estimate the magnetic interactions in \( \text{Ca}_4\text{RhO}_6 \) in a similar fashion as done for \( \text{Sr}_4\text{RhO}_6 \) and obtained values are listed in Table III below.

| Term | Bond-type | A  | B  | C  |
|------|-----------|----|----|----|
| \( J \) |            | 0.447 | –1.944 | 5.119 |
| \( K \) |            | 0.038 | 3.104 | 0.460 |
| \( \zeta \) |            | 0.000 | 0.483 | –0.180 |
| \( \eta \) |            | 0.052 | –1.362 | 0.694 |
| \( \eta' \) |            | 0.000 | –2.832 | 0.560 |
| \( \eta'' \) |           | –0.040 | 1.989 | –0.460 |
| \( D \) |            | 0.000 | 2.911 | 0.000 |
| \( D' \) |            | 0.000 | 1.565 | 0.000 |
| \( D'' \) |           | 0.000 | –2.176 | 0.000 |

TABLE III. Estimated first neighbor (NN) Heisenberg \( J \), Kitaev \( K \) and diagonal \( \zeta \) and off-diagonal \( \eta \), \( \eta' \) and \( \eta'' \) anisotropic terms for \( \text{Ca}_4\text{RhO}_6 \) given in meV. Parameters used are \( U = 2.474 \) eV, \( J_H = 0.106 \) eV and \( \lambda = 140 \) meV.

As one can see from the table, most of the magnetic interactions are substantially enhanced when compared to their \( \text{Sr}_4\text{RhO}_6 \) counterparts, except on the A-bond. This is due to enhanced hopping amplitudes among \( d \) orbitals of Rh atoms. Such an enhancement is consistent with the reduced volume in the current case due to the reduction of lattice parameters. In \( \text{Ca}_4\text{RhO}_6 \), the Rh-Rh 1NN bond lengths were found to be substantially smaller than that of \( \text{Sr}_4\text{RhO}_6 \) and are \( \sim 5.62 \) (for A-bonds) and 5.71 Å (other six B/C/D bonds), resulting in enhanced hopping amplitudes of Rh-\( d \) orbitals. Thus, \( \text{Ca}_4\text{RhO}_6 \) maybe a better material candidate belonging to the rare class of \( 4d \)-transition metal-based magnetic compound and calls for an experimental exploration.

V. Conclusion

In the quest for new Kitaev candidates, in this work, we have investigated the electronic and magnetic properties of \( \text{Sr}_4\text{RhO}_6 \). Through \textit{ab initio} calculations and a TB model, we show the lowering of cubic symmetry of Rh-O\(_6\) octahedra due to additional trigonal-like distortions which are in contradiction to the previous experimental proposal. Using the exact diagonalization technique, we show that despite such a distortion, electronic and magnetic properties of \( \text{Sr}_4\text{RhO}_6 \) can be well described with the pseudo-spin 1/2 framework. The magnetic interactions between these pseudo-spins were found to be highly bond-dependent anisotropic in nature. We found two particularly noticeable features of the 1NN magnetic interactions in \( \text{Sr}_4\text{RhO}_6 \) which are, appearance of antiferromagnetic Kitaev term and DMI. This may place \( \text{Sr}_4\text{RhO}_6 \) in a distinct class of materials as previously proposed Kitaev candidates shown to have ferromagnetic Kitaev couplings and DMI appears on the 2nd neighbor bonds \([56]\). The analysis of spin-wave spectra obtained employing linear spin-wave theory considering these interactions reveals the crucial role of diagonal and off-diagonal magnetic interactions in producing a gaped spectrum of \( \text{Sr}_4\text{RhO}_6 \). In the end, we also propose \( \text{Ca}_4\text{RhO}_6 \) in the \( 4d \) category of transition metal compounds as a better magnetic candidate with larger magnetic interaction than \( \text{Sr}_4\text{RhO}_6 \). Our theoretical study provides deeper insights of structural, electronic and magnetic properties of these compounds and calls for further experimental investigations of these compounds.

Appendix A: First neighbors Rh-Rh hopping amplitudes in \( \text{Sr}_4\text{RhO}_6 \) expressed in the basis \([d^\dagger_{i,2}, d^\dagger_{i,-y,2}, d^\dagger_{i,x}, d^\dagger_{i,y}, d^\dagger_{i,z}]\).
A-bond

B-bond

C-bond

TABLE A-1. First neighbor Rh-Rh hopping amplitudes on different types of bonds shown in Fig. 1(c)

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