



Review of honeycomb-based Kitaev materials with zigzag magnetic ordering

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The search for a Kitaev quantum spin liquid in crystalline magnetic materials has fueled intense interest in the two-dimensional honeycomb systems. Many promising candidate Kitaev systems are characterized by a long-range-ordered magnetic structure with an antiferromagnetic zigzag-type order, where the static moments form alternating ferromagnetic chains. Recent experiments on high-quality single crystals uncovered the existence of intriguing multi-**k** magnetic structures, which evolved from zigzag structures. Those discoveries have sparked new theoretical developments and amplified interest in these materials. We present an overview of the honeycomb materials known to display this type of magnetic structure and provide detailed crystallographic information for the possible single- and multi-**k** variants.

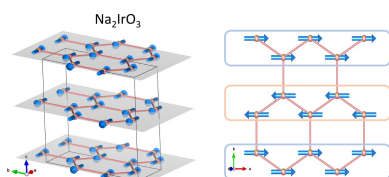
1. Introduction

Honeycomb materials have been the subject of much interest over the last few decades for their unique properties and promise in a wide range of applications (Seepersad *et al.*, 2004; Zhang *et al.*, 2015; Qi *et al.*, 2021). Magnetic honeycomb materials, where magnetic ions decorate the corners of a 2D honeycomb network, have been investigated in the search for a quantum spin liquid (QSL) – an exotic phase of matter where strong quantum fluctuations disrupt formation of long-range order while preserving a highly correlated entangled ground state (Balents, 2010; Savary & Balents, 2016; Broholm *et al.*, 2020). The closely related triangular lattice system has remained the paradigmatic example of a geometrical-frustration-driven QSL, ever since it was first proposed by P. W. Anderson (1973). Likewise, honeycomb systems also show great promise toward the realization of a QSL, aided both by a reduced nearest neighbor connectivity (3 in honeycomb systems versus 6 in triangular systems) of the magnetic ions within the layers [Fig. 1(a)], as well as a pronounced 2D nature of the magnetism, which emerges from the well separated layers.

In the decoupled 2D limit, the magnetic ground states of a single honeycomb layer were explored extensively by Fouet *et al.* (2001) in the context of a Heisenberg Hamiltonian of the form

$$H = J_1 \sum_{\langle ij \rangle_1} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle ij \rangle_2} \mathbf{S}_i \cdot \mathbf{S}_j + J_3 \sum_{\langle ij \rangle_3} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where J_1 represents the strength of the nearest neighbor (NN) bond, J_2 the second NN bond, J_3 the third NN bond, and the brackets, $\langle ij \rangle_n$, indicate the sum be carried over all n th neighbor bonds. For both an antiferromagnetic (AFM) NN ($J_1 > 0$) and a ferromagnetic (FM) NN ($J_1 < 0$), Fouet *et al.* fully characterized the exchange-space phase diagrams in the



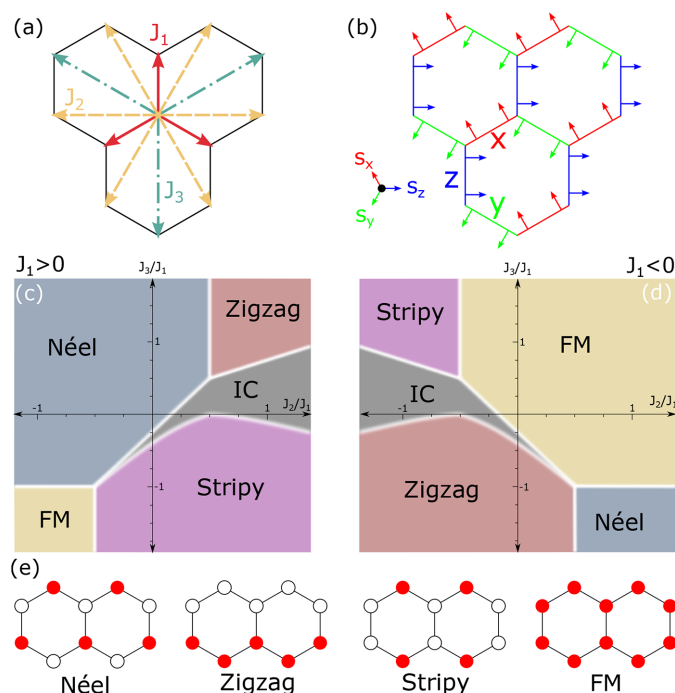


Figure 1

(a) Near-neighbor connectivity on the 2D honeycomb lattice. Here first nearest neighbor interactions (J_1) are shown by solid red arrows, second nearest neighbor interactions (J_2) are shown by gold dashed lines and third nearest neighbor interactions (J_3) are shown by teal dot-dashed lines. (b) Bond-dependent nearest neighbor Ising interactions of the Kitaev model (for ferromagnetic Kitaev coupling), showing strong exchange-driven frustration between three incompatible orthogonal spin axes. J_1 – J_2 – J_3 Heisenberg classical phase diagrams of the honeycomb lattice for (c) antiferromagnetic (AFM) and (d) ferromagnetic (FM) nearest neighbor interactions (adapted from Fouet *et al.*, 2001). The two phase diagrams are very similar and show six possible ground-state configurations: one collinear FM state, three commensurate AFM orders (Neel, stripy and zigzag states), and two incommensurate states (presented here together as one IC phase). (e) Visual depiction of the four collinear magnetic orders described above. Red and open white circles represent oppositely aligned moments.

classical limit and found six distinct magnetic ground states, shown in Figs. 1(c) and (d). These are characterized by one FM order, two different incommensurate (IC) orders and three AFM orders: a standard Néel state, a stripy state and a zigzag state where FM chains are coupled antiferromagnetically. The four collinear phases are shown in Fig. 1(e) for visualization.

Fouet *et al.* (2001) also explored the impact of quantum fluctuations on phase diagrams, and showed that while the collinear classical ground states persist, the boundaries can undergo significant shifts. Moreover, they reported evidence of unconventional states, especially in proximity to phase boundaries. Further investigation of the quantum phase diagram by the community showed the quantum fluctuations can stabilize many unconventional phases, including valence-bond crystal phases, quantum dimer phases and quantum spin liquid phases (Moessner *et al.*, 2001; Sindzingre *et al.*, 2003; Zhang & Lamas, 2013).

While the isotropic Heisenberg interactions can accurately describe the Hamiltonians of many magnetic systems, several honeycomb materials feature either an easy-plane or easy-axis

anisotropy, which slightly modifies the Hamiltonian above to be an XXZ type Hamiltonian of the form

$$H = \sum_{n=1}^3 J_n \sum_{\langle ij \rangle_n} [S_i^x S_j^x + S_i^y S_j^y + \lambda S_i^z S_j^z], \quad (2)$$

where now λ corresponds to the anisotropy in the system, either being constrained to $\lambda \in [0, 1]$ for an easy-plane type exchange anisotropy or $\lambda > 1$ for an easy-axis anisotropy (with $\lambda = 1$ being the Heisenberg model described above). While there have been investigations of the J_1 – J_2 XXZ model (Li *et al.*, 2014), the zigzag phase cannot be stabilized by a J_1 – J_2 model and thus more recent theoretical work has shifted toward a J_1 – J_3 XXZ model. Density matrix renormalization group (DMRG) approaches show a similar phase diagram to the isotropic case described by Fouet *et al.* where the zigzag is stabilized across a wide parameter range for an FM nearest neighbor and AFM third neighbor interaction (Jiang *et al.*, 2023; Bose *et al.*, 2023).

A separate mechanism of exchange frustration was explored by Alexei Kitaev (2006) using a toy model of a $S = 1/2$ bond-dependent Ising Hamiltonian on a honeycomb lattice, where each nearest neighbor bond uniquely couples a separate spin component [depicted in Fig. 1(b) for an FM case]. Via a transform into a Majorana framework, Kitaev was able to show that this model is exactly solvable and contains a QSL ground state: either a gapless QSL phase if all three bond-dependent exchanges were similar in strength, or gapped in the case of one exchange being dominant over the other two. More interestingly, Kitaev showed that for the gapless case, application of a perturbative magnetic field was able to realize a state with non-Abelian anyonic statistics, which was previously discussed as a possible framework for the development of topological quantum computation (Bravyi & Kitaev, 2002; Freedman *et al.*, 2002; Kitaev, 2003).

While the search for Kitaev materials represents an important focus in the search for fault-tolerant topological quantum computing, there already exist multiple comprehensive review articles covering Kitaev physics and materials (see for instance: Winter *et al.*, 2017; Hermanns *et al.*, 2018; Takagi *et al.*, 2019; Trebst & Hickey, 2022). In this work, rather than focusing on the QSL ground state of the pure Kitaev model, we instead focus on the mechanisms for realizing the commonly observed zigzag magnetic structure in honeycomb materials, which many of the promising Kitaev candidate materials have been found to exhibit.

The extension of Kitaev's model to real materials was made later by Jackeli & Khaliullin (2009) centered on $5d^5$ Ir⁴⁺ (and later $4d^5$ Ru³⁺) with a combination of spin–orbit coupling, octahedral crystal field effects and edge-sharing geometry of neighboring octahedral clusters. For an ideal octahedral coordination the three orthogonal spin axes lie canted out of the honeycomb planes [$\alpha = \arcsin(1/\sqrt{3}) \sim 35.26^\circ$], naturally lying perpendicular to the three magnetic–ligand–magnetic bonding planes. In this limit, non-bond-dependent interactions cancel, leaving only the Kitaev term surviving.

Table 1
List of honeycomb compounds with a zigzag AFM ground state.
 S_{eff} is effective spin. tbd is to be determined.

Compound	S_{eff}	Crystal[?] space group	k -vector	T_N (K)	References
Na_2IrO_3	$\frac{1}{2}$	$C2/m$	$(0, 1, \frac{1}{2})$	18	Ye <i>et al.</i> (2012)
$\text{Na}_3\text{Co}_2\text{SbO}_6$	$\frac{1}{2}$	$C2/m$	$(\frac{1}{2}, \frac{1}{2}, 0)$	6.7–8	Wong <i>et al.</i> (2016); Yan <i>et al.</i> (2019); Li <i>et al.</i> (2022)
$\text{Na}_2\text{Co}_2\text{TeO}_6$	$\frac{1}{2}$	$C2/m$	$(\frac{1}{2}, \frac{1}{2}, 0)$	9.6	Dufault <i>et al.</i> (2023)
$\text{Li}_3\text{Ni}_2\text{SbO}_6$	1	$C2/m$	$(\frac{1}{2}, \frac{1}{2}, 0)$	15	Kurbakov <i>et al.</i> (2017); Zvereva <i>et al.</i> (2015)
$\text{Na}_3\text{Ni}_2\text{SbO}_6$	1	$C2/m$	$(\frac{1}{2}, \frac{1}{2}, 0)$	16	Zvereva <i>et al.</i> (2015); Werner <i>et al.</i> (2019)
$\text{Na}_3\text{Ni}_2\text{BiO}_6$	1	$C2/m$	$(0, 1, 0)$	10.4	Seibel <i>et al.</i> (2013); Shangguan <i>et al.</i> (2023)
$\text{Li}_3\text{Ni}_2\text{BiO}_6$	1	$C2/m$	tbd	5.5	Berthelot <i>et al.</i> (2012)
$\text{Cu}_3\text{Co}_2\text{SbO}_6$	$\frac{1}{2}$	$C2/c$	$(1, 0, 0)$	18.5	Roudebush <i>et al.</i> (2013)
$\text{Cu}_3\text{Ni}_2\text{SbO}_6$	1	$C2/c$	$(1, 0, 0)$	22.3	Roudebush <i>et al.</i> (2013)
$\text{Ag}_3\text{Co}_2\text{SbO}_6$	$\frac{1}{2}$	$C2/m$	tbd	21.2	Zvereva <i>et al.</i> (2016)
CoPS_3	$\frac{1}{2}$	$C2/m$	$(0, 1, 0)$	122	Wildes <i>et al.</i> (2017)
NiPS_3	1	$C2/m$	$(0, 1, 0)$	155	Wildes <i>et al.</i> (2015)
NiPSe_3	1	$C2/m$	tbd	212	Basnet <i>et al.</i> (2022)
$\text{Na}_2\text{Co}_2\text{TeO}_6$	$\frac{1}{2}$	$P6_322$	$(\frac{1}{2}, 0, 0)$	27	Lefrançois <i>et al.</i> (2016); Bera <i>et al.</i> (2017); Samarakoon <i>et al.</i> (2021)
$\text{K}_2\text{Co}_2\text{TeO}_6$	$\frac{1}{2}$	$P6_3/mcm$	tbd	12.3	Xu <i>et al.</i> (2023)
$\text{Na}_2\text{Ni}_2\text{TeO}_6$	1	$P6_3/mcm$	$(\frac{1}{2}, 0, \frac{1}{2})$	27–30	Samarakoon <i>et al.</i> (2021); Bera <i>et al.</i> (2022)
$\text{Na}_2\text{Ni}_2\text{TeO}_6$	1	$P6_3/mcm$	$(\frac{1}{2}, 0, 0)$	27.5	Karna <i>et al.</i> (2017); Kurbakov <i>et al.</i> (2020)
$\text{Na}_{2.4}\text{Ni}_2\text{TeO}_6$	1	$P6_3/mcm$	$(\frac{1}{2}, 0, 0)$	25	Samarakoon <i>et al.</i> (2021)
$\text{K}_2\text{Ni}_2\text{TeO}_6$	1	$P6_3/mcm$	tbd	23–27	Matsubara <i>et al.</i> (2020); Vasilchikova <i>et al.</i> (2022)
$\text{BaNi}_2(\text{AsO}_4)_2$	1	$R\bar{3}$	$(\frac{1}{2}, 0, \frac{1}{2})$	18	Regnault <i>et al.</i> (1980); Gao <i>et al.</i> (2021)
$\alpha\text{-RuCl}_3$	$\frac{1}{2}$	$R\bar{3}$	$(0, \frac{1}{2}, 1)$	6.3–14	Park <i>et al.</i> (2024); Cao <i>et al.</i> (2016)
$\text{Ru}_{0.9}(\text{Ir,Rh})_{0.1}\text{Cl}_3$	$\frac{1}{2}$	$R\bar{3}$	$(0, \frac{1}{2}, 1)$	6	Morgan <i>et al.</i> (2024)
$\alpha\text{-RuBr}_3$	$\frac{1}{2}$	$R\bar{3}$	$(0, \frac{1}{2}, 1)$	34	Imai <i>et al.</i> (2022)
KNiAsO_4	1	$R\bar{3}$	$(\frac{3}{2}, 0, 0)$	19	Bramwell <i>et al.</i> (1994); Taddei <i>et al.</i> (2023)
KCoAsO_4	$\frac{1}{2}$	$R\bar{3}$	$(\frac{3}{2}, 0, 0)$	13	Sarkis <i>et al.</i> (2024)
			$(\frac{1}{2}, 0, \frac{1}{2})$		

The detection of zigzag magnetic order in the primary candidate materials, Na_2IrO_3 and $\alpha\text{-RuCl}_3$, ultimately led to the development of a more comprehensive Kitaev model that respects symmetry and accounts for the stabilization of order in these materials:

$$H = \sum_{n=1}^3 \sum_{\langle ij \rangle_n} J_n \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\langle ij \rangle} \sum_{\alpha, \beta, \gamma} [K^\gamma S_i^\gamma S_j^\gamma + \Gamma(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha) + \Gamma'(S_i^\alpha S_j^\gamma + S_i^\gamma S_j^\alpha + S_i^\beta S_j^\gamma + S_i^\gamma S_j^\beta)], \quad (3)$$

where alongside the Kitaev term, K^γ , there exist nearest neighbor off-diagonal terms Γ and Γ' , as well as Heisenberg interactions up the third nearest neighbor. Here n in the first sum indicates the n th rank nearest neighbor, and α, β, γ sum over the three bond directions dictated by the local x, y, z coordinates. In the applicable isotropic Kitaev limit, the Kitaev term reduces to $|K|^\gamma = |K|^\alpha = |K|^\beta = K$.

Shortly after the proposal by Jackeli and Khaliullin, multiple extensions of realizing Kitaev materials were proposed in relatively low spin–orbit-coupled $3d$ materials, holding promise in opening up the relatively scarce materials landscape (Liu & Khaliullin, 2018; Stavropoulos *et al.*, 2019;

Liu *et al.*, 2020; Motome *et al.*, 2020). The primary focus on the $3d$ materials has been on cobaltates and nickelates relying on high-spin ($S = 3/2$) Co^{2+} and ($S = 1$) Ni^{2+} . Most notably for cobalt in the presence of an intermediate strength octahedral crystal field, Co^{2+} has shown a spin–orbit-coupled Kramers ground state doublet in multiple materials thanks to its relatively unquenched orbital momentum. This mechanism has made many cobalt materials hallmark examples of $S = 1/2$ pseudospin materials (Holden *et al.*, 1971; Buyers *et al.*, 1971; Goff *et al.*, 1995; Ringler *et al.*, 2022).

While initial experimental studies reported a dominant Kitaev exchange in various cobaltates, more recent theoretical approaches have indicated that the presence of multiple hopping channels and low spin–orbit coupling typically results in a suppression of Kitaev exchange, leaving the cobaltates more at the mercy of fine tuning of local environments (Das *et al.*, 2021; Winter, 2022; Maksimov *et al.*, 2022; Liu & Kee, 2023). Many reports also highlight a large third nearest neighbor interaction (J_3), due to exchange pathways through neighboring ligand complexes (Songvilay *et al.*, 2020; Kim *et al.*, 2022; Samarakoon *et al.*, 2021; Sanders *et al.*, 2022; Yao *et al.*, 2022).

Of the multiple ground state configurations found, most candidate Kitaev materials have shown either an incommen-

surate spin spiral state or the collinear zigzag AFM phase. Stabilization of the zigzag phase can be realized either through combination of an FM J_1 and AFM J_3 , or by dominant Kitaev with subdominant off-diagonal nearest neighbor (Γ , Γ') interaction terms. While these two opposing mechanisms for development of zigzag order have been the subject of much debate in the search for Kitaev materials, the prevalence of the unusual zigzag order in honeycomb magnets is clear. Table 1 highlights the stability of the zigzag structure, which remains the ground-state configuration across a wide range of crystal space groups ($C2/m$, $C2/c$, $P6_322$, $P6_3/mcm$, $R\bar{3}$ etc.) and magnetic ion species (Co^{2+} , Ni^{2+} , Ru^{3+} , Ir^{4+}).

While quantum and thermal fluctuations often stabilize collinear structures (Price & Perkins, 2013; Rau *et al.*, 2018), more exotic non-collinear structures can be stabilized by interactions beyond standard bilinear exchange (Korshunov, 1993; Krüger *et al.*, 2023). In the honeycomb material $\text{Na}_2\text{Co}_2\text{TeO}_6$, Krüger *et al.* (2023) demonstrated that ring exchange stabilizes a non-collinear C_3 symmetric triple- $\mathbf{k}$ state, a finding that has been corroborated by recent experimental results (Chen *et al.*, 2021; Yao *et al.*, 2022, 2023). An extension to a C_2 symmetric double- $\mathbf{k}$ state in the case of monoclinic $\text{Na}_3\text{Co}_2\text{SbO}_6$ has also been suggested (Gu *et al.*, 2024). While there is currently still much debate in the community as to the true nature of these ground states, in light of these reports we will review and provide detailed crystallographic descriptions of the possible multi- $\mathbf{k}$ structures that were proposed to emerge in the aforementioned systems.

2. Monoclinic honeycomb systems with zigzag-type magnetic structures

Among the earliest and most notable candidates for the Kitaev model are the $A_2\text{IrO}_3$ iridates ($A = \text{Na}$, Li , Cu), renowned for their intriguing magnetic and electronic behaviors. These phenomena result from the combined effects of crystal field interactions, spin–orbit coupling and electron correlations. The $A_2\text{IrO}_3$ compounds crystallize in the monoclinic space group $C2/m$ and are characterized by a layered arrangement with edge-sharing octahedra. Central to these layers are iridium (Ir^{4+}) ions with a pseudospin $1/2$ ($J_{\text{eff}} = 1/2$), situated at the core of the edge-sharing oxygen octahedra, which form a honeycomb pattern. The structure also includes three inequivalent cation (A^{1+}) sites. A notable feature of these materials is a certain level of disorder, often due to the mixing of cation sites, leading to heterogeneous magnetic ground states. In this class of materials, only Na_2IrO_3 was found to display a zigzag antiferromagnetic order (Ye *et al.*, 2012). The three structural polytypes of Li_2IrO_3 (known as α -, β - and γ - Li_2IrO_3) exhibit incommensurate magnetic orders with counter-rotating moments on nearest neighbor sites (Williams *et al.*, 2016; Biffin *et al.*, 2014). Meanwhile, the magnetic ground state of Cu_2IrO_3 (Kenney *et al.*, 2019) was shown to consist of coexistent static and dynamic (spin liquid) magnetic states originating from a mixed copper valence $\text{Cu}^+/\text{Cu}^{2+}$. For $\text{H}_3\text{LiIr}_2\text{O}_6$ (Kitagawa *et al.*, 2018) and $\text{Ag}_3\text{LiIr}_2\text{O}_6$ (Chakraborty *et al.*, 2021), experimental evidence

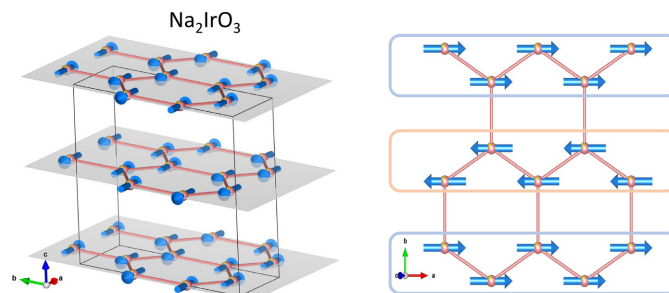


Figure 2
Magnetic structure of Na_2IrO_3 and view along $\mathbf{c}^*$ of the honeycomb layer consisting of alternating ferromagnetic zigzag chains. Magnetic structures in this article were drawn using VESTA software (Momma & Izumi, 2011)

suggest the existence of a quantum spin liquid state and coexisting incommensurate Néel and stripe ordered magnetic domains, respectively.

The zigzag magnetic structure of Na_2IrO_3 was unveiled by Ye *et al.* (2012) from single-crystal neutron diffraction data. The magnetic propagation vector was identified as $\mathbf{k} = (0, 1, \frac{1}{2})$, indicating the possibility of either stripy or zigzag-type order, below the Néel temperature $T_N = 18.1$ (2) K. The zigzag arrangement with ferromagnetic chains running along the a axis, depicted in Fig. 2, was inferred from the relative intensities of three magnetic reflections. A comprehensive crystallographic description of the magnetic structure of Na_2IrO_3 is provided in Table 2. This magnetic structure is described by the magnetic space group C_c2/m (No. 12.63) in a magnetic cell ($\mathbf{a}$, $\mathbf{b}$, $2\mathbf{c}$). The magnetic space group confines the magnetic moment to be in the ac plane. However, data from magnetic susceptibility, polarized X-ray measurements and neutron experiments suggest that the moment is primarily oriented along the a axis. The fitted neutron scattering intensities resulted in a magnetic moment of 0.22 (1) μ_B per Ir, which is significantly smaller than expected for the expected $J_{\text{eff}} = 1/2$ state. This reduced moment is attributed to the strong hybridization between the Ir $5d$ orbitals and the ligand oxygen $2p$ orbitals.

Another important category of compounds featuring honeycomb magnetic lattices is characterized by the general formula $A_{2,3}M_2M'O_6$, where A represents an alkali metal (Na , Li , K), M denotes a transition-metal ion such as Co^{2+} or Ni^{2+} and M' is a heavy metal such as Sb , Te or Bi . Kanyolo *et al.* (2023) offered an exhaustive review of honeycomb layered oxides within this group, encompassing detailed synthesis methods. Viciu *et al.* (2007) identified the layered compounds $\text{Na}_3\text{Co}_2\text{SbO}_6$ and $\text{Na}_2\text{Co}_2\text{TeO}_6$, which are akin to the layered Na_xCoO_2 , albeit with a third of the Co sites substituted by the non-magnetic ions $\text{Sb}^{5+}/\text{Te}^{6+}$. These compounds exhibit complete ordering of Co and $\text{Sb}^{5+}/\text{Te}^{6+}$ ions, forming a honeycomb lattice. However, the Na distribution amidst the honeycomb layers is markedly disordered. $\text{Na}_3\text{Co}_2\text{SbO}_6$ was found to have a single-layer monoclinic structure (space group $C2/m$), whereas $\text{Na}_2\text{Co}_2\text{TeO}_6$ possesses a two-layer hexagonal structure ($P6_322$). Notably, a monoclinic ($C2/m$) polymorph of

Table 2
Crystallographic description of zigzag magnetic structures observed in monoclinic honeycomb systems (I).
MSG is magnetic space group.

Compound	Na ₂ IrO ₃	Na ₃ Co ₂ SbO ₆	Na ₂ Co ₂ TeO ₆
MAGNDATA No.	1.10	1.788	1.259
Reference	Ye (2012)	Yan <i>et al.</i> (2019)	Dufault <i>et al.</i> (2023)
Parent space group	<i>C2/m</i>		<i>C2/m</i>
k -vector	(0, 1, $\frac{1}{2}$)		($\frac{1}{2}$, $\frac{1}{2}$, 0)
Transformation from parent to magnetic cell	(a _p , b _p , 2 c _p)		(2 a _p , 2 b _p , c _p)
MSG symbol	<i>C_c2/m</i>		<i>P_S1</i>
UNI notation	<i>C2/m.1'</i> [<i>C2/m</i>]		<i>P1.1'</i> [<i>P1</i>]
MSG No.	12.63		2.7
Transformation to MSG standard setting	a – c , b , c ; 0, 0, $\frac{1}{4}$	c , $-\frac{1}{4}$ a + $\frac{1}{4}$ b , $-\frac{1}{2}$ a – $\frac{1}{2}$ b ; $\frac{1}{8}$, $\frac{1}{8}$, 0	
Magnetic point group	2/m1'		$\bar{1}.1'$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.32, 9.215, 11.07	10.741, 18.578, 5.653	10.656, 18.387, 5.769
α , β , γ (°)	90, 108.67, 90	90, 108.56, 90	90, 108.95, 90
MSG symmetry operations	<i>x</i> , <i>y</i> , <i>z</i> , +1 $-x$, <i>y</i> , $-z + \frac{1}{2}$, +1 $-x$, $-y$, $-z + \frac{1}{2}$, +1 <i>x</i> , $-y$, <i>z</i> , +1		<i>x</i> , <i>y</i> , <i>z</i> , +1 $-x + \frac{1}{4}$, $-y + \frac{1}{4}$, $-z$, +1
MSG centering operations	<i>x</i> , <i>y</i> , <i>z</i> , +1 $x + \frac{1}{2}$, $y + \frac{1}{2}$, $z + \frac{1}{2}$, +1 <i>x</i> , <i>y</i> , $z + \frac{1}{2}$, –1 $x + \frac{1}{2}$, $y + \frac{1}{2}$, <i>z</i> , –1		<i>x</i> , <i>y</i> , <i>z</i> , +1 $x + \frac{1}{4}$, $y + \frac{3}{4}$, <i>z</i> , +1 $x + \frac{1}{2}$, $y + \frac{1}{2}$, <i>z</i> , +1 $x + \frac{3}{4}$, $y + \frac{1}{4}$, <i>z</i> , +1 $x + \frac{3}{4}$, $y + \frac{3}{4}$, <i>z</i> , –1 x , $y + \frac{1}{2}$, <i>z</i> , –1 $x + \frac{1}{4}$, $y + \frac{1}{4}$, <i>z</i> , –1 $x + \frac{1}{2}$, <i>y</i> , <i>z</i> , –1
Positions of magnetic atoms	Ir1 0, 0.333, 0 Ir2 0, 0, 0	Co 0, 0.333, 0	Co 0, 0.337, 0
Non-magnetic atoms	Na1 0, 0, 0.333 Na2 0, 0, 0 Na3 0, 0.836, 0.25 Na4 0, 0.5, 0.25 O1 0.26, 0.329, 0.396 O2 0.27, 0, 0.396	Sb 0, 0, 0 Na1 0, 0.25, 0.5 Na2 0, 0.413, 0.5 O11 0.136, 0.17, 0.794 O12 0.863, 0.17, 0.205 O2 0.375, 0, 0.20	Te 0, 0, 0 Na1 0, 0.25, 0.5 Na2 0, 0.413, 0.5 O11 0.14, 0.172, 0.80 O12 0.86, 0.172, 0.197 O2 0.381, 0, 0.192
Magnetic moments (μ_B), symmetry constraints and total magnitudes	Ir1 (0.22, 0, 0) (<i>m_x</i> , 0, <i>m_z</i>) 0.22 Ir2 (0, 0, 0) (0, 0, 0) 0	Co (0, 0.9, 0) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 0.9	Co (0.48, 1.5, 1.2) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 1.83

Na₂Co₂TeO₆ was recently documented by Dufault *et al.* (2023).

The zigzag-type magnetic structure of Na₃Co₂SbO₆ has been corroborated by multiple research groups, as defined by a propagation vector **k** = ($\frac{1}{2}$, $\frac{1}{2}$, 0) and a magnetic space group *P_S1* (No. 2.7). The magnetic symmetry permits the orientation of the magnetic moment along any crystallographic axis. An initial powder neutron diffraction study suggested that the Co magnetic moments align parallel to the *c* axis (Wong *et al.*, 2016). However, this model was subsequently contested by a single-crystal study (Yan *et al.*, 2019), which proposed a zigzag configuration with moments of 0.9 μ_B directed along the *b* axis. Confinement of the moment within the *ab* plane, orthogonal to the wavevector, was later substantiated by further single-crystal studies employing neutron polarization analysis (Li *et al.*, 2022; Gu *et al.*, 2024). Additionally, in-plane magnetic field experiments suggested a potential non-collinear double-**k** structure, indicative of XXZ easy-plane anisotropy, as opposed to Kitaev anisotropy (Gu *et al.*, 2024).

The magnetic structure of the monoclinic variant of Na₂Co₂TeO₆ was refined using powder neutron diffraction data, with magnetic intensities indexed by the identical **k** vector ($\frac{1}{2}$, $\frac{1}{2}$, 0) (Dufault *et al.*, 2023). The Rietveld refinement yielded an out-of-plane canted moment with the components *m_x* = 0.48, *m_y* = 1.5 (1) and *m_z* = 1.2 (1) μ_B . The single-**k** zigzag-like magnetic structure models of both Sb and Te cobaltates are shown in Fig. 3. Detailed crystallographic information is given in Table 2.

The past decade has seen a rapid increase in the number of new compounds within the *A_{2.3}M₂M'O₆* class. The list of *C2/m* monoclinic single-layer honeycomb systems with verified zigzag magnetic structures now includes several Ni-based (*S* = 1) compounds such as Li₃Ni₂SbO₆, Na₃Ni₂SbO₆ and Na₃Ni₂BiO₆ (Fig. 3). The nickel antimonide compounds are characterized by a magnetic supercell (2**a**, 2**b**, **c**), which originates from the propagation vector ($\frac{1}{2}$, $\frac{1}{2}$, 0). The ordered magnetic moments are slightly inclined from the *c* axis by about 17 ± 1° towards the *a* axis, rendering the moments

Table 3

Crystallographic description of zigzag magnetic structures observed in monoclinic honeycomb systems (II).

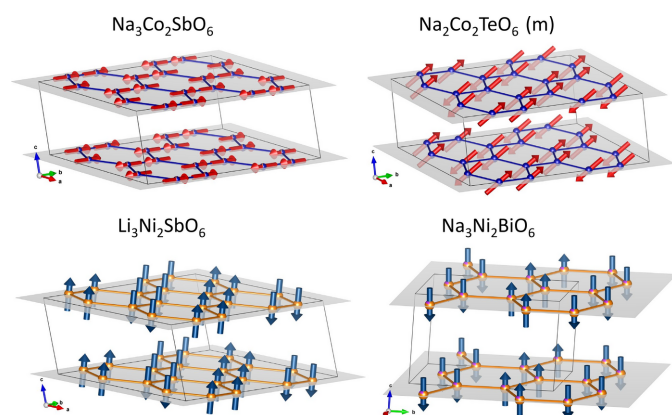
MSG is magnetic space group.

Compound	$\text{Li}_3\text{Ni}_2\text{SbO}_6$	$\text{Na}_3\text{Ni}_2\text{SbO}_6$	$\text{Na}_3\text{Ni}_2\text{BiO}_6$
MAGNDATA No.	1.373	—	1.789
Reference	Kurbakov <i>et al.</i> (2017)	This work	Seibel <i>et al.</i> (2013)
Parent space group		$C2/m$	$C2/m$
k -vector		$(\frac{1}{2}, \frac{1}{2}, 0)$	$(0, 1, 0)$
Transformation from parent to magnetic cell		$(2\mathbf{a}_p, 2\mathbf{b}_p, \mathbf{c}_p)$	$(\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p)$
MSG symbol		$P_5\bar{1}$	P_2C_2/m
UNI notation		$P\bar{1}.1'_c[P\bar{1}]$	$P2_1/m.1'_c[C2/m]$
MSG No.		2.7	11.57
Transformation to MSG standard setting		$\mathbf{c}, -\frac{1}{4}\mathbf{a} + \frac{1}{4}\mathbf{b}, -\frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b}; \frac{1}{8}, \frac{1}{8}, 0$	$\mathbf{a}, \mathbf{b}, \mathbf{c}; \frac{1}{4}, \frac{1}{4}, 0$
Magnetic point group		$\bar{1}.1'$	$2/m1'$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.368, 17.942, 5.16	10.488, 18.331, 5.581	5.399, 9.352, 5.68
α , β , γ (°)	90, 109.7, 90	90, 108.27, 90	90, 108.56, 90
MSG symmetry operations		$x, y, z, +1$ $-x + \frac{1}{4}, -y + \frac{1}{4}, -z, +1$	$x, y, z, +1$ $-x + \frac{1}{2}, y + \frac{1}{2}, -z, +1$ $-x + \frac{1}{2}, -y + \frac{1}{2}, -z, +1$ $x, -y, z, +1$
MSG centering operations		$x, y, z, +1$ $x + \frac{1}{4}, y + \frac{3}{4}, z, +1$ $x + \frac{1}{2}, y + \frac{1}{2}, z, +1$ $x + \frac{3}{4}, y + \frac{1}{4}, z, +1$ $x + \frac{3}{4}, y + \frac{3}{4}, z, -1$ $x, y + \frac{1}{2}, z, -1$ $x + \frac{1}{4}, y + \frac{1}{4}, z, -1$ $x + \frac{1}{2}, y, z, -1$	$x, y, z, +1$ $x + \frac{1}{2}, y + \frac{1}{2}, z, -1$
Positions of magnetic atoms	Ni 0, 0.1666, 0	Ni 0, 0.333, 0	Ni 0, 0.666, 0
Non-magnetic atoms	Sb 0, 0, 0	Sb 0, 0, 0	Bi1 0, 0, 0
	O1 0.379, 0, 0.225	O11 0.136, 0.175, 0.79	O1 0.226, 0.84, 0.20
	O21 0.118, 0.08, 0.233	O12 0.863, 0.175, 0.21	O2 0.748, 0, 0.213
	O22 0.88, 0.078, 0.766	O2 0.378, 0, 0.205	Na1 0, 0.5, 0.5
	Li1 0, 0.08, 0.5	Na1 0, 0.25, 0.5	Na2 0, 0.836, 0.5
	Li2 0, 0.25, 0.5	Na2 0, 0.419, 0.5	
Refined moments components (μ_B), symmetry constraints and total magnitudes	Ni (0.58, 0, 1.72) (m_x, m_y, m_z) 1.62	Ni (0.68, -0.05, 1.9) (m_x, m_y, m_z) 1.8	Ni (0.71, 0.0, 2.32) ($m_x, 0, m_z$) 2.2

nearly orthogonal to the honeycomb plane. The moment magnitudes are in the range 1.6–1.8 μ_B , marginally less than the expected value for an $S = 1$ system. The bismuth analog $\text{Na}_3\text{Ni}_2\text{BiO}_6$ exhibits ordered magnetic moments also perpendicular to the honeycomb plane, yet the zigzag chain orientation differs (Seibel *et al.*, 2013). Interestingly, the propagation vector $\mathbf{k} = (0, 1, 0)$, defining the magnetic order in this material, results in ferromagnetic chains along the *a* axis and alternating directions along the *b* axis. This model is described using the magnetic space group P_2C_2/m (No. 11.57). Crystallographic details of the magnetic structure are provided in Table 3. Given the small distortion of the honeycomb lattice in the monoclinic structure, it is inferred that the FM zigzag chains along the *a* axis consist of uniform Ni–Ni bonds, whereas the Sb and Te compounds feature chains with alternating Ni–Ni bonds. The Néel temperature typically declines when transitioning from Sb to Bi, with the same alkali metal. A recent study revealed that when subjected to an external magnetic field, $\text{Na}_3\text{Ni}_2\text{BiO}_6$ exhibits a one-third magnetization plateau. This is indicative of a ferromagnetic state, which implies the presence of bond-anisotropy

tropic Kitaev interactions in this phase (Shangguan *et al.*, 2023). This discovery has attracted significant interest, broadening the scope of fractional magnetization plateau phase research to honeycomb-lattice compounds with $S = 1$. Meanwhile, the sister compound $\text{Li}_3\text{Ni}_2\text{BiO}_6$ (Berthelot *et al.*, 2012) has yet to be thoroughly investigated and awaits neutron scattering studies to confirm zigzag magnetic ordering.

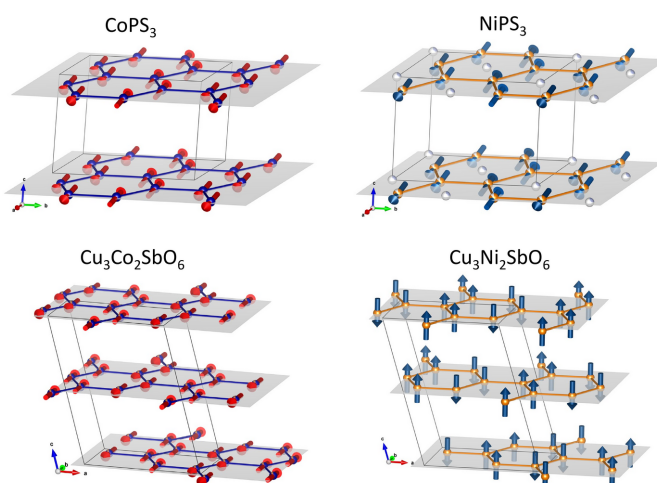
The delafossite-type structures have a similar formula, $A_3M_2M'O_6$, where the monovalent ion (*A*) can be either Cu^{1+} or Ag^{1+} . Unlike alkali-metal systems, these structures feature linear O–Cu–O coordination instead of octahedral. Notable examples include the $\text{Cu}_3\text{Co}_2\text{SbO}_6$ and $\text{Cu}_3\text{Ni}_2\text{SbO}_6$ compounds, which exhibit a monoclinic distortion of the hexagonal delafossite polytype. Their structure is described by the space group $C2/c$ and contains two honeycomb layers per unit cell. Antiferromagnetic ordering occurs at 22.3 K for the nickel variant and at 18.5 K for the cobalt variant. The magnetic structures are defined by a propagation vector $\mathbf{k} = (1, 0, 0)$ and involve FM zigzag chains along the *b* axis, antiferromagnetically coupled to neighboring chains (see Fig. 4). In the Co delafossite, magnetic moments align parallel to the *b*

**Figure 3**

Zigzag magnetic structures of monoclinic honeycomb systems $A_2M_2M'O_6$ with $A = \text{Na, Li}$ and $M = \text{Co and Ni}$. The Co moments are mainly confined to the ab plane, while the Ni moments are orthogonal to the honeycomb plane. The magnetic structures of the Sb and Te compounds are defined by $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$, forming ferromagnetic zigzag chains running along the diagonal direction. In contrast, the magnetic structure of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is defined by a propagation vector $\mathbf{k} = (0, 1, 0)$, which produces ferromagnetic chains along the a axis.

axis, while in the Ni compound, they are nearly orthogonal to the honeycomb plane. Adjacent honeycomb layers exhibit antiferromagnetic coupling. These magnetic models were described within same monoclinic crystal frame by magnetic space groups P_C2_1/c (No. 1.258) for Co and P_C2/c (No. 1.259) for Ni. Additional structural details are summarized in Table 4. Notably, the Ni compound exhibits a second polytype described by the hexagonal space group $P6_3$, with its magnetic order defined by a propagation vector $\mathbf{k} = (\frac{1}{2}, 0, 0)$. Another identified delafossite-honeycomb material is $\text{Ag}_3\text{Co}_2\text{SbO}_6$ (Zvereva *et al.*, 2016). Although *ab initio* GGA + U calculations predict a zigzag-type magnetic structure, no experimental confirmation exists to date.

The metal phosphorous trichalcogenides MPX_3 formed from transition metals (M) and chalcogen atoms ($X = \text{S, Se, Te}$) hold promise as single-layer van der Waals materials with potential applications in spintronics. The crystal structures have monoclinic symmetry with space group $C2/m$. Specifically, CoPS_3 and NiPS_3 were found to exhibit zigzag-type structures, stemming from dominant antiferromagnetic third-neighbor exchange coupling J_3 (Wildes *et al.*, 2015; 2017; Kim *et al.*, 2020; Wildes *et al.*, 2022; 2023; Scheie *et al.*, 2023). Both compounds order with a propagation vector $\mathbf{k} = (0, 1, 0)$ below the Néel temperature of 122 K (for Co) and 155 K (for Ni). The magnetic structures are depicted in Fig. 4. The magnetic structure of CoPS_3 was refined from neutron single-crystal data using a model described by the magnetic space group P_C2_1/m (No. 11.57). Refinement results allowed the moments to have components along the a and c axes, as constrained by symmetry. The total moment was found to be $3.3 \mu_B$, with the components $m_x = 3.13$ (8) and $m_z = -0.6$ (1) μ_B , consistent with an absence of a spin–orbit exciton in neutron scattering suggesting a pure $S = 3/2$ state (Kim *et al.*, 2020). Structural studies on NiPS_3 reported a site disorder between the main Ni1 (4g) and the minority Ni2 (2a) sites, with an occupancy

**Figure 4**

Zigzag magnetic structures of MPS_3 and delafossite-derived $\text{Cu}_3\text{M}_2\text{SbO}_6$, where $M = \text{Co and Ni}$.

ratio of approximately 88:12. The magnetic structure was refined from neutron single-crystal data. The zigzag-type structure involves three irreducible representations (irreps) to accommodate the magnetic ordering of both sites. The model, defined by the magnetic space group P_51 (No. 1.3), breaks all the point-group symmetry operations. While the magnetic refinement of the Ni1 (4g) site appeared to be robust, there has been less confidence in the moment direction for the minority 2a site. The moment magnitudes were found to be $1.05 \mu_B$ [$m_x = 0.94$ (3), $m_y = 0$, $m_z = -0.26$ (4)] for the Ni1 site and $1.06 \mu_B$ [$m_x = 1.0$ (5), $m_y = 0.5$ (6), $m_z = 0.0$ (9)] for the Ni2 site. The moment direction predominantly aligns with the a axis, consistent with spin-wave analyses that revealed a significant XY-like anisotropy accompanied by a minor uniaxial component (Wildes *et al.*, 2022; Scheie *et al.*, 2023). One notes that, considering only the Ni1 order, the zigzag structure can be equally well described by the magnetic space group P_C2_1/m , similar to that proposed for the Co compound. For further details, refer to Table 4.

3. Hexagonal honeycomb systems with zigzag-type magnetic structures

The hexagonal honeycomb systems known to exhibit zigzag magnetic ordering belong to the $A_2M_2M'O_6$ class with $M' = \text{Te}^{6+}$. In particular, $\text{Na}_2\text{Co}_2\text{TeO}_6$ presents an exciting opportunity for exploring quantum magnetism and exotic magnetic states. Its zigzag magnetic order and potential connection to the Kitaev model have made it a captivating subject of study within the condensed matter community. Its crystal structure is described by the $P6_322$ space group and the successive Co honeycomb planes are shifted by a $[\frac{1}{3}, \frac{2}{3}, 0]$ translation. The honeycomb networks are formed by two nonequivalent Co sites, Co1 in the $2b$ $(0, 0, \frac{1}{4})$ site and Co2 in the $2d$ $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ site. Crystal electric field excitations provided evidence that Co^{2+} ions have a spin–orbital entangled $S_{\text{eff}} = 1/2$ state (Songvilay *et al.*, 2020). Magnetic susceptibility showed a long-range

Table 4

Crystallographic description of zigzag magnetic structures observed in monoclinic honeycomb systems (III).

MSG is magnetic space group.

Compound	CoPS ₃	NiPS ₃	Cu ₃ Co ₂ SbO ₆	Cu ₃ Ni ₂ SbO ₆
MAGNDATA No.	1.264	1.231	1.258	1.259
Reference	Wildes <i>et al.</i> (2015)	Wildes <i>et al.</i> (2017)	Roudebush (2013)	Roudebush (2013)
Parent space group	<i>C2/m</i>	<i>C2/m</i>	<i>C2/c</i>	<i>C2/c</i>
k -vector	(0, 1, 0)	(0, 1, 0)	(1, 0, 0)	(1, 0, 0)
Transformation from parent to magnetic cell	(a_p , b_p , c_p)	(a_p , b_p , c_p)	(a_p , b_p , c_p)	(a_p , b_p , c_p)
MSG symbol	<i>P_C2₁/m</i>	<i>P_S1</i>	<i>P_C2₁/c</i>	<i>P_C2/c</i>
UNI notation	<i>P2₁/m.1'c</i> [<i>C2/m</i>]	<i>P1.1'c</i> [<i>P1</i>]	<i>P2₁/c.1'c</i> [<i>C2/c</i>]	<i>P2/c.1'c</i> [<i>C2/c</i>]
MSG No.	11.57	1.3	14.84	13.74
Transformation to MSG standard setting	a , b , c ; $\frac{1}{4}, \frac{1}{4}, 0$	− c , b , a + b ; 0, 0, 0	a , b , a + c ; 0, 0, 0	a , b , c ; 0, 0, 0
Magnetic point group	<i>2/m1'</i>	<i>1.1'</i>	<i>2/m1'</i>	<i>2/m1'</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.90, 10.22, 6.658	5.811, 10.064, 6.594	9.327, 5.385, 11.911	9.192, 5.309, 11.915
α , β , γ (°)	90, 107.17, 90	90, 106.997, 90	90, 105.13, 90	90, 104.88, 90
MSG symmetry operations	<i>x</i> , <i>y</i> , <i>z</i> , +1 − <i>x</i> + $\frac{1}{2}$, <i>y</i> + $\frac{1}{2}$, − <i>z</i> , +1 − <i>x</i> + $\frac{1}{2}$, − <i>y</i> + $\frac{1}{2}$, − <i>z</i> , +1 <i>x</i> , − <i>y</i> , <i>z</i> , +1	<i>x</i> , <i>y</i> , <i>z</i> , +1	<i>x</i> , <i>y</i> , <i>z</i> , +1 − <i>x</i> + $\frac{1}{2}$, <i>y</i> + $\frac{1}{2}$, − <i>z</i> + $\frac{1}{2}$, +1 − <i>x</i> , − <i>y</i> , − <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, − <i>y</i> + $\frac{1}{2}$, <i>z</i> + $\frac{1}{2}$, +1	<i>x</i> , <i>y</i> , <i>z</i> , +1 − <i>x</i> , <i>y</i> , − <i>z</i> + $\frac{1}{2}$, +1 − <i>x</i> , − <i>y</i> , − <i>z</i> , +1 <i>x</i> , − <i>y</i> , <i>z</i> + $\frac{1}{2}$, +1
MSG centering operations	<i>x</i> , <i>y</i> , <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> + $\frac{1}{2}$, <i>z</i> , −1	<i>x</i> , <i>y</i> , <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> + $\frac{1}{2}$, <i>z</i> , −1	<i>x</i> , <i>y</i> , <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> + $\frac{1}{2}$, <i>z</i> , −1	<i>x</i> , <i>y</i> , <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> + $\frac{1}{2}$, <i>z</i> , −1
Positions of magnetic atoms	Co 0, 0.331, 0	Ni1 0, 0.333, 0 Ni2 0, 0.666, 0 Ni2 0, 0, 0	Co1 0.08, 0.249, 0.499	Ni1 0.08, 0.249, 0.499
Non-magnetic atoms	P 0.057, 0, 0.169 S 0.746, 0, 0.244 S 0.252, 0.17, 0.247	P11 0.059, 0, 0.17 P12 0.44, 0.5, 0.83 P21 0.059, 0.333, 0.17 P22 0.44, 0.166, 0.83 P23 0.059, 0.666, 0.17 P24 0.44, 0.833, 0.83 S11 0.242, 0.5, 0.244 S12 0.257, 0, 0.755 S21 0.249, 0.33, 0.756 S22 0.25, 0.17, 0.243 S23 0.249, 0.67, 0.756 S24 0.25, 0.83, 0.243	Cu1 0.823, 0.09, 0.249 Cu2 0, 0.587, 0.25 O1 0.624, 0.593, 0.09 O2 0.72, 0.57, 0.41 O3 0.442, 0.085, 0.09 Sb 0.25, 0.25, 0	Cu1 0.825, 0.09, 0.249 Cu2 0, 0.585, 0.25 O1 0.62, 0.588, 0.09 O2 0.723, 0.576, 0.41 O3 0.44, 0.08, 0.088 Sb 0.25, 0.25, 0
Refined moments components (μ_B), symmetry constraints and total moment	Co (3.13, 0, −0.6) (<i>m_x</i> , 0, <i>m_z</i>) 3.36	Ni11 (0.94, 0, −0.26) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 1.05 Ni12 (−0.94, 0, 0.26) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 1.05 Ni2 (1.0, 0.5, 0) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 1.12	Co1 (0, 2.4, 0) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 2.4	Ni1 (0.44, 0, 1.49) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 1.44

magnetic order at about 27 K followed by two spin reorientation transitions at 15 and 5 K (Lefrançois *et al.*, 2016; Bera *et al.*, 2017; Samarakoon *et al.*, 2021). The magnetic order is described by the propagation vector **k** = ($\frac{1}{2}$, 0, 0). The zigzag magnetic model, described by the magnetic space group *P_C2₁2₁2₁* (No. 19.29) in a (2**a**, **b**, **c**) magnetic cell base, provided the best description of neutron scattering intensities. Ferro-magnetic chains align along the *b* direction (orthogonal to **k**), and the magnetic moments lie in the *bc* plane. The magnetic moments alternate their directions in successive layers. The out-of-plane component (*m_z*) is particularly relevant in the context of the Kitaev-type anisotropic bond-directional couplings model. Refined magnetic moments for the two Co positions were *m_y* = 2.07 (7) μ_B and *m_z* = 0.5 (2) μ_B for Co1, and *m_y* = −1.95 (10) μ_B and *m_z* = 0.5 (2) μ_B for Co2 (Samarakoon *et al.*, 2021). Other reported values, when only

in-plane components were considered, were *m_{Co1}* = 2.7 μ_B and *m_{Co2}* = 2.45 μ_B (Bera *et al.*, 2017). Fig. 5 illustrates the magnetic structures and Table 5 provides crystallographic details. A 3-**k** magnetic structure model was recently proposed by several studies (Chen *et al.*, 2021; Yao *et al.*, 2022, 2023; Krüger *et al.*, 2023), and further details will be discussed in Section 5. The magnetic field evolution of the magnetic structure of Na₂Co₂TeO₆ was recently explored by Yao *et al.* (2023), Zhang *et al.* (2023) and Bera *et al.* (2023).

A single crystal of the compound K₂Co₂TeO₆ was recently synthesized and its structural analysis revealed a *P6₃/mcm* space group (Xu *et al.*, 2023). Unlike the Na variant, the honeycomb layers in K₂Co₂TeO₆ have a different stacking arrangement, with Co atoms stacked directly on top of each other. The honeycomb lattices contain a single Co site (4*d*), and K ions are distributed in a disordered way between the

Table 5

Crystallographic description of zigzag magnetic structures observed in hexagonal honeycomb systems.

MSG is magnetic space group.

Compound	Na ₂ Co ₂ TeO ₆	Na ₂ Ni ₂ TeO ₆	Na ₂ Ni ₂ TeO ₆
MAGNDATA No.	1.645	1.646	1.258
Reference	Samarakoon <i>et al.</i> (2021)	Samarakoon <i>et al.</i> (2021)	Kurbakov <i>et al.</i> (2020)
Parent space group	<i>P</i> 6 ₃ 22	<i>P</i> 6 ₃ / <i>mcm</i>	
k -vector	($\frac{1}{2}$, 0, 0)	($\frac{1}{2}$, 0, $\frac{1}{2}$)	($\frac{1}{2}$, 0, 0)
Transformation from parent to magnetic cell	(2 a _p , b _p , c _p)	(2 a _p , b _p , 2 c _p)	(2 a _p , b _p , c _p)
MSG symbol	<i>P</i> _C 2 ₁ 2 ₁ 2 ₁	<i>I</i> _a <i>mm</i> 2	<i>P</i> _A <i>nma</i>
UNI notation	<i>P</i> 2 ₁ 2 ₁ 2 ₁ .1' _C [<i>C</i> 222 ₁]	<i>Imm</i> 2.1' _a [<i>Amm</i> 2]	<i>Pnma</i> .1' _A [<i>Amma</i>]
MSG No.	19.29	44.234	62.453
Transformation to MSG standard setting	a + b , b , c ; $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	c , a + b , b ; 0, 0, $\frac{1}{8}$	c , a + b , b ; $\frac{1}{4}$, 0, 0
Magnetic point group	2221'	<i>mm</i> 21'	<i>mmm</i> 1'
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.517, 5.258, 11.17	10.382, 5.191, 22.182	10.403, 5.201, 11.172
α , β , γ (°)	90, 90, 120	90, 90, 120	90, 90, 120
MSG symmetry operations	<i>x</i> , <i>y</i> , <i>z</i> , +1 − <i>x</i> , −2 <i>x</i> + <i>y</i> , − <i>z</i> , −1 <i>x</i> , 2 <i>x</i> − <i>y</i> , − <i>z</i> + $\frac{1}{2}$, −1 − <i>x</i> , − <i>y</i> , <i>z</i> + $\frac{1}{2}$, +1	<i>x</i> , <i>y</i> , <i>z</i> , +1 − <i>x</i> , −2 <i>x</i> + <i>y</i> , − <i>z</i> + $\frac{1}{4}$, +1 <i>x</i> , <i>y</i> , − <i>z</i> + $\frac{1}{4}$, +1 − <i>x</i> , −2 <i>x</i> + <i>y</i> , <i>z</i> , +1	<i>x</i> , <i>y</i> , <i>z</i> , +1 − <i>x</i> , − <i>y</i> , <i>z</i> + $\frac{1}{2}$, +1 <i>x</i> + $\frac{1}{2}$, 2 <i>x</i> − <i>y</i> , − <i>z</i> , +1 − <i>x</i> + $\frac{1}{2}$, −2 <i>x</i> + <i>y</i> , − <i>z</i> + $\frac{1}{2}$, +1 − <i>x</i> + $\frac{1}{2}$, − <i>y</i> , − <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> , − <i>z</i> + $\frac{1}{2}$, +1 − <i>x</i> , −2 <i>x</i> + <i>y</i> , <i>z</i> , +1 <i>x</i> , 2 <i>x</i> − <i>y</i> , <i>z</i> + $\frac{1}{2}$, +1
MSG centering operations	<i>x</i> , <i>y</i> , <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> , <i>z</i> , −1	<i>x</i> , <i>y</i> , <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> , <i>z</i> + $\frac{1}{2}$, +1 <i>x</i> , <i>y</i> , <i>z</i> + $\frac{1}{2}$, −1 <i>x</i> + $\frac{1}{2}$, <i>y</i> , <i>z</i> , −1	<i>x</i> , <i>y</i> , <i>z</i> , +1 <i>x</i> + $\frac{1}{2}$, <i>y</i> , <i>z</i> , −1
Positions of magnetic atoms	Co1 0, 0, 0.25 Co2 0.166, 0.666, 0.75	Ni 0.167, 0.667, 0	Ni 0.167, 0.667, 0
Positions of non-magnetic atoms	Te 0.166, 0.666, 0.25 O11 0.32, 0.974, 0.345 O12 0.51, 0.668, 0.345 O13 0.165, 0.356, 0.345 Na21 0, 0, 0 Na31 0.35, 0.066, 0.99 Na32 0.967, 0.636, 0.99 Na33 0.68, 0.298, 0.99	Te 0, 0, 0 O11 0.163, 0, 0.296 O12 0, 0.327, 0.296 O13 0.836, 0, 0.546 O14 0, 0.672, 0.546 Na11 0.174, 0, 0.125 Na12 0, 0.349, 0.125 Na13 0.825, 0, 0.375 Na14 0, 0.65, 0.375 Na21 0.166, 0.667, 0.125 Na22 0.333, 0.333, 0.375	Te 0, 0, 0 O11 0.159, 0, 0.594 O12 0, 0.318, 0.594 Na11 0.173, 0, 0.25 Na12 0, 0.347, 0.25 Na2 0.167, 0.667, 0.25 Na3 0, 0, 0.25
Refined moments components (μ_B), MSG constraints and total magnitudes	Co1 (0, 2.07, 0.5) (0, <i>m_y</i> , <i>m_z</i>) 2.1 Co2 (0, −1.95, 0.5) (0, <i>m_y</i> , <i>m_z</i>) 2.0	Ni (0, 0, 1.55) (<i>m_x</i> , <i>m_y</i> , <i>m_z</i>) 1.55	Ni (0, 0.41, 1.67) (0, <i>m_y</i> , <i>m_z</i>) 1.72

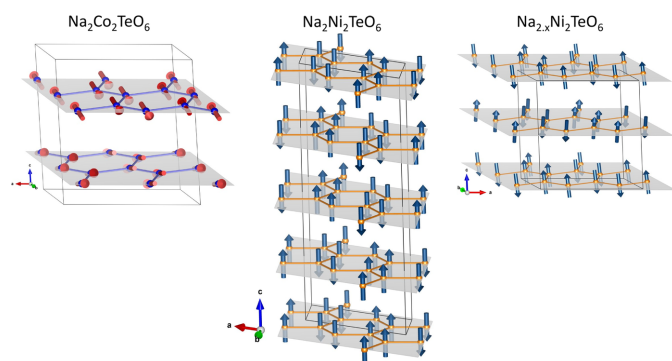


Figure 5

Zigzag magnetic structures of hexagonal Na₂Co₂TeO₆ and two layer stacking variants of Na₂Ni₂TeO₆ defined by the wavevectors **k** = ($\frac{1}{2}$, 0, $\frac{1}{2}$) and ($\frac{1}{2}$, 0, 0).

honeycomb layers. The system exhibits antiferromagnetic order below 12.3 K, although no magnetic diffraction studies have been reported to date.

The Ni-based compounds A₂Ni₂TeO₆ are isostructural to K₂Co₂TeO₆. Notably, the magnetic order of these systems is influenced by the alkali-ion site occupancies. Samarakoon *et al.* (2021) reported a propagation vector **k** = ($\frac{1}{2}$, 0, $\frac{1}{2}$) for the stoichiometric Na₂Ni₂TeO₆ and **k** = ($\frac{1}{2}$, 0, 0) for the doped Na_{2.4}Ni₂TeO₆. Earlier neutron diffraction studies on Na₂Ni₂TeO₆ reported a ($\frac{1}{2}$, 0, 0) wavevector (Karna *et al.*, 2017; Kurbakov *et al.*, 2020), while Bera *et al.* (2022) observed a mixture of the two **k** vectors. This discrepancy likely arises from variations in Na composition and sample homogeneity. The key difference in the ordered state lies in the stacking sequence of adjacent honeycomb layers, which changes from

an A - B - A - B type to A - A - B - B , where A and B represent opposite moment directions. This suggests that the out-of-plane coupling is highly sensitive to the amount and distribution of Na within the Na monolayer.

For the undoped material, the magnetic structure is described using the magnetic space group I_4mm2 (No. 44.234) in the supercell (2a, b, 2c). Moments align parallel to the c axis, forming a zigzag structure with ferromagnetic chains along the b direction. The refined static moment is $1.55(6) \mu_B$, with an in-plane component less than $0.05 \mu_B$ (Samarakoon *et al.*, 2021). In contrast, the zigzag-type magnetic structure of $\text{Na}_{2.4}\text{Ni}_2\text{TeO}_6$ is described by the magnetic space group P_4nma (No. 62.453) on the magnetic lattice (2a, b, c). The ordered moment exhibits canting away from the c axis, with the magnetic components $m_y = 0.7(1) \mu_B$ and $m_z = 1.30(5) \mu_B$. Graphical representations of $\text{Na}_{2-x}\text{Ni}_2\text{TeO}_6$ magnetic structures are shown in Fig. 5. The magnetic structure of the potassium variant $\text{K}_2\text{Ni}_2\text{TeO}_6$ has not yet been examined through neutron scattering. However, spin-polarized DFT + U calculations indicate that the honeycomb layers of this compound also adopt a zigzag order (Vasilchikova *et al.*, 2022).

4. Honeycomb materials with a rhombohedral lattice

The honeycomb material α - RuCl_3 has remained arguably one of the most topical magnets of the last decade. After numerous experimental and theoretical investigations, α - RuCl_3 has emerged as a leading candidate material for observing Kitaev physics. The observation of a suppression of magnetic order under an applied magnetic field within the honeycomb plane above 7.3 T (Banerjee *et al.*, 2018; Balz *et al.*, 2021) has led to the proposal that α - RuCl_3 is a proximate Kitaev QSL in a narrow field range of 7.3–10 T. Fractionalized excitations have been reported in neutron scattering experiments (Banerjee *et al.*, 2016, 2017, 2018; Do *et al.*, 2017; Balz *et al.*, 2019), Raman scattering (Sandilands *et al.*, 2015) and THz spectroscopy (Little *et al.*, 2017), along with reports of quantized thermal Hall plateaus matching the half-integer value expected from Kitaev's model (Kasahara *et al.*, 2018; Yokoi *et al.*, 2021). Despite strong support for Kitaev physics, there have been several conflicting reports from various groups on α - RuCl_3 as a candidate material, and to this day discussion of the nature of the field-induced disordered phase remains a centerpiece in the field. As work on α - RuCl_3 can easily spawn its own rich review article, in this work we focus mostly on its low-temperature crystal and magnetic structure.

The low-temperature crystal structure of α - RuCl_3 has been a topic of extensive debate due to its structural fragility and apparent sensitivity to the crystal growth method (Johnson *et al.*, 2015; Sears *et al.*, 2015, 2020; Cao *et al.*, 2016). The anti-ferromagnetic transition temperature falls within the range 6–14 K and is also highly sensitive to the specific details of the sample synthesis and handling, with high-quality stacking-fault-free samples showing a single $T_N = 7$ K. Although all studies of the room-temperature structure confirm a monoclinic $C2/m$ structure, multiple groups report a strongly first

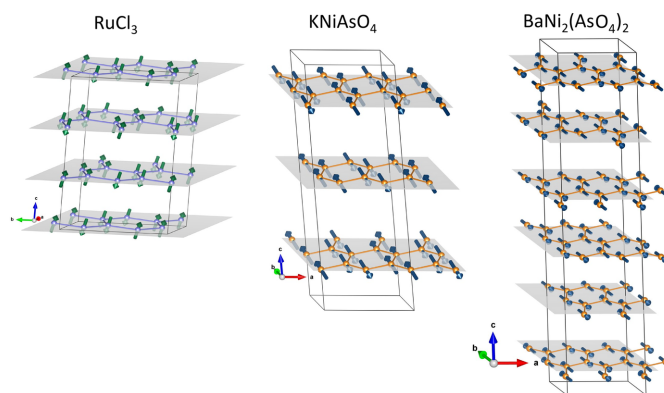


Figure 6

Zigzag magnetic structures observed in the honeycomb materials α - RuCl_3 , KNiAsO_4 and $\text{BaNi}_2(\text{AsO}_4)_2$ with trigonal $R\bar{3}$ parent symmetry.

order transition around 150 K (Kubota *et al.*, 2015; Lampen-Kelley *et al.*, 2018; Gass *et al.*, 2020), below which α - RuCl_3 adopts a BiI_3 -type structure with an ideal honeycomb lattice described by the $R\bar{3}$ space group (Mu *et al.*, 2022; Park *et al.*, 2024). The magnetic structure exhibits an alternating FM zigzag pattern, but uncertainties related to its low-temperature crystal symmetry and the prevalence of structural domains have hindered a precise determination of the magnetic moment orientation. Park *et al.* (2024) reported a magnetic ordering with $\mathbf{k} = (0, \frac{1}{2}, 1)$ and a refined magnetic moment of $0.73(3) \mu_B$ per Ru atom. The magnetic moments lie within the ac plane, tilted at an angle of $48(3)^\circ$ from the hexagonal plane (see Fig. 6). This structure is described with the magnetic space group $P_5\bar{1}$ for a cell doubled along the b axis (a, 2b, c).

Chemical substitution with non-magnetic ions is an attractive strategy for tuning the magnetic behavior of α - RuCl_3 and, potentially, for inducing a quantum spin liquid state. In this context, $\text{Ru}_{0.9}\text{R}_{0.1}\text{Cl}_3$ ($R = \text{Rh}^{3+}$ and Ir^{3+}) single crystals were prepared and characterized using neutron diffraction (Morgan *et al.*, 2024). The study revealed that the structural transition from the monoclinic $C2/m$ to the trigonal $R\bar{3}$ crystal structure persists, although at a lower temperature of approximately 70 K. The Néel temperature is also slightly suppressed to around 6 K in the Ir-substituted compound, which exhibits a much reduced ordered moment of $0.32(5) \mu_B$ per Ru and a smaller canting angle of $15(4)^\circ$.

A similar magnetic structure was also reported for RuBr_3 , which crystallizes in the $R\bar{3}$ structure and shows no structural transition. At 34 K, it undergoes a transition to the zigzag magnetic order characterized by the propagation vector $\mathbf{k} = (0, \frac{1}{2}, 1)$ (Imai *et al.*, 2022). The magnitude of the magnetic moment is determined to be $0.74(12) \mu_B$ and its angle from the ab plane is $64(12)^\circ$. Crystallographic details for α - RuCl_3 and RuBr_3 are provided in Table 6.

Another Kitaev physics candidate is the spin-1 honeycomb compound KNiAsO_4 , which orders magnetically below 19 K. It crystallizes in the trigonal $R\bar{3}$ space group, featuring edge-sharing NiO_6 octahedra that form layered structures. Each layer of NiO_6 octahedra is enclosed by two sheets of AsO_4 tetrahedra, and the interlayers contain offset triangular lattice sheets of K ions. Early neutron diffraction work suggested an

Table 6
Crystallographic description of zigzag magnetic structures observed in rhombohedral honeycomb systems.
MSG is magnetic space group.

Compound	RuCl ₃	RuBr ₃	KNiAsO ₄	BaNi ₂ (AsO ₄) ₂
MAGNDATA No.	1.787	1.786	1.742	1.257
References	Park <i>et al.</i> (2024)	Imai <i>et al.</i> (2022)	Taddei <i>et al.</i> (2023)	Regnault <i>et al.</i> (1980)
Parent space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
k -vector		$(0, \frac{1}{2}, 1)$	$(\frac{2}{3}, 0, 0)$	$(\frac{1}{2}, 0, \frac{1}{2})$
Transformation from parent to magnetic cell		$(\mathbf{a}_p, 2\mathbf{b}_p, \mathbf{c}_p)$	$(2\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p)$	$(2\mathbf{a}_p, \mathbf{b}_p, 2\mathbf{c}_p)$
MSG symbol		$P_5\bar{1}$	$P_5\bar{1}$	$P_5\bar{1}$
UNI notation		$P\bar{1}.1'_c[P\bar{1}]$	$P\bar{1}.1'_c[P\bar{1}]$	$P\bar{1}.1'_c[P\bar{1}]$
MSG No.		2.7	2.7	2.7
Transformation to MSG standard setting		$\frac{1}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} - \frac{1}{3}\mathbf{c}, \frac{1}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{2}{3}\mathbf{c}, \frac{1}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{2}{3}\mathbf{c}; 0, \frac{1}{4}, 0$	$\frac{1}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{1}{3}\mathbf{c}, \mathbf{b}, -\frac{1}{3}\mathbf{a} - \frac{4}{3}\mathbf{b} + \frac{2}{3}\mathbf{c}; \frac{1}{4}, 0, 0$	$\frac{1}{6}\mathbf{a} - \frac{1}{3}\mathbf{b} - \frac{1}{6}\mathbf{c}, \frac{1}{6}\mathbf{a} + \frac{2}{3}\mathbf{b} - \frac{1}{6}\mathbf{c}, \frac{2}{3}\mathbf{a} + \frac{2}{3}\mathbf{b} + \frac{1}{3}\mathbf{c}; 0, 0, 0$
Magnetic point group	$\bar{1}.1'$		$\bar{1}.1'$	$\bar{1}.1'$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.973, 11.946, 16.93	6.295, 12.591, 17.91	9.973, 4.986, 28.619	9.89, 4.945, 47.220
α , β , γ (°)	90, 90, 120	90, 90, 120	90, 90, 120	90, 90, 120
MSG symmetry operations		$x, y, z, +1$ $-x, -y + \frac{1}{2}, -z, +1$	$x, y, z, +1$ $-x + \frac{1}{2}, -y, -z, +1$	$x, y, z, +1$ $-x, -y, -z, +1$
MSG centering operations		$x, y, z, +1$ $x + \frac{1}{3}, y + \frac{1}{3}, z + \frac{2}{3}, +1$ $x + \frac{2}{3}, y + \frac{2}{3}, z + \frac{1}{3}, +1$ $x + \frac{2}{3}, y + \frac{1}{6}, z + \frac{1}{3}, -1$ $x, y + \frac{1}{2}, z, -1$ $x + \frac{1}{3}, y + \frac{2}{6}, z + \frac{2}{3}, -1$	$x, y, z, +1$ $x + \frac{1}{3}, y + \frac{1}{3}, z + \frac{1}{3}, +1$ $x + \frac{2}{3}, y + \frac{2}{3}, z + \frac{2}{3}, +1$ $x + \frac{5}{6}, y + \frac{1}{3}, z + \frac{1}{3}, -1$ $x + \frac{1}{6}, y + \frac{2}{3}, z + \frac{2}{3}, -1$ $x + \frac{1}{2}, y, z, -1$	$x, y, z, +1$ $x + \frac{1}{6}, y + \frac{2}{3}, z + \frac{5}{6}, +1$ $x + \frac{1}{3}, y + \frac{1}{3}, z + \frac{2}{3}, +1$ $x + \frac{1}{2}, y, z + \frac{1}{2}, +1$ $x + \frac{2}{3}, y + \frac{2}{3}, z + \frac{1}{3}, +1$ $x + \frac{5}{6}, y + \frac{1}{3}, z + \frac{1}{3}, +1$ $x + \frac{1}{3}, y + \frac{1}{3}, z + \frac{1}{6}, -1$ $x + \frac{1}{2}, y, z, -1$ $x + \frac{2}{3}, y + \frac{2}{3}, z + \frac{5}{6}, -1$ $x + \frac{5}{6}, y + \frac{1}{3}, z + \frac{5}{6}, -1$ $x, y, z + \frac{1}{3}, -1$ $x + \frac{1}{6}, y + \frac{2}{3}, z + \frac{1}{3}, -1$
Positions of magnetic atoms	Ru 0, 0, 0.333	Ru 0, 0, 0.323	Ni 0, 0, 0.1652	Ni 0, 0, 0.083
Non-magnetic atoms	Cl1 0.317, 0.167, 0.41 Cl2 0.665, 0.991, 0.41 Cl3 0.016, 0.841, 0.41	Br1 0.329, 0.49, 0.08 Br2 0.016, 0.67, 0.08 Br3 0.654, 0.835, 0.08	K 0, 0, 0.289 As 0, 0, 0.556 O11 0, 0.345, 0.124 O12 0.83, 0.66, 0.124 O13 0.17, 0.99, 0.124 O2 0, 0, 0.62	Ba 0, 0, 0 As 0, 0, 0.213 O1 0, 0, 0.177 O21 0.164, 0.328, 0.06 O22 0.836, 0, 0.06 O23 0, 0.672, 0.06
Magnetic moments (μ_B), MSG constraints and total magnitudes	Ru (0.49, 0, 0.54) (m_x, m_y, m_z) 0.73	Ru (−0.3, 0.04, 0.66) (m_x, m_y, m_z) 0.74	Ni (−0.2, 1.6, 0.7) (m_x, m_y, m_z) 1.8	Ni (0, 2.0, 0) (m_x, m_y, m_z) 2.0

ordering vector of $\mathbf{k} = (\frac{1}{2}, 0, 0)$ with an AFM chain structure that results in a stripy-type structure (Bramwell *et al.*, 1994). New, higher-resolution neutron powder measurements revealed a different propagation vector $\mathbf{k} = (\frac{2}{3}, 0, 0)$ due to the observed extinction rule $-h + k + l = 3n$. The determined magnetic structure features FM zigzag chains along the *a* axis, described using the magnetic space group $P_5\bar{1}$ (No. 2.7) with doubled *a* lattice parameter. The magnetic symmetry allows the magnetic moments to have non-zero components in all three crystallographic directions, and the refined components were $m_x = -0.2$ (1), $m_y = 1.6$ (1) and $m_z = 0.7$ (1) μ_B . The magnetic moments mainly lie in the *ab* plane with a small component along *c* to produce a 22° canting, as depicted in Fig. 6. The modeling of spin wave spectra indicates that the extended Kitaev spin Hamiltonian is essential for reproducing the observed canted zigzag-type order (Taddei *et al.*, 2023). In the more recent study, the novel compound KCoAsO₄ was added to this series. The static and dynamic magnetic prop-

erties were characterized, revealing a disordered ground state with two types of stacking sequences for the honeycomb layers (Sarkis *et al.*, 2024). Two sets of magnetic reflections indexed by the **k**-vectors $(\frac{2}{3}, 0, 0)$ and $(\frac{1}{2}, 0, \frac{1}{2})$ were modeled using a zigzag-type magnetic arrangement. Interestingly, the Co magnetic moment was determined to be nearly parallel to the *c* axis, with a small canting of about 7°. This suggests opposite magnetic anisotropies for the Ni and Co compounds, but in a reversed manner compared to that observed in the $A_{2,3}M_2M'O_6$ series.

A third family of honeycomb materials with rhombohedral structures is BaM₂(XO₄)₂ (*M* = Ni, Co, and *X* = P, As, V). These layered compounds consist of staggered honeycomb layers formed by edge-sharing MO₆ octahedra, separated by non-magnetic Ba and XO₄ layers. The magnetic properties and spin Hamiltonians were investigated by Regnault and colleagues approximately four decades ago (Regnault *et al.*, 1977, 1980). Each material exhibits a different magnetic

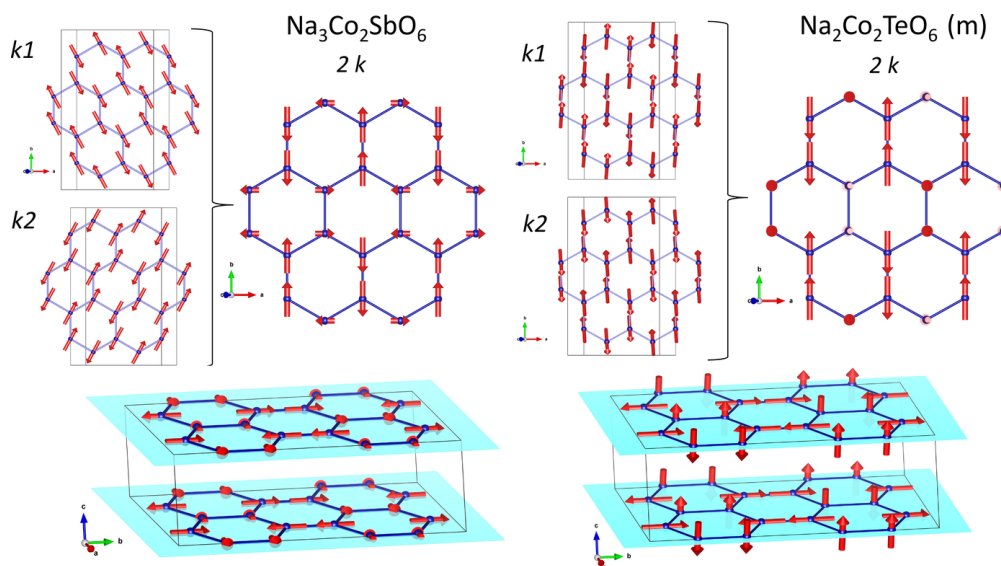


Figure 7

Spin patterns of two types of zigzag domains and the 2- $\mathbf{k}$ structures for $\text{Na}_3\text{Co}_2\text{SbO}_6$ and monoclinic $\text{Na}_2\text{Co}_2\text{TeO}_6$.

propagation vector: $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$ for $\text{BaNi}_2(\text{AsO}_4)_2$, $(0, 0, \frac{3}{2})$ for $\text{BaNi}_2(\text{VO}_4)_2$ and $(0, 0, 0)$ for $\text{BaNi}_2(\text{PO}_4)_2$. Among the compounds in this class, the nickel arsenate is the only one that exhibits a zigzag magnetic structure. On the other hand, the vanadate and phosphate variants display Néel-type order, where the magnetic moments couple antiferromagnetically to their three nearest neighbors. The zigzag magnetic order in $\text{BaNi}_2(\text{AsO}_4)_2$ follows the symmetry of the magnetic space group $P_5\bar{1}$ (No. 2.7) inside the magnetic lattice (2a, b, 2c). The magnetic moment was determined to be 2.0 (2) μ_B along the b axis, although the symmetry permits canting away from that axis. A much more complicated magnetic structure was observed in $\text{BaCo}_2(\text{AsO}_4)_2$ (Regnault *et al.*, 1977). This system orders with an incommensurate propagation vector $\mathbf{k} = (0.261, 0, -1.31)$ and the inferred helical order consists of stacking weakly coupled quasi-ferromagnetic chains (Regnault *et al.*, 2018). Weak in-plane magnetic fields can suppress the long-range magnetic order, suggesting it as a potential quantum spin liquid candidate (Halloran *et al.*, 2023).

5. Multiple- $\mathbf{k}$ magnetic structures derived from zigzag structures

While the majority of magnetic structures involve a single propagation vector, there are cases when several $\mathbf{k}$ vectors can operate concomitantly to form fascinating multi- $\mathbf{k}$ structures. Theoretical investigations indicated that multi- $\mathbf{k}$ states can become energetically favorable over a single- $\mathbf{k}$ zigzag state when symmetry-allowed nonbilinear exchange perturbations are present (Krüger *et al.*, 2023; Wang & Liu, 2023). Distinguishing between single- $\mathbf{k}$ and multi- $\mathbf{k}$ ordered states presents a significant experimental challenge. In crystals, multiple domains may be ordered according to different single- $\mathbf{k}$ domains, resulting in the same contribution to magnetic scattering as the multi- $\mathbf{k}$ structure. To resolve ambiguity, scattering

experiments on high-quality single crystals under external uniaxial stress or magnetic fields are necessary. These conditions can favor the population of a specific $\mathbf{k}$ domain to clarify the structure. A 1- $\mathbf{k}$ zigzag structure is expected to have one type of domain noticeably depopulated after magnetic field training, but a multi- $\mathbf{k}$ state will maintain the original ratio of the magnetic Bragg peaks. A recent neutron diffraction study on a twin-free crystal of monoclinic $\text{Na}_3\text{Co}_2\text{SbO}_6$, subjected to strong in-plane magnetic fields along a low-symmetry direction, revealed the presence of double- $\mathbf{k}$ order (Gu *et al.*, 2024). On the other hand, when magnetic fields were applied along the a axis of a hexagonal $\text{Na}_2\text{Co}_2\text{TeO}_6$ single crystal, evidence emerged of a triple- $\mathbf{k}$ magnetic structure with C_3 symmetry, deviating from the expected multi-domain zigzag structure (Yao *et al.*, 2023). Measuring spin-wave spectra is another valuable approach for distinguishing multi- $\mathbf{k}$ features. The distinct shapes of magnetic Brillouin zones result in different symmetries of the magnetic excitation spectra, allowing identification and characterization of these structures. By using this approach the triple- $\mathbf{k}$ state with a vortex spin structure was further confirmed in the hexagonal $\text{Na}_2\text{Co}_2\text{TeO}_6$ compound (Chen *et al.*, 2021; Yao *et al.*, 2022; Krüger *et al.*, 2023).

In this section we will provide crystallographic descriptions for such double- or triple- $\mathbf{k}$ magnetic structures that can emerge from zigzag-type structures. Magnetic structure models have been constructed using the magnetic symmetry tools available at the Bilbao Crystallographic Server (BCS) (Perez-Mato *et al.*, 2015).

5.1. Double- $\mathbf{k}$ magnetic structures in the monoclinic $\text{Na}_3\text{Co}_2\text{SbO}_6$ and $m\text{-Na}_2\text{Co}_2\text{TeO}_6$ systems

For the monoclinic $\text{Na}_3\text{Co}_2\text{SbO}_6$ and $\text{Na}_2\text{Co}_2\text{TeO}_6$ compounds, the 1- $\mathbf{k}$ zigzag-type magnetic structures can be defined by either $\pm(\frac{1}{2}, \frac{1}{2}, 0)$ or $\pm(\frac{1}{2}, -\frac{1}{2}, 0)$ wavevectors. Each

possibility gives rise to coexisting $\mathbf{k}$ domains, related by a 180° rotation about the b axis. For a 2- $\mathbf{k}$ scenario, the configuration of the magnetic moment is derived by superimposing the two zigzag components. The resulting vector depends on the actual orientation of the magnetic moment in the zigzag chains relative to the $\mathbf{k}$ -vector. It is worth noting that the magnetic space group $P_5\bar{1}$, which describes the 1- $\mathbf{k}$ structures, allows the orientation of the magnetic moment along any crystallographic axis. For $\text{Na}_3\text{Co}_2\text{SbO}_6$, one proposed model suggested the alignment of the magnetic moments along the b axis (Yan *et al.*, 2019). A more recent model proposed that the moments are aligned within the ab plane, perpendicular to the wavevector (Li *et al.*, 2022; Gu *et al.*, 2024). In the former model, the vector superposition in the 2- $\mathbf{k}$ structure results in two magnetic sublattices where half of the moments align along the b axis, while the other half do not have a static ordered moment. Conversely, a pair of single- $\mathbf{k}$ structures with moments perpendicular to $\mathbf{k}$ will produce components that are nearly 60° or 120° apart, due to proximity to the C_3 symmetry. In this case, the 2- $\mathbf{k}$ structure will consist of two orthogonal sublattices with a ratio between moment amplitudes close to $\sqrt{3}:1$.

A crystallographic representation of this 2- $\mathbf{k}$ magnetic structure was obtained using the *k-SUBGROUPSMAG* program hosted at the BCS (Perez-Mato *et al.*, 2015). The magnetic space group C_a2/m (No. 12.64) was utilized in the (2a, 2b, c) magnetic unit cell, which divides the Co position into two non-equivalent sites with distinct symmetry constraints. One site (Co1) confines the magnetic moment to the ac plane, while the second site (Co2) aligns the moment parallel to the b axis. To evaluate the moment magnitudes, we used as the starting point the b component ($0.9 \mu_B$) reported by Yan *et al.* (2019), and added an a projection ($\approx 0.49 \mu_B$) to ensure orthogonality to the $\mathbf{k}$ -vector (as proposed by Gu *et al.*, 2024). The moments of the 2- $\mathbf{k}$ model were refined using the *Fullprof* program (Rodríguez-Carvajal, 1993) against the simulated data from the single- $\mathbf{k}$ model. The obtained moments for the two Co sublattices are $m_{\text{Co1}} = (0.69, 0, 0) \mu_B$ and $m_{\text{Co2}} = (0, 1.27, 0) \mu_B$.

The 1- $\mathbf{k}$ zigzag magnetic structure of the monoclinic polymorph of $\text{Na}_2\text{Co}_2\text{TeO}_6$ was shown to exhibit an out-of-plane magnetic component (Dufault *et al.*, 2023). Consequently, its corresponding 2- $\mathbf{k}$ variant will represent a more generalized case, with a c component on half of the Co moments. We computed the moments for a potential 2- $\mathbf{k}$ magnetic structure, described by C_a2/m , to match the diffraction intensities simulated from the single- $\mathbf{k}$ structure. The magnetic moments on the two non-equivalent Co positions are found to be $m_{\text{Co1}} = (-0.69, 0, -1.69) \mu_B$ and $m_{\text{Co2}} = (0.0, 2.1, 0.0) \mu_B$. The in-plane spin patterns of two types of zigzag domains and the 2- $\mathbf{k}$ structures are illustrated in Fig. 7 for both $\text{Na}_3\text{Co}_2\text{SbO}_6$ and $m\text{-Na}_2\text{Co}_2\text{SbO}_6$. The complete descriptions of the 2- $\mathbf{k}$ models are given in Table 7. The magnetic CIF files are available as supporting information.

5.2. Triple- $\mathbf{k}$ magnetic structures in the hexagonal $\text{Na}_2\text{Co}_2\text{TeO}_6$ systems

The triple- $\mathbf{k}$ state in hexagonal $\text{Na}_2\text{Co}_2\text{TeO}_6$ is formed by combining three C_3 -related single- $\mathbf{k}$ zigzag components, each with a different orientation. In the 1- $\mathbf{k}$ zigzag model, the ferromagnetic chains and the moments align perpendicular to the wavevector, with the magnetic moments positioned in the bc plane and a minor ($\approx 0.5 \mu_B$) out-of-plane component (Samarakoon *et al.*, 2021). By superposing contributions of the three wavevectors, $(\frac{1}{2}, 0, 0)$, $(0, -\frac{1}{2}, 0)$ and $(-\frac{1}{2}, \frac{1}{2}, 0)$, the magnetic moments form spin vertices, where canted moments at the corner of hexagons are rotated by 60° and alternate in their canting direction. The vertices are separated by sites with the alternating c -axis moments, as depicted in Fig. 8. From a crystallographic perspective, this structure can be described using the magnetic space group $P6_32'2'$ (No. 182.183) in a magnetic supercell that is doubled along both the a and b axes (2a, 2b, c). In this symmetry, each of the two non-identical Co sites of the parent structure is divided into two additional magnetic sites (with multiplicities 6 and 2), leading to four magnetic sublattices. Two of the sites, which represent $1/3$ of the Co sites, confine the magnetic moments to the c direction. The other two sites ($2/3$ of the total sites) allow components in- and out-of-plane with a constrained 60° rotation within the ab plane. Using the moment values of the 1- $\mathbf{k}$ model reported by Samarakoon *et al.*, we derived the actual moment values for the alternative triple- $\mathbf{k}$ model. As was done previously for the zigzag model, we assigned the same moment amplitudes to Co sites with similar magnetic symmetries. The obtained moments components in the triple- $\mathbf{k}$ model were: $m_{\text{Co11}} = (2.31, 0, -0.5) \mu_B$, $m_{\text{Co12}} = (0, 0, 0.5) \mu_B$, $m_{\text{Co21}} = (2.31, 2.31, 0.5) \mu_B$ and $m_{\text{Co22}} = (0, 0, -0.5) \mu_B$. Further description of this 3- $\mathbf{k}$ model is provided in Table 7. The magnetic CIF file is provided as supporting information.

6. Concluding remarks

Layered materials with a honeycomb lattice are incredibly versatile and can host a variety of magnetic ground states. These states are dictated by the relative ratio and signs of the nearest neighbor (J_1), next-nearest neighbor (J_2) or third-nearest neighbor (J_3) couplings. In this review article, our focus has been on materials that exhibit alternating FM zigzag chains, as they appear to be, aside from some spiral orders, a dominant magnetic ground state in Kitaev-type candidate materials. This type of structure can be stabilized by a combination of an FM J_1 and an AFM J_3 interaction. They are interesting in the context of Kitaev physics due to their prevalence in material candidates proximate to the elusive quantum spin liquid state. The studies of zigzag-type structures in materials have also led to the development of extended Kitaev Hamiltonians, which include additional symmetry-allowed perturbing interactions, necessary to describe real materials. These lead to an alternative route for stabilizing the zigzag structure at a nearest neighbor level via off-diagonal exchange terms Γ and Γ' .

Table 7

Crystallographic description of multi-**k** magnetic structures derived from zigzag structures.

MSG is magnetic space group.

Compound	Na ₃ Co ₂ SbO ₆	Na ₂ Co ₂ TeO ₆	Na ₂ Co ₂ TeO ₆
Parent space group	<i>C2/m</i>		<i>P6₃22</i>
k -vector	$2\text{-}\mathbf{k}: (\frac{1}{2}, \frac{1}{2}, 0) + (\frac{1}{2}, -\frac{1}{2}, 0)$		$3\text{-}\mathbf{k}: (\frac{1}{2}, 0, 0) + (0, -\frac{1}{2}, 0) + (-\frac{1}{2}, \frac{1}{2}, 0)$
Transformation from parent to magnetic cell	$(2\mathbf{a}_p, 2\mathbf{b}_p, \mathbf{c}_p)$		$(2\mathbf{a}_p, 2\mathbf{b}_p, \mathbf{c}_p)$
MSG symbol	<i>C_a2/m</i>		<i>P6₃2'2'</i>
UNI notation	<i>C2/m.1'_a[P2/m]</i>		<i>P6₃2'2'</i>
MSG No.	12.64		182.183
Transformation to MSG standard setting	a, b, c: $\frac{1}{4}, 0, 0$		a, b, c: $\frac{1}{4}, 0, 0$
Magnetic point group	<i>2/m1'</i>		<i>62'2'</i>
<i>a, b, c</i> (Å)	10.741, 18.578, 5.653	10.656, 18.387, 5.769	10.517, 10.517, 11.17
α, β, γ (°)	90, 108.56, 90	90, 108.95, 90	90, 90, 120
MSG symmetry operations	$x, y, z, +1$ $-x, -y, -z, -1$ $x, -y, z, +1$ $-x, y, -z, -1$		$x, y, z, +1$ $x - y, x + \frac{1}{2}, z + \frac{1}{2}, +1$ $-y + \frac{1}{2}, x - y + \frac{1}{2}, z, +1$ $-x, -y, z + \frac{1}{2}, +1$ $-x + y, -x + \frac{1}{2}, z, +1$ $y + \frac{1}{2}, -x + y + \frac{1}{2}, z + \frac{1}{2}, +1$ $x - y, -y, -z, -1$ $y + \frac{1}{2}, x + \frac{1}{2}, -z, -1$ $-x, -x + y + \frac{1}{2}, -z, -1$ $x, x - y + \frac{1}{2}, -z + \frac{1}{2}, -1$ $-x + y, y, -z + \frac{1}{2}, -1$ $-y + \frac{1}{2}, -x + \frac{1}{2}, -z + \frac{1}{2}, -1$ $x, y, z, +1$
MSG centering operations	$x, y, z, +1$ $x + \frac{1}{2}, y + \frac{1}{2}, z, +1$ $x, y + \frac{1}{2}, z, -1$ $x + \frac{1}{2}, y, z, -1$		
Positions of magnetic atoms	Co1 0, 0.333, 0 Co2 0.25, 0.583, 0	Co1 0, 0.334, 0 Co2 0.25, 0.584, 0	Co11 0, 0, 0.25 Co12 0.5, 0, 0.25 Co21 0.333, 0.166, 0.25 Co22 0.166, 0.333, 0.75
Non-magnetic atoms	Sb1 0, 0, 0 Sb2 0.25, 0.25, 0 Na11 0, 0.25, 0.5 Na12 0.25, 0, 0.5 Na21 0, 0.413, 0.5 Na22 0.25, 0.66, 0.5 O11 0.136, 0.17, 0.794 O12 0.386, 0.42, 0.79 O21 0.375, 0, 0.204 O22 0.625, 0.25, 0.204	Te1 0, 0, 0 Te2 0.25, 0.25, 0 O11 0.14, 0.172, 0.80 O12 0.390, 0.422, 0.80 O21 0.132, 0, 0.19 O22 0.382, 0.25, 0.19 Na11 0, 0.164, 0.5 Na12 0.25, 0.414, 0.5 Na21 0.0, 0.25, 0.5 Na22 0.25, 0, 0.5	Te1 0.166, 0.333, 0.25 Te2 0.333, 0.166, 0.75 O11 0.324, 0.49, 0.345 O12 0.51, 0.835, 0.345 O13 0.164, 0.675, 0.345 O14 0.824, 0.488, 0.345 Na21 0, 0, 0 Na22 0.5, 0, 0 Na31 0.349, 0.033, 0.99 Na32 0.966, 0.316, 0.99 Na33 0.683, 0.650, 0.99 Na34 0.849, 0.033, 0.99
Magnetic moments (μ_B), symmetry constraints and total magnitudes	Co1 (0.69, 0, 0) ($m_x, 0, m_z$) 0.69 Co2 (0, 1.27, 0) (0, m_y , 0) 1.27	Co1 (−0.68, 0, −1.68) ($m_x, 0, m_z$) 1.60 Co2 (0, 2.09, 0) (0, m_y , 0) 2.09	Co11 (2.31, 0, −0.5) ($m_x, 0, m_z$) 2.36 Co12 (0, 0, 0.5) (0, 0, m_z) 0.5 Co21 (2.31, 2.31, 0.5) (m_x, m_x, m_z) 2.36 Co22 (0, 0, −0.5) (0, 0, m_z) 0.5

In this work, we have highlighted the stability of the zigzag structure across a wide range of parent crystal symmetries (*C2/m*, *C2/c*, *P6₃22*, *P6₃/mcm*, *R3*) in representative compounds. These compounds contain *5d*, *4d* or *3d* transition-metal magnetic ion species (Ir^{4+} , Ru^{3+} , Co^{2+}) with an effective spin 1/2. The Kitaev model, originally formulated for spin-1/2 systems, has been a cornerstone in the study of quantum spin

liquids due to its exactly solvable nature. Extending the Kitaev model to larger spins $S \geq 1$ is seen as an exciting opportunity to unveil new physics and broaden the scope of Kitaev materials. Therefore, we have also included in our review the Ni^{2+} -based honeycomb materials, as recent experimental studies on these $S = 1$ materials have provided evidence for the presence of bond-anisotropic Kitaev interactions.

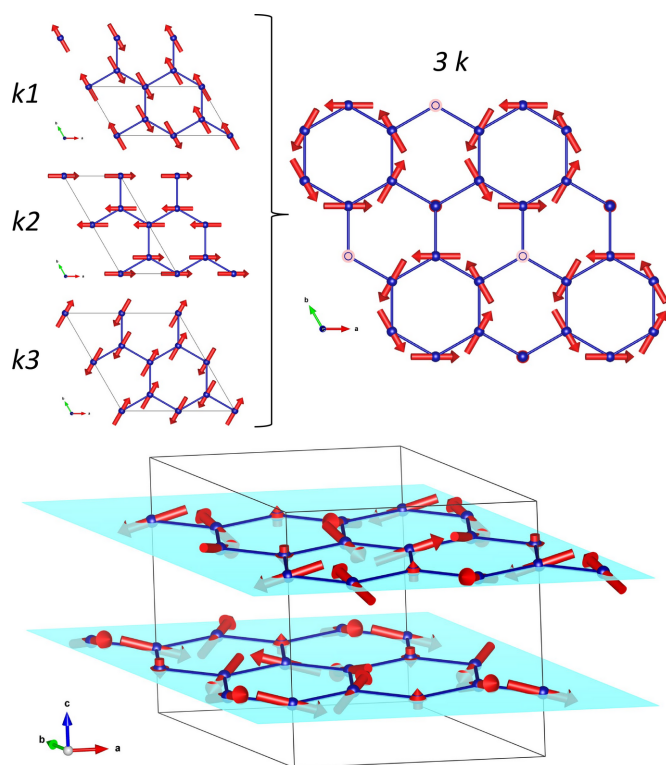


Figure 8
The spin patterns of three distinct zigzag domains and the alternative 3- $\mathbf{k}$ magnetic structure within hexagonal $\text{Na}_2\text{Co}_2\text{TeO}_6$.

The crystallographic details of the zigzag structures observed in several classes of materials have been reviewed and tabulated. Notably, the magnetic moments in Na_2IrO_3 and cobaltates in the $A_2\text{Co}_2M'\text{O}_6$ series primarily reside within the honeycomb plane or display minor canting angles. The out-of-plane canting is relevant in the context of the anisotropic bond-directional Kitaev interaction. For some of these materials, the presence of out-of-plane components is still awaiting experimental confirmations. In contrast, the Ni compounds exhibit an easy-axis anisotropy that tends to orient the moment along the c axis. Reversed anisotropies are noted in the KMASO_4 compounds, where the Ni moments are predominantly in the ab plane and Co moments are nearly along the c axis. The magnetic moments also lie in, or close to, the honeycomb plane in $\text{BaNi}_2(\text{AsO}_4)_2$ and in the van der Waals materials MPX_3 . In RuCl_3 the canting angle, reported to be about 48° , is more pronounced than in any other compound. This canting demonstrates a strong dependence on the chemical composition, with a 10% substitution of Ru by Rh or Ir leading to a 15° angle.

The slightly distorted honeycomb lattices of the monoclinic compounds exhibit two distinct types of propagation vector: $(\frac{1}{2}, \frac{1}{2}, 0)$ or $(0, 1, 0)$. The direction of the wavevector defines the direction of the ferromagnetic chain and thus the nature of the bonds involved in the magnetic coupling. While $\mathbf{k} = (0, 1, 0)$ or $(1, 0, 0)$ implies the formation of zigzag chains with uniform bond length, $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ produces ferromagnetic chains in the diagonal direction that involve alternating bonds. The latter ordering vector is also susceptible to forming multi- $\mathbf{k}$ struc-

tures. Variations in the ordering wavevector are also encountered in the hexagonal or rhombohedral systems that are intrinsically susceptible to stacking faults. In such systems, the magnetic propagation vectors can involve a doubling of the lattice along the c direction, which is very sensitive to the sample composition. In particular, the alkali-metal distribution amidst the honeycomb layers can be markedly disordered and inhomogeneous, and that can contribute to the stacking sequence of the magnetic layers. Mixed propagation vectors, suggesting stacking disorder, were observed in the $\text{Na}_2\text{Ni}_2\text{TeO}_6$ and KCoAsO_4 compounds.

Inspired by recent elastic and inelastic neutron scattering experiments on high-quality single crystals that uncovered the existence of multi- $\mathbf{k}$ magnetic structures in the $\text{Na}_3\text{Co}_2\text{SbO}_6$ and $\text{Na}_2\text{Co}_2\text{TeO}_6$ compounds, we have provided detailed crystallographic information to better define these structures. Such structures suggest the presence of non-trivial, symmetry-allowed, non-bilinear exchange perturbations. As a result, we anticipate that a new course in probing and examining the multi- $\mathbf{k}$ variants will emerge. There are many more honeycomb compounds with zigzag-type order that are yet to be discovered or are awaiting confirmation of their magnetic structures by neutron scattering experiments. It is our hope that this review will stimulate further interest and research efforts in exploring these fascinating systems.

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