Spin interaction and magnetism in cobaltate Kitaev candidate materials: an \textit{ab initio} and model Hamiltonian approach

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In the quest for materials hosting Kitaev spin liquids, much of the efforts have been focused on the fourth- and fifth-row transition metal compounds, which are spin-orbit coupling assisted Mott insulators. Here, we study the structural and magnetic properties of 3d transition metal oxides, Na$_2$Co$_2$TeO$_6$ and Na$_3$Co$_2$SbO$_6$. The partial occupancy of sodium in former compound is addressed using a cluster expansion, and a honeycomb lattice of sodiums is found to be energetically favored. Starting from the \textit{ab initio} band structures, a many-body second order perturbation theory leads to a pseudospin-$\frac{1}{2}$ Hamiltonian with estimated magnetic interactions. We show that the experimentally observed zigzag magnetic state is stabilised only when the first neighbour Kitaev coupling dominates over the Heisenberg term, both of which are highly suppressed due to presence of $e_g$ orbitals. A third neighbour Heisenberg interaction is found dominant in both these compounds. We also present a phase diagram for Na$_3$Co$_2$TeO$_6$ by varying the electron-electron and spin-orbit interactions. The computed spin excitation spectra are found to capture essential features of recent experimental magnon spectrum, lending support to our results.

I. Introduction

Strong quantum fluctuations in the ground state of a many-spin system can produce a quantum spin liquid state, in which spins are highly entangled even at large separations without any long-range order. Re-alisation of quantum spin liquid in actual materials is clearly attractive, especially for its potential application in quantum computation. Realisation of quantum spin liquid in actual materials is clearly attractive, especially for its potential application in quantum computation. One of the early solvable spin models is the Kitaev's honeycomb lattice model, proposed as a material candidates for realising the Kitaev spin liquid, are questions worth pursuing. Additionally, whether the small structural difference in the two compounds, explained later, can bring some noticeable changes.

In transition metal compounds, the origin of anisotropic magnetic interactions such as Kitaev interaction is attributed to a combination of the directional nature of transition metal $d$ orbitals and the interaction of unquenched orbital moments with spin moments via spin-orbit interaction (SOI), which may give rise to this type of non-trivial anisotropic exchange coupling. Under the large CF present in these 4/5$d$ compounds, the low energy excitations of 5$d^5$ configuration of transition metal ions can be described by a single hole with an effective spin moment $S = 1/2$ and an effective orbital angular momentum $L = 1$ within the $t_{2g}$ manifold. The SOI then leads to an effective total angular momentum of $J_{total} = S + L$, forming for a pseudospin-1/2 corresponding to doubly degenerate ground state.

Based on the above discussions, several interesting questions arises about structural, electronic and magnetic properties of cobaltates. Whether cobaltates are a Kitaev-type material, and if so, how close it is to a quantum spin liquid, are questions worth pursuing. Additionally, whether the small structural difference in the two compounds, explained later, can bring some noticeable changes.

A host of transition-metal compounds have been proposed as a material candidates for realising the Kitaev physics. Nevertheless, compounds containing a 3$d$ element distinguishes themselves from 4/5$d$ compounds. On the one hand, crystal fields (CF) and spin-orbit coupling (SOC) are believed to be substantially stronger in 4/5$d$ compounds than in their third-row counterparts. On the other hand, 3$d$ elements are considerably more compact and the localisation of $d$ orbitals results in larger Hubbard $U$ and intra-atomic Hund’s coupling compared to 4/5$d$ compounds. Much of previous attention has been paid to 4/5$d$ magnetic materials, in which the interplay of Hubbard interaction ($U$), intra-atomic Hund’s exchange ($J_h$), CF ($\Delta$) and the SOC ($\lambda$) leads to intricate Mott insulating states. The studies focusing 3$d$ material are few and limited mostly to theoretical models. A quantitative examination based on \textit{ab initio} electronic structure methods of the electronic and magnetic structure of the co-based compounds, Na$_2$Co$_2$TeO$_6$ and Na$_3$Co$_2$SbO$_6$, is evidently in order.

Each Co$^{2+}$ with seven $d$ electrons in a nearly octahedral CF of oxygen in these materials shows a high-spin $t_{2g}e_g^2$ configuration. The $d$ electrons on an isolated Co ion is then described by an effective spin $S = 3/2$ and orbital angular momentum $L = 1$, giving rise to a low-energy pseudospin-1/2 doublet after application of SOC. Similar to iridates or RuCl$_3$, experiments propose zigzag magnetic ground state also for Na$_2$Co$_2$TeO$_6$ and Na$_3$Co$_2$SbO$_6$. What makes these $d^5$ cobaltates even more intriguing, compared to those of $d^5$ iridates or RuCl$_3$, is the additional presence of spin-only active $e_g$ orbitals.

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changes in the magnetic interactions would be a crucial information from an experimental perspective. Pertaining to the structure-property relation, how the Na partial occupancy in Na$_2$Co$_2$TeO$_6$ impacts its electronic or the magnetic properties clearly requires investigation.

In the present study, the fractional occupancy of Na in Na$_2$Co$_2$TeO$_6$ is first resolved computationally using the cluster expansion technique, with which we obtain particular pattern formation of Na atoms in the supercell of Na$_2$Co$_2$TeO$_6$. Subsequently, the magnetic interactions between the Co$^{2+}$ ions in terms of pseudospins-1/2 for both Na$_2$Co$_2$TeO$_6$ and Na$_3$Co$_2$SbO$_6$ are obtained based on the second-order perturbation theory. The hopping amplitudes and CF splitting considered in this method are estimated from tight-binding (TB) models obtained from fitting the ab initio electronic structures. We show that Heisenberg interactions as well as off-diagonal couplings are all highly suppressed and the dominant interaction is Kitaev-type for first nearest-neighbour (1NN) Co atoms. Trigonal CF splitting, albeit comparable to the strength of SOC in these materials, does not alter the pseudospin-1/2 picture. The second nearest-neighbour (2NN) and inter-layer magnetic interactions are found to be negligibly small. Contrary to $4d/5d$ based Kitaev-materials, quite surprisingly, the third nearest-neighbor (3NN) magnetic interactions are significantly larger than the 1NN ones. Remarkably, a suppressed Kitaev coupling and appearance of off-diagonal terms are revealed for 3NNs. The spin wave spectra obtained using these magnetic interactions in a Heisenberg-Kitaev model shows qualitative agreement with experiments. By varying parameters Hubbard $U$ and SOC strength-$\lambda$ we obtain a phase diagram for Na$_2$Co$_2$TeO$_6$. We find different type of zigzag magnetic ordering stabilised in major portion of the phase diagram. We extensively discuss the properties of Na$_2$Co$_2$TeO$_6$ in this study and finish our discussion in the end with a brief comparison between the properties of Na$_2$Co$_2$TeO$_6$ and Na$_3$Co$_2$SbO$_6$.

II. Methods

Before proceeding to the discussions of the crystal and basic electronic structures, let us briefly describe the computational details of the ab initio calculations for basic electronic structure and total energies, and of the cluster expansion and Monte Carlo simulation employed to understand the Na vacancy in Na$_2$Co$_2$TeO$_6$.

A. Ab initio and TB calculations

To calculate the total energies and electronic structure of cobaltates, we perform density-functional theory (DFT) calculations with the generalized-gradient approximation (GGA) within Perdew-Burke-Ernzerhof framework\cite{perdew1996generalized}. Calculations were performed using Vienna ab initio simulation package (VASP: version-5.4.4)\cite{vasp}. Planewave basis set with a cutoff at 550 eV with projected augmented wave potentials\cite{blochl1994projector, kresse1999ultrasoft} is used, with a 8 × 8 × 4/6 × 3 × 6 $k$-grid for the Brillouin zone sum for calculations on the primitive cell of Na$_2$Co$_2$TeO$_6$/Na$_3$Co$_2$SbO$_6$, and a 6 × 6 × 3 $k$-grid for the supercell to be described later. To account for the correlation in Co(II) $d$-states, a static on-site $U$ is used in the GGA+$U$ formalism\cite{hedin1970relativistic}. SOI was included along with spinor wavefunctions in the nonrelativistic approximation. The total energies are calculated self-consistently till the energy difference between successive steps was better than 0.5 × 10$^{-6}$ eV/formula unit. All results are sufficiently converged for this choice of basic computational parameters. Using Na vacancy configuration obtained from our cluster expansion calculations (discussed next) along with the experimentally observed zigzag magnetic ground state, a full structural optimization relaxing both ion positions and lattice parameters using $U = 3$ eV leads to lattice parameters within 1.4% of the experimental values. We hence use the experimental crystal structures in all subsequent ab initio band structure calculations.

To extract the CF matrix and hopping matrix elements, a TB Hamiltonian describing the low-energy states of both the materials were constructed using the maximally localized Wannier function implemented in Wannier90 package\cite{mostofi2008wannier90}. We consider all the five Co $d$ orbitals in the TB basis. The strength of SOI $\lambda = 65$ meV is determined by fitting the SOC included ab initio band structure with the TB model after explicitly introducing the intratomic SOC term $(\sum_i \lambda \vec{L}_i \cdot \vec{s}_i$, where $i$ is site index) in the model. The band structure fit is shown in Fig. 3(b).

B. Cluster expansion and Monte Carlo simulations

The issue of Na partial occupancy in Na$_2$Co$_2$TeO$_6$ is resolved using a cluster-expansion model to aid a global survey of the energy landscape of the vacancy disorder. The total energy of Na$_2$Co$_2$TeO$_6$ with 2/3 Na occupancy in Na$_2$Co$_2$TeO$_6$ is expressed as a cluster expansion up to the 4th order, as

$$E(C) = E_0 + \sum_\alpha g_\alpha V_\alpha \varphi_\alpha, \quad (1)$$

where a configuration $C$ refers to particular occupation of the lattice conforming to 2/3 occupancy of a Na monolayer, $V_\alpha$ are the effective cluster interactions associated with the symmetry inequivalent cluster $\alpha$ with multiplicity $g_\alpha$, and $\varphi_\alpha$ are the cluster correlations calculated as symmetrized averages of the products of all lattice sites (1, 2, 3 and 4 for one, two, three and four-point clusters) over the number of unit cells needed to form the cluster $\alpha$ in configuration $\{C\}$. Cluster spaces with up to four-point clusters (quadruplets) comprised of 132 distinct clusters are considered. Further improvement on the model is not seen upon inclusion of higher order clusters. The effective cluster interactions $V_\alpha$ are obtained...
using least absolute shrinkage and selection operator as implemented in the ICET package. The total energies of a $2 \times 2 \times 1$ supercell obtained from \textit{ab initio} calculations are used to train and cross-validate the model in Eq.(1). The model is subsequently employed in Monte Carlo simulations in the canonical ensemble to obtain the lowest energy configuration with Na vacancies. The Monte Carlo annealing processes start from a sufficiently high temperature of 1000 K, to avoid trapping into local minima. The annealing proceeds by lowering the temperature as a function of Monte Carlo steps with function $T_{\text{start}} - (T_{\text{start}} - T_{\text{stop}}) \times \log(\text{step} + 1) / \log(n_{\text{steps}})$ where $T_{\text{start}}$ ($T_{\text{stop}}$) is the starting (target) temperatures, and $n_{\text{steps}}$ (step) is the total number of Monte Carlo steps (current step). We obtain the ground state at 300 K in each case which remain so with further lowering of temperature close to zero. We set the lower temperature at 225 K in our Monte Carlo simulations. The Na monolayer $n \times n$ supercells with ($n = 4,10,14$) were used in our simulations. Typically, a system is annealed in $2^6 - 2^8$ steps, depending on system size, to avoid mode collapsing. MC simulations were performed using the same ICET package.

III. \textbf{Na}_2\text{Co}_2\text{TeO}_6

A. Structure and Na vacancies

In this section, we present the results concerning the basic structure and electronic structure of \textbf{Na}_2\text{Co}_2\text{TeO}_6 obtained from \textit{ab initio} calculations. We will discuss properties of \textbf{Na}_3\text{Co}_2\text{SbO}_6 later in Sec. IV. As shown in Fig. 1(a), in the experimental crystal structure of \textbf{Na}_2\text{Co}_2\text{TeO}_6,\textit{12,14,15,38–40} Co(II) ions are caged in edge-sharing oxygen octahedra, forming a honeycomb lattice with a Te ion sitting in the center of each hexagon. These 2-dimensional Co-O-Te sheets are joined by hexagonal close-packed Na monolayers to form a 3-dimensional array, with hexagonal lattice in the space group \textit{P}6_3\textit{mm}. It was found that the intercalated Na layers has a 2/3 overall occupancy, though the six-fold symmetry remains intact. Not only this presents a challenge to DFT calculations, the charge pattern of the partially occupied Na layers can also influence the spin states and interactions which is the central topic of present study. Therefore, we begin by sorting out this issue before performing further analysis of the electronic and spin structures.

To this end, we perform cluster expansion calculations in which random starting vacancy configurations conforming to 2/3 occupancy invariably converge to a honeycomb lattice, when annealed from over 1000 K steadily down to 300 K. The energy evolution for different supercells in the simulated annealing processes is shown in Fig. 2(a), which all evidently converge to the same ground state. We stress that the energy in this plot is the configurational potential energy of Na vacancies, which shows several steps in various temperature ranges before plateauing at 300 K for ground state configuration. Lowering the temperature further to 225 K does not change the energy, reassuring that the system is well equilibrated. The evolution of coordination numbers of Na for a $10 \times 10$ supercell during a typical annealing is shown in Fig. 2(b). The population of triply coordinated Na-sites increases gradually as the annealing proceeds, while the population of atoms with other coordination numbers diminish. The resultant structure at 300 K only has triply coordinated sites, corresponding to a honeycomb lattice. These results point to the honeycomb net as a most probable ground state monolayer configuration. However, when we stack two of such honeycomb lattices together in a given experimental unit cell, where the original hexagonal close-packed sheets adopt a \textit{ABAB} type periodic stacking, it is seen the unit cell cannot have 3-fold rotational symmetry. As shown in Fig. 1(b), the three replica of such bilayer stacking with a unit cell interrelated by $C_3$ rotations are shown. Clearly, these replica do not coincide with each other, demonstrating the the lack of 3-fold symmetry in this ordered Na vacancy configuration.

We thus come to the following interpretation of the computed Na vacancy configuration, in order to reconcile with the experimentally established crystal structure with an apparent 3-fold symmetry. Within each layer, the Na vacancies are arranged to produce an ordered hon-
energy for various supercells. Horizontal dashed line represents the ground state energy. Different plateaus of energy in the equilibration process (dashed lines) is clearly visible with the flat plateau in range 300-225 K revealing that ground state has reached. (b) Change in coordination of Na-sites with temperature for 10×10×1 supercell. For ground state, only 3-point clusters are present with population of all other clusters vanishing with lowering of temperature.

The total energy for various magnetic configurations (in eV) is listed in Table I and shown in Fig. 1(c).

| Mag. config | Spin-direction |
|-------------|----------------|
| Zig-zag     | 010 001 100    |
| Stripy      | 0.0 0.226 0.231|
| Neel        | 0.338 1.688 0.116|
| FM          | 0.724 0.737 0.758|
|             | 0.252 0.073 0.086|

TABLE I. Energies of various magnetic configurations (in eV) relative to the zigzag antiferromagnetic configuration.

In order to extract the magnetic interactions, we constructed a TB Hamiltonian as described in the methods section. The crystal structure of cobaltates have a C3 axis along crystallographic c-axis. We choose the local axes x, y, z along Co-O bonds such that x + y + z = c, i.e., the local axes respects 3-fold symmetry of the crystal structure. Mapping in this setting of local axes was done considering a basis formed by all the five orbitals on Co atoms. The Brillouin zone of Na2Co2TeO6 is shown in Fig. 3(a). The \textit{ab initio} band structure for the non-magnetic phase shown in Fig. 3(b) in a calculation involving SOC shows that the low-energy excitation involves both the c\textgreek{g} and t\textgreek{z} states. Thus the Wannier functions involve the full set of d orbitals on Co. Using the basis \( \psi_{i\sigma} = [d_{x^2-y^2}, d_{x^2-z^2}, d_{y^2-z^2}, d_{xy} \, \lambda L_i \cdot \mathbf{s}_i] \) for site \( i \) and spin \( \sigma \), the TB Hamiltonian then reads

\[
H_0 = H_{\text{cf}} + H_{\text{hop}} + H_{\text{soc}} = \sum_{i,\sigma} \psi_{i\sigma}^{\dagger} \Delta_i \psi_{i\sigma} + \sum_{i\sigma,j,\sigma} \psi_{i\sigma}^{\dagger} T_{ij} \psi_{j\sigma} + \sum_i \lambda L_i \cdot \mathbf{s}_i
\]

(2)

in which the CF \( (\Delta_i) \) and the hopping amplitudes \( (T_{ij}) \) are obtained from the TB model without SOI. The so-determined spin-independent CF matrix (in eV) is

\[
\Delta_i = \begin{bmatrix}
1.377 & 0.045 & 0.045 & 0.000 & 0.0897 \\
0.045 & 0.015 & 0.006 & 0.078 & -0.006 \\
0.045 & 0.006 & 0.051 & -0.077 & -0.006 \\
0.000 & 0.078 & -0.078 & 1.377 & 0.000 \\
0.000 & -0.006 & -0.006 & 0.000 & 0.015
\end{bmatrix}
\]

(3)

This CF matrix has explicit \( C_3 \) symmetry. The spin-independent hopping amplitudes are listed in Appendix A. These parameters are used in the next set of calculations. The last term in Eq. (2) is the atomic SOI. It is observed that the strength of SOI \( (\lambda = 65 \text{ meV}, \text{see Methods section}) \) in Na2Co2TeO6 is considerably smaller than that of Ir- and Ru-based materials, for which \( \lambda \approx 400 \text{ meV}^{16} \) and 150 meV\(^{18}\), respectively.
As $\lambda$ is an order of magnitude larger than the trigonal CF, the SOC strength ($\Delta$) is expected to be of the same order as $\lambda$; this difference manifests itself in terms of enhanced direct (\(\sigma\)-type) hopping amplitudes between \(d\) orbitals of Co atoms\(^{49}\). For example, in Appendix A, \(d_{yz} - d_{yz}\) hopping on a X bond is larger when compared to other hopping interactions. The same is true for \(d_{zx} - d_{yz}\) and \(d_{xy} - d_{xy}\) hopping on Y and Z bonds. Opposite has been observed in case of Na\(^2\)IrO\(_3\)\(^{49}\).

To be concrete, let’s consider the interaction Hamiltonian

\[
H_{\text{int}} = \frac{U}{2} \sum_{i,\sigma} n_{i\sigma} n_{i\sigma'} + \frac{U'}{2} \sum_{i\neq j,\sigma\sigma'} n_{i\sigma} n_{j\sigma'} - \frac{J_{\text{H}}}{2} \sum_{i,\sigma,\sigma',\alpha\neq\beta} \langle \psi_{i\sigma}^{\dagger} \psi_{i\sigma'}^{\dagger} \psi_{j\beta} \psi_{j\beta'} \rangle - \frac{J'}{2} \sum_{i,\sigma,\sigma',\alpha\neq\beta} \langle \psi_{i\sigma}^{\dagger} \psi_{i\sigma'}^{\dagger} \psi_{j\beta} \psi_{j\beta'} \rangle.
\]

Here, \(U/U'\) are intraorbital/interorbital Hartree energies; and \(J_{\text{H}}\) and \(J'\) are Hund’s coupling and pair hopping interaction, respectively. Rotational invariance in the single atom limit dictates the relationships: \(U' = U - 2J_{\text{H}}\) and \(J_{\text{H}} = J'\).

The key here is the \(d^2\) manifold has a two-fold degenerate ground state, which form a Kramers doublet and can be treated as a pseudospin-1/2. In order to extract the magnetic interactions of these pseudospin states, we first project the full TB Hamiltonian onto the pseudospin \(S_{1/2}\) space \(\{\phi_{\alpha\sigma}\}, \alpha = \uparrow, \downarrow\), where \(\uparrow, \downarrow\) refer to the SOC pseudospin-1/2 states. We note here that due to consideration of local axes \(x, y\) and \(z\) in the forthcoming calculations, up/down axis of the pseudo-spins are along \(c\) axis which is also the trigonal distortion axis of Co-O octahedra in Na\(^2\)CoO\(_6\). We start in the isolated atom limit, where \(H_{\text{atom}} = H_{\text{eff}} + H_{\text{soc}} + H_{\text{int}}\), and introduce the hopping contribution \(H_{\text{hop}}\) as a perturbation. In the second-order perturbation theory, the Hamiltonian is written as,

\[
H^{(2)} = \sum_{ij} \sum_{\alpha\beta\alpha'\beta'} H(i, j)_{\alpha\beta\alpha'\beta'} |i\alpha, j\beta\rangle \langle i\alpha', j\beta'|,
\]

where \(1/\Delta E = \frac{1}{2}[1/(E_{i\alpha} + E_{j\beta} - E_{k\lambda} - E_{l\gamma}) + 1/(E_{i\alpha'} + E_{j\beta'} - E_{k\lambda} - E_{l\gamma})]\). Here, \(|i\alpha, j\beta\rangle\) and \(|i\alpha', j\beta'\rangle\) are two-
site states in the $J_{1/2}$ ground states, and $|k\lambda,l\gamma\rangle$ are two-site excited states, both in the isolated atom limit. $H_{\text{hop}}$ connects a two-site ground state to an excited state with $(d^6, d^8)$ configuration, the dimensions of whose Hilbert spaces are 210 and 45, respectively. The eigenstates of isolated Co with 6, 7 and 8 $d$ electrons are obtained by exact diagonalization.

Considering the scenario when magnitude of Hubbard $U$ and CF splitting are much larger than the hopping amplitudes and also when the SOC strength is much larger than $t^2/U$, the low energy space is formed by the lowest two degenerate many body states of the “onsite” Hamiltonian ($H_{\text{atom}}$). These states behaves exactly as pseudospin-1/2 Kramers doublet in the limit of an infinite CF and in the absence of any lattice distortions which can further split the $t_{2g}$ orbitals such as trigonal distortions. Writing the pseudospin $J_{1/2}$ as $S^\mu = \frac{1}{2}\sigma^\mu$, Eq. (6) can be mapped to a spin Hamiltonian of the form

$$H_{\text{spin}} = S^\mu_i \Gamma(i,j)^{\mu\nu} S^\nu_j$$

$$= \frac{1}{4} \Gamma(i,j)^{\mu\nu} \phi^\mu_\alpha \sigma^\alpha_\alpha \phi^\nu_{\alpha'} \phi^\alpha_{\beta} \phi^\nu_{\beta'} \phi^\alpha_{\beta'} \phi^\nu_{\beta'} \phi^\alpha_{\beta'} \phi^\nu_{\beta'}, \quad (7)$$

where $\mu, \nu = 0, x, y, z$, $\sigma^\mu$ are Pauli matrices, and summation over all repeated indices is implied. The map can be achieved by solving the linear equations

$$- \frac{1}{4} \sigma^\mu_{\alpha\alpha'} \sigma^\nu_{\beta\beta'} = H(i,j)_{\alpha\beta\alpha'\beta'}$$

(8)

The spin Hamiltonian thus can be rewritten as,

$$H_{\text{spin}} = \sum_{\langle i,j \rangle \in \ell(mn)} \left[ J^1_{ij} \sigma_i \cdot \sigma_j + K^1_{ij} \sigma_i^l \sigma_j^l \right] + \sum_{\langle \langle i,j \rangle \rangle \in \ell(mn)} \left[ J^2_{ij} \sigma_i \cdot \sigma_j + K^2_{ij} \sigma_i^l \sigma_j^l \right] + \sum_{\langle \langle (i,j) \rangle \rangle \in \ell(mn)} \left[ J^3_{ij} \sigma_i \cdot \sigma_j + K^3_{ij} \sigma_i^l \sigma_j^l \right]$$

Above $\langle i,j \rangle$ and $\langle (i,j) \rangle$ represent 1NN/3NN pairs. The 2NN interaction is omitted as they are negligibly small. $J$, $K$ and $\eta$ are, respectively, the Heisenberg, Kitaev and off-diagonal interactions on any $t \in Z/X/Y$ bond. E.g., for Z-type bond, $(mn)$ is $(xy)$ and so on.

We now comment briefly on the results obtained from diagonalization of the “onsite” Hamiltonian, $H_{\text{atom}} = H_{\text{ex}} + H_{\text{soc}} + H_{U}$, before going into a detailed discussion of the magnetic interactions in Na$_2$Co$_2$TeO$_6$.

1. **Onsite Hamiltonian: $H_{\text{atom}}$**

There are four parameters in $H_{\text{atom}}$ viz., $U$, $J_{\text{H}}$, $\lambda$ and $\Delta$. From the optical spectra on CoO$^{31}$, estimated value of Hund’s splitting ($J_{\text{H}}$) is $\sim 0.8$ eV. $J_{\text{H}}/U$ ratio in cobaltates is believed to be $< 0.2^{10}$, hence $U = 5$ eV was initially fixed in our calculation of magnetic interactions. $\lambda = 65$ meV obtained from band structure fitting is slightly larger than an estimated value of $\sim 0.015$ eV (corresponding to $J_{\text{eff}}$=1/2 to $J_{\text{eff}}$=3/2 transition) from inelastic neutron scattering experiment$^{12}$. Later, we will vary both $U$ and $\lambda$ to examine their effect on the magnetic interactions. $\Delta$ obtained from the atomic Hamiltonian of the TB model is consistent with what is expected for such materials$^{10,13}$.

The energy separation between $J_{\text{eff}}$=1/2 and $J_{\text{eff}}$=3/2 states, obtained after diagonalizing $H_{\text{atom}}$ with above mentioned parameter values, is $\sim 24$ meV which is in close agreement with the experimentally observed value of $\sim 21$ meV in Na$_2$Co$_2$TeO$_6$,$^{12}$ and is much smaller than the expected value of $\sim 100$ meV corresponding to $\frac{3}{2} \lambda$ (for $\lambda$=0.065 eV). We attribute this difference to be arising from large mixing between $t_{2g}$-$e_g$ orbitals through the trigonal distortions present in Na$_2$Co$_2$TeO$_6$. Compression of Co-O octahedra along c-axis causes large deviation of O-Co-O angles from the ideal 90° with the smallest and largest angles being $\sim 78°$ and 97°, respectively. This non-orthogonal local environment causes mixing between different $d$ orbitals. It is worth mentioning here that estimate of $\lambda$ from experiments would yield a value of 15 meV and yet we obtained $J_{\text{eff}}$=1/2 - 3/2 separation consistent with experimentally observed value using $\lambda$= 65 meV. This calls for scrupulous attention while estimating $\lambda$ in the systems with active $e_g$ orbitals and large trigonal distortions. The $J_{\text{eff}}$=3/2 states were found to split into two doublets with an energy separation of $\sim 7$ meV. To examine the effect of “imperfect” CF due to additional trigonal distortions, we compare the result to a perfect octahedral geometry with $\Delta = 1.36$ eV. In this case, $J_{\text{eff}}$=1/2 and $J_{\text{eff}}$=3/2 separation increased to 34 meV while the $J_{\text{eff}}$=3/2 states regained their four fold degeneracy. Although the CF heavily mixes $J_{\text{eff}}$=1/2-3/2 states, pseudospin-1/2 picture is still relevant in Na$_2$Co$_2$TeO$_6$ as both, the $U$ and CF splitting $\Delta_{t_{2g}-e_g}$ are much larger than the hopping amplitudes ($t$) and $\lambda \gg t^2/U$ still holds in our case.

2. **Magnetic interactions**

The magnetic interaction on X/Y/Z bonds (see Fig. 3(c)), estimated from the process described above, are tabulated in Table II. Owing to the local site symmetry $C_5$, we have identical magnetic interactions on all the three bonds. Indeed, the 1NN Heisenberg term is highly suppressed and antiferromagnetic as was expected in this case due to opposite sign of $e_g$-$e_g$ and $t_{2g}$-$e_g$ exchange process$^{10,13}$. However, contrary to the previous speculations, the ferromagnetic Kitaev term is also small compared with recent experimental estimation from the fitting of spin-wave dispersion data$^{12}$. The same is true for a comparison with Ru$^{36}$ and Ir$^{35}$ based compounds. There can be mainly two reasons behind such a reduction. First, smaller hopping amplitudes and large $U$ in our case.
when compared to 4d/5d materials can contribute to this huge reduction. The effect of the latter is verified by reducing $U$ to 2.5 eV while keeping the $J_H/U$ ratio fix at 0.16, in which case the magnitude of both $J_1$ and $K_1$ are substantially enhanced, to 1.93 and $-1.616$ meV, respectively. The other factor contributing to the reduction is the weaker SOI in Na$_2$Co$_2$TeO$_6$. We will examine the effect of varying $X$ in a later section to understand how it affects the magnetic interactions.

| Bond type | First NN | Second NN |
|-----------|----------|-----------|
| X/Y/Z     | $J$      | $K$       |
| $\eta/\eta'$ |         | 0.261 $-0.678$ | 0.0 $3.153$ $-0.04$ | (0.76) |

TABLE II. Estimated 1NN and 3NN Heisenberg $J$, Kitaev $K$ and off-diagonal $\eta$, $\eta'$ terms in Na$_2$Co$_2$TeO$_6$ given in meV. The 2NN interactions as well as terms other than $J$ and $K$ for 1NN were found to be negligibly small. Parameters used are $U = 5$ eV, $J_H = 0.8$ eV and $\lambda = 65$ meV.

Interestingly, all other first-neighbour off-diagonal spin interactions $\eta$ and $\eta'$ are found to be negligibly small for this particular set of parameters, in contrast to what was obtained for Ir- and Ru-based compounds. Previous arguments for the suppression of the Heisenberg interaction in this material also apply to these off-diagonal interactions. We find the second-neighbour as well as inter-layer coupling to be negligibly small, ruling out the possibility of any inter-layer interactions and effect of Na-vacancies which separates these Co-hexagons in $c$-direction. This again is in complete agreement with the some experimental observations of negligible inter-layer spin interactions. The limited magnetic correlations between Co honeycomb layers along $c$ axis observed in the experiments on Na$_2$Co$_2$TeO$_6$ was attributed to disordered distribution of Na$^+$ ions which disrupts any out-of-plane magnetic coupling making it essentially intra-layer. Not to a complete surprise, the 3NN in Na$_2$Co$_2$TeO$_6$ are also non-zero, similar to the cases of iridates and RuCl$_3$.

Surprisingly, however, antiferromagnetic $J_3$ is larger in magnitude than $K_1$, hence being the dominant interaction in Na$_2$Co$_2$TeO$_6$. At first glance, it seems unusual given that 3d orbitals are more compact compared to their 4d/5d counterparts. In Na$_2$Co$_2$TeO$_6$, the 3NN hopping can be mediated via Te ions sitting at the center of a Co-hexagon. Orbital projected density of states for Te-$s/p$ orbitals (not shown) precludes any significant contribution near the Fermi-level where Co-$d$ and O-$p$ have their main contributions. This rules out any direct interaction between Co-$d$ and Te-$s/p$ orbitals. A second possibility for the 3NN interaction is through shared O-$p$ orbitals between these ions, which is favored by the highly suppressed 3NN Kitaev interaction due to a cancellation of anistropic interactions from multiple long-distance pathways. This then allows $J_3$ to become the largest magnetic interaction in this compound. Off-diagonal couplings of a smaller magnitude appears on these bonds. On a Z-bond, $\eta_3$ is found to be antiferromagnetic, while $\eta_3'$ ferromagnetic. However, on X or Y bond, signs of these couplings do not follow a specific pattern. On these two bonds, $\eta_3'$ never becomes ferromagnetic while $\eta_3$ can be either ferro- or antiferro-magnetic.

In order to examine whether the obtained parameters can reproduce the magnetic ground state of Na$_2$Co$_2$TeO$_6$, we optimize the magnetic structure using Hamiltonian of Eq. (9) with spins allowed to rotate in the $a$-$b$ plane. We find that the classical ground state was zigzag-type with the ferromagnetic chains running along $a$-direction coupled antiferromagnetically in direction perpendicular to $a$ (see Fig. 4(b)) with propagation vector $\sim (0.0, 0.5, 0.0)$. We call it Z2 structure. This structure is different than the experimentally proposed magnetic structure with propagation vector $(0.5, 0.0, 0.0)$ which we call Z1. However, in the next section we show that one can also obtain Z1 as the classical ground by tuning the parameters of perturbation theory.

![Phase diagram](image)

FIG. 4. (a) The $U$-$\lambda$ phase diagram for Na$_2$Co$_2$TeO$_6$ at $J_H/U = 0.16$. Magnetic ground state obtained classically with magnetic interactions extracted in different regions of the phase space brings four distinct phases, a Neel and three zigzag phases Z1, Z2, Z3 shown in (b). These three zigzag phases differ by the direction of antiferromagnetic coupling between the two ferromagnetic chains in a hexagon. Z1 is the experimentally proposed magnetic state in which antiferromagnetic coupling is along the X-bond shown in Fig. 3(c).

### 3. Phase diagram

We varied $U$ and SOC strength ($\lambda$) to study their effect on magnetic interactions and on the ground state. A phase diagram, obtained from optimization of classical ground with magnetic interactions obtained at different $U$-$\lambda$ values, is shown in Fig. 4(a). $J_H/U$ ratio has been kept fixed at 0.16 in all these calculations. We obtain four distinct phase viz, Neel and three types of zigzag magnetic order (Fig. 4(b)) differentiated by direction of antiferromagnetic coupling between the ferromagnetic chains. Phase diagram can be read in the following manner.
In a smaller $U$ range (close to 3 eV), classical magnetic ground state is Neel-type and independent of $\lambda$ in this region, antiferromagnetic $J_1$ is dominant over other types of first neighbour interactions. All these interactions increase with increase in $\lambda$ with $K_1$ more rapidly than $J_1$. At a particular $\lambda$, with the increase in $U$, we find decreasing $J_1$ and $K_1$ with $J_1$ decreasing more rapidly than $K_1$. After critical values of $U$ and $\lambda$, situated on the phase boundary of Neel-$Z_1/Z_2$ phase, $K_1$ term starts to compete with $J_1$. Only when $K_1 \geq J_1$, the magnetic ground state changes from Neel to one of the zigzag types. $Z_1$ configuration (Fig. 4(b)) with propagation vector $\sim (0.5, 0.0, 0.0)$ is the experimentally observed magnetic state of $Na_2Co_2TeO_6$. In $Z_3$ configuration with propagation vector $\sim (0.5, 0.5, 0.0)$, antiferromagnetic coupling between ferromagnetic zigzag layers is along (1 1 0) direction. At some of the phase points, spin moments of our classical ground state was found to slightly deviate from $b$-direction owing to small $\eta/\eta'$ terms.

Here, a couple of remarks are in order. First, neither $J_1$, $K_1$ terms nor $J_3$, $\eta_3/\eta_3'$ terms alone can produce the zigzag ground state of $Na_2Co_2TeO_6$ which is a collective efforts of all these terms. Second, these three zigzag spin configurations are distinct and hence break the three fold rotational symmetry. To verify this point we compared the energies of these three configurations at same phase point, $U = 4$ eV and $\lambda = 0.60$ eV, the phase boundary point between $Z_1$ and $Z_2$ configurations. At this point, the obtained magnetic ground state was $Z_1$ type and energies of $Z_2$ and $Z_3$ configurations were higher in energy by 0.010 meV and 0.015 meV per spin. These differences, when compared with the scale of magnetic coupling strengths, are significant and hence establish the fact of these three zigzag magnetic configurations being distinct. Our three zigzag configurations differ from those proposed in Chen et al. as in the latter, the three domains of zigzag configurations are related by three fold rotational symmetry. For further validation of our obtained magnetic interactions, spin-wave spectra are computed and analyzed next.

D. Spin wave spectra

Recently, several inelastic neutron scattering experiments on $Na_2Co_2TeO_6$ have reported spin wave spectra of this material. The main feature of these reported spectra is gapped dispersive modes with lowest dispersive branch of width around 3 meV and some flat modes around 4.5 meV and 7 meV. A natural question about how well our estimated magnetic interactions can reproduce these experimental findings is inevitable. The spin Hamiltonian in Eq. (9) with estimated magnetic interactions is solved using the linear spin wave theory to obtain the spin wave spectra as implemented in SpinW package. These calculations were performed for the four distinct magnetic phases in Fig. 4(a), and are shown in Fig. 5.

IV. $Na_3Co_2SbO_6$

The crystal of $Na_3Co_2SbO_6$ is shown Fig. 6(a). As for $Na_3Co_2SbO_6$, Co-O-Sb environment is similar to that of Co-O-Te in $Na_2Co_2TeO_6$, except that the 2-dimensional sheets of Co-O-Sb are joined by a triangular lattice of Na atoms stacking into the three-dimensional lattice along the direction with space group $C2/m$. Thus, similar to $Na_2Co_2TeO_6$, the magnetic lattice comprised of a honeycomb network in $Na_3Co_2SbO_6$ is quasi-two dimensional and magnetic ground state is again zigzag type.
antiferromagnet described by propagation vector (1/2, 1/2, 0) with the spins aligned along the crystallographic $b$ axis. However, Co-Co distances in Na$_2$Co$_2$SbO$_6$ are 10% shorter than Na$_2$Co$_2$TeO$_6$. It would hence be interesting to investigate whether such differences in structural features can affect magnetic interactions in Na$_2$Co$_2$SbO$_6$.

The Brillouin zone of Na$_2$Co$_2$SbO$_6$ is shown in Fig. 6(b). Following similar computational procedures to that of Na$_2$Co$_2$TeO$_6$, we extracted the CF matrix and hopping interactions for Na$_2$Co$_2$SbO$_6$ and fitting of $ab$ initio band structure to a Wannier TB model is shown in Fig. 6(c).

The obtained CF matrix and hopping amplitudes are given in Eq. 10 and Appendix B, respectively. Inspection of O-Co-O angles in an octahedra reveal a deviation from ideal case of 90° to the largest angle being ∼ 96° and smallest one is ∼ 81°. Thus, the lower symmetry of $C2/m$ space group along with the trigonal CF causes the additional splitting of 15 meV within $e_g$ orbitals and two types of splitting within 6 meV, 12 meV splitting within the $t_{2g}$ orbitals. This is consistent with the previous findings on Iridates$^{35}$ and RuCl$_3$$^{36}$. Co-O-Co angles across a pair of edge-sharing octahedra are ∼ 93.5°, again close to 90° but slightly larger than the case of Na$_2$Co$_2$TeO$_6$. In our “onsite” Hamiltonian for Na$_2$Co$_2$SbO$_6$, $U$ and $\lambda$ were kept the same to 5 eV and 65 meV as before. Similar to the case of Na$_2$Co$_2$TeO$_6$, in this case too, the lowest six states are three Kramer’s doublet with energy separation of 28 and ∼ 13 meV, between the lowest and the higher two doublets, respectively.

For the lower symmetry space group of Na$_2$Co$_2$SbO$_6$, symmetry-inequivalent nearest-neighbour bonds have two types, viz-a-viz, $Z_1$ bonds || to crystallographic $b$ axis with a local $C_{2h}$ point group symmetry and $X_1/Y_1$ bonds lying in the $ab$ plane with a (lower) $C_1$ point group symmetry. This arrangement of bonds is shown in Fig. 7(a).

In such a case, on these $X/Y$ type bonds, in addition to $J$, $K$, $\Gamma$ and $\Gamma'$, one needs additional parameters $\zeta$ and $\xi$ as explained in Winter et. al.$^{35}$ to describe the magnetic interactions. The magnetic interactions estimated in this case using the second-order perturbation theory is listed in Table III.

| Bond type | $J$ | $K$ | $\eta$ | $\eta'$ | $\xi$ | $\zeta$ |
|-----------|-----|-----|-------|--------|-----|------|
| $Z_1$     | 0.3 | −0.757 | 0.0  | 0.0    | 0.0 | 0.0  |
| $X_1/Y_1$ | 0.186 | −0.211 | 0.0  | −0.15 | −0.421 | 0.0  |
| $Z_3$     | 1.7 | 0.4  | 0.34  | −0.31 | 0.0  | 0.0  |
| $X_3/Y_3$ | 1.823 | −0.189 | 0.31 | 0.0 | −0.211 | 0.302 |

By comparing with Na$_2$Co$_2$TeO$_6$, we find that the 1NN magnetic interactions are more or less similar in this case. However, a subtle difference can be found for the 3NN interactions as in Na$_2$Co$_2$SbO$_6$, the magnitudes are half of their values of Na$_2$Co$_2$TeO$_6$. One more difference between these two materials is that the Kitaev coupling on $Z_3$ bond, though again smaller, is found to be antiferromagnetic in this case. Additionally, the $\eta_3/\eta_3'$ terms are much smaller (almost half) in this case when compared to Na$_2$Co$_2$TeO$_6$.

With these magnetic parameters, in optimization of classical ground state using the Hamiltonian in Eq. 9, only in-plane movement of spins was allowed first which brings the same zigzag type magnetic ground which was obtained experimentally. However, we find a small deviation of spin from $b$ direction along $a$-axis in our optimized structure in this case too. In terms of propagation vector, the optimized magnetic structure is described by ∼ (0.498, 0.492, 0). Using this optimized magnetic structure we calculated the spin wave spectra of Na$_2$Co$_2$SbO$_6$ shown in Fig. 7(b). Most of the intensity of this spectra is found in 3-4 meV energy range which is in reasonably good agreement with the recent experiment$^{12}$. However, the negative magnon frequencies imply that the optimized magnetic ground state may not be fully consistent with the magnetic interactions of Table III. A full
FIG. 7. (a) Lattice of Co\textsuperscript{4+2} in Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6}. 1NN, 2NN and 3NN are shown by solid, dotted and dashed lines. Orange, dark gray and skyblue color represent the Z, X and Y bonds respectively. a, b and c are the crystallographic axes and cubic axes of Co-O octahedra are denoted by x, y and z. (b) Spin wave spectra obtained from linear spin wave theory for optimized classical ground state of Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6} (at \( U = 5.0 \text{ eV}, \lambda = 0.065 \text{ eV} \)), for the case when only in-plane movements of spins were allowed during the optimization. (c) Spectra obtained after full classical optimization of magnetic ground state for which a large out-of-plane deviation of magnetic moments is observed while zigzag configuration remains the ground state.

classical optimization of magnetic structure again leads to a zigzag ground state, in which spins show significant out-of-plane tilting. Spectra obtained with this structure is shown in Fig. 7(c), which clearly is free of negative frequencies and and show a 2 meV Goldstone gap. This gapped spectral feature is consistent with the previous experimental finding\textsuperscript{12}.

We now will briefly compare the properties of these two materials. Structurally, the crucial difference is the stacking of the Co honeycomb layers. For Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6}, the layers are staggered while for Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6}, these layers are exactly on the top of each other. However, the estimated interlayer magnetic interactions in our calculations are found to be negligibly small ruling out any possibility of coupling between the honeycomb layers of Co in both these materials. Co-Co distance in these two materials is very similar and comparatively larger deviation of Co-O-O angle from 90° between edge shared octahedra is found in Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6} (~ 93.5°) when compared to the Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6} (92°)\textsuperscript{14} as discussed earlier. This small difference does not seem to substantially affect the nearest-neighbour magnetic interactions. So, while the INN interactions have similar strengths in both the materials (after averaging of two type of bonds in Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6}), the smaller 3NN magnetic interactions in Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6} can be the reason behind its lower \( T_X \) (~ 7 K) than Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6} (\( T_X \sim 18 \text{ K} \)). Also, the smaller off-diagonal \( \eta_3/\eta_5^\prime \) in Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6} can be seen as a manifestation of the lower trigonal CF in Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6} as been explained in Liu et. al\textsuperscript{13}. Thus, the smaller “undesirable” off-diagonal and 3NN terms make Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6} a more suitable candidate than Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6} in the quest of spin-liquid behaviour.

In a recent study by Das et. al\textsuperscript{53} on cobalt-based Kitaev materials, the authors commented, en passant, on the magnetic interactions in Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6}. They found 1NN ferromagnetic Heisenberg and off-diagonal, antiferromagnetic 1NN Kitaev and 3NN Heisenberg couplings, all are of equal strength for this compound, differing from our results. It is important to verify that the combination of their magnetic interactions stabilizes the zigzag ground state, from following two considerations. First, the consensus seems to be that the zigzag ground state in these materials is a result of a combination of ferromagnetic \( K_1 \) and antiferromagetic \( J_1 \) and \( J_3 \)\textsuperscript{10,13}. Second, though with 1NN antiferro Kitaev coupling where the nature of Heisenberg term is of lesser consequence, one may also realize a zigzag ground state. However, in this case the role of longer-range Heisenberg interaction requires further clarification.\textsuperscript{10,13}

V. Summary and remarks

In this paper, we investigated the structural and magnetic properties of Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6} and Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6}. Using a cluster expansion model, we find a particular pattern of hexagonal lattice formation by Na-vacancies in Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6}. Using a multiband Hubbard model and the second-order perturbation theory valid in the large \( U \) regime, we have estimated the magnetic interactions in these material and showed that a zigzag magnetic order can only be stabilized when Kitaev term is either comparable to or larger than the first neighbour Heisenberg term. However, we find the third neighbour Heisenberg interaction to be the dominant magnetic interactions in both these compounds. In addition, we have also presented a phase diagram for Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6} by varying \( U \) and \( \lambda \), a majority portion of which is shared by different zigzag magnetic ground state. Based on the spin Hamiltonian, we have calculated spin wave spectra and showed that our findings are in qualitative agreement with the recent neutron-scattering experiments. A comparison between these two materials establish the fact that Na\textsubscript{3}Co\textsubscript{2}SbO\textsubscript{6} is might be a better candidate than Na\textsubscript{2}Co\textsubscript{2}TeO\textsubscript{6} in the quest for Kitaev materials due to smaller off-diagonal and 3NN magnetic interactions in the former.

The trigonal CF present in these materials is believed to be the main hurdle for realization of a quantum spin liquid phase and has been recently suggested as an experimentally tuneable parameter.\textsuperscript{13} Previously, this type of tuning has been achieved experimentally by means of strain in CoO\textsuperscript{54} and would be an interesting future direction of research at both theoretical and experimental fronts. For another interesting aspect from an experi-
mental perspective, it will be worth investigating whether magnetic field can induce a quantum spin liquid phase in these cobalt-based compounds, alluding to another Kitaev candidate material \( \alpha\)-RuCl\(_3\). 

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### Appendix A. 1NN and 3NN hopping amplitudes in Na\(_2\)Co\(_2\)TeO\(_6\)

| Hopping | 1st NN | 3rd NN |
|---------|--------|--------|
|         | X      | Y      | Z      | X      | Y      | Z      |

| \( d_{z} \rightarrow d_{z} \) | -0.0307 | -0.0307 | -0.0709 | 0.0086 | 0.0086 | -0.0335 |
| \( d_{z} \rightarrow d_{x} \) | 0.0364  | -0.0364 | 0.0364  | 0.0047 | -0.0327 | 0.0047 |
| \( d_{y} \rightarrow d_{y} \) | -0.1699 | 0.0364  | 0.0364  | -0.0327 | 0.0047 | -0.0327 |
| \( d_{x} \rightarrow d_{x} \) | 0.0364  | 0.0364  | -0.1699 | 0.0047 | 0.0047 | -0.0327 |
| \( d_{x,y} \leftrightarrow d_{x} \) | -0.0184 | 0.0638  | 0.0071  | 0.0082 | 0.0080 | -0.0010 |
| \( d_{y} \leftrightarrow d_{z} \) | 0.0638  | -0.0148 | 0.0071  | 0.0085 | 0.0073 | -0.0010 |

### Appendix B. 1NN and 3NN hopping amplitudes in Na\(_2\)Co\(_2\)SbO\(_6\)

| Hopping | 1st NN | 3rd NN |
|---------|--------|--------|
|         | X      | Y      | Z      | X      | Y      | Z      |

| \( d_{z} \rightarrow d_{z} \) | 0.0001 | -0.0096 | -0.0590 | 0.0060 | 0.0011 | 0.0244 |
| \( d_{z} \rightarrow d_{x} \) | -0.1478 | 0.0390 | 0.0352  | 0.0049 | 0.0073 | -0.0010 |
| \( d_{y} \rightarrow d_{y} \) | 0.0483 | -0.1449 | 0.0272  | 0.0055 | 0.0047 | -0.0071 |
| \( d_{x} \rightarrow d_{x} \) | -0.0624 | -0.0463 | 0.0060  | 0.0060 | 0.0206 | -0.0018 |
| \( d_{x,y} \rightarrow d_{x} \) | 0.0365 | 0.0365 | -0.1312 | 0.0009 | -0.0103 | 0.0029 |
| \( d_{y} \rightarrow d_{y} \) | -0.0482 | 0.0074 | -0.0219 | -0.0124 | 0.0176 | -0.0159 |
| \( d_{z} \rightarrow d_{y} \) | -0.0021 | 0.0616 | 0.0220  | -0.0158 | 0.0089 | 0.0096 |
| \( d_{z} \rightarrow d_{x} \) | 0.0167 | 0.0270 | -0.0223 | 0.0175 | -0.0150 | 0.0016 |
| \( d_{y} \rightarrow d_{z} \) | 0.0142 | 0.0059 | -0.1213 | -0.0018 | 0.0016 | -0.0167 |
| \( d_{x} \rightarrow d_{y} \) | -0.0106 | -0.0336 | 0.0234  | 0.0059 | -0.0019 | 0.0147 |
| \( d_{x} \rightarrow d_{z} \) | -0.1229 | 0.0032 | 0.0057  | -0.0167 | -0.0061 | 0.0134 |
| \( d_{y} \rightarrow d_{z} \) | -0.0094 | 0.0239 | -0.0497 | 0.0030 | 0.0042 | -0.0094 |
| \( d_{x} \rightarrow d_{y} \) | 0.0079 | -0.1114 | 0.0205  | -0.0154 | -0.0171 | 0.0134 |
| \( d_{y} \rightarrow d_{y} \) | -0.0221 | 0.0359 | 0.0529  | -0.0423 | -0.0026 | -0.0060 |
| \( d_{x,y} \rightarrow d_{x} \) | 0.0066 | 0.0189 | -0.0246 | -0.0278 | 0.0229 | 0.0013 |
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