A realistic first-principle-based spin Hamiltonian is constructed for the type-II multiferroic NiI₂, using a symmetry-adapted cluster expansion method. Besides single ion anisotropy and isotropic Heisenberg terms, this model further includes the Kitaev interaction and a biquadratic term, and can well reproduce striking features of the experimental helical ground state, that are, e.g., a proper screw state, canting of rotation plane, propagation direction and period. Using this model to build a phase diagram, it is demonstrated that, (i) the in-plane propagation direction of (110) is determined by the Kitaev interaction, instead of the long-believed exchange frustrations; and (ii) the canting of rotation plane is also dominantly determined by Kitaev interaction, rather than interlayer couplings. Furthermore, additional Monte Carlo simulations reveal three equivalent domains and different topological defects. Since the ferroelectricity is induced by spins in type-II multiferroics, our work also implies that Kitaev interaction is closely related to the multiferroicity of NiI₂.

Another interesting but still elusive point is the canting of the spin rotation plane. Measurements find that the normal of the rotation plane is not along the in-plane ⟨110⟩ propagation direction, but rather forms an angle of 55° with the out-of-plane direction of NiI₂ bulk [8]. Such canting has been believed to be natural, as the presumed PS state should have its rotation plane being perpendicular to its propagation direction and the PS state of NiI₂ does have an out-of-plane propagation component [9, 15]. However, common mechanisms can not explain such canting, as (i) single ion anisotropy (SIA) does not favor specific canting angle; (ii) the Dzyaloshinskii-Moriya interaction (DMI) is not allowed by the inversion symmetry of NiI₂ (Note that incommensurate spin patterns are too weak to generate non-negligible DMI); and (iii) interlayer Heisenberg terms are proved to have effects neither on propagation directions nor cantings [16]. On the other hand, new forms of interactions, i.e., Kitaev interaction [11, 12, 17] and biquadratic interactions [13], have recently been proposed to be non-negligible in NiI₂, but their effects and interplays are still not clearly understood. Hence, any highly desired realistic model of NiI₂ has to not only incorporate all these aforementioned important mechanisms, but also reproduce the correct ground state — which is currently lacking.

In this work, we build a first-principle-based spin Hamiltonian for NiI₂, taking advantage of a symmetry-adapted cluster expansion and machine learning methods. The resulting Hamiltonian can well reproduce the observed PS state of NiI₂, with the propagation, period
and canting angle comparing well with experiments on bulk systems. By further developing a phase diagram, it is demonstrated that (i) Heisenberg terms actually lead to \(\langle 110\rangle\) propagation; and (ii) it is the Kitaev interaction that not only results in the actual \(\langle 1\bar{1}0\rangle\) propagation, but also dominantly determines the canting of the rotation plane. The roles of biquadratic interaction and interlayer couplings are also carefully examined. Monte Carlo (MC) simulations further predict diverse spin textures and topological defects.

Our newly developed symmetry-adapted cluster expansion method, as implemented in the PASP software, is applied to build the spin Hamiltonian of NiI\(_2\) \([18, 19]\). Such method roots in cluster expansion that goes over all isomers and topological defects. The Hamiltonian of NiI\(_2\) is determined employing the Hamiltonian of Eq. (1) within MC and conjugate gradient (CG) methods. The predicted ground state indeed yields a canted PS state with an in-plane \(\langle 1\bar{1}0\rangle\) propagation and antiparallel interlayer alignments, which agree

| NiI\(_2\) | HSE | PBE |
|---------|-----|-----|
| \(A_{zz}\) | 0.140 (-0.03) | 0.212 (-0.05) |
| \(J\) | -4.976 (1.00) | -4.338 (1.00) |
| \(K\) | 0.858 (-0.17) | 1.433 (-0.33) |
| \(B\) | -0.719 (0.14) | -0.685 (0.16) |
| \(J_2\) | -0.155 (0.03) | -0.121 (0.03) |
| \(J_3\) | 2.250 (-0.45) | 3.155 (-0.73) |
| \(J_{1}^{+}\) | -0.048 (0.01) | -0.060 (0.01) |
| \(J_{1}^{-}\) | 0.685 (-0.14) | 1.103 (-0.25) |
| \(J_{3}^{+}\) | 0.105 (-0.02) | 0.195 (-0.04) |

with \(n = 1, 2, 3\) and where \(\langle i, j\rangle_n\) denotes pairs of \(n\)th nearest neighbors (NN) within each layer, while the \(\perp\) symbol refers to interlayer couplings; \(\gamma\) chooses its value from \(X, Y\) and \(Z\) from the Kitaev basis (see Fig. 1d and SM [21]), which shows the bond-dependent feature. Note that the SOC effects are reflected by the Kitaev term and SIA. For the sum running over \(\langle i, j\rangle_1\), \(J\) quantifies the isotropic exchange coupling, \(K\) the Kitaev interaction, and \(B\) a biquadratic term. Note that one can also define \(J_1 = \frac{1}{3}(3J + K)\), which can be thought of as the real isotropic exchange. \(A_{zz}\) denotes the SIA. As shown in Table I, the NN isotropic exchange favors FM since \(J = -4.976\) meV, which is the largest coefficient in magnitude. \(J_2\) also favors FM because of its negative sign, but is relatively very small. On the other hand, \(J_3 = 2.250\) meV favors AFM and thus competes with the NN \(J\). Regarding the interlayer couplings, \(J_{1}^{\perp}\) is FM in nature but very small in magnitude. In contrast, \(J_{3}^{\perp} = 0.685\) meV favors AFM and is the strongest interlayer coupling. Moreover, sizable AFM Kitaev \(K = 0.858\) meV and \(B = -0.719\) meV biquadratic interactions are predicted, which are in line with previous studies \([11–13, 17, 24, 25]\). Such spin Hamiltonian of Eq. (1) yields a very small mean averaged error (MAE) of 0.063 meV/\(\text{Ni}\), as indicated in the SM [21].

The ground state of NiI\(_2\) is determined employing the Hamiltonian of Eq. (1) within MC and conjugate gradient (CG) methods. The predicted ground state indeed yields a canted PS state with an in-plane \(\langle 1\bar{1}0\rangle\) propagation and antiparallel interlayer alignments, which agree

![FIG. 1. Schematics of (a) NiI\(_2\) crystal structure and common helical spin structures, (b) proper screw, (c) in-plane cycloid and (d) vertical cycloid. Panel (e) displays the PS\(_{\text{conf}}\) state of NiI\(_2\), where spins rotate in a canted plane that is spanned by the NiI\(_2\) clusters. The hollow red, green and blue arrows denote the Kitaev basis \{XYZ\}.](image-url)
comes IC \langle \end{verbatim}

well with measurements. The period is determined to be $\lambda = 7.3a$ if neglecting interlayer couplings, which compares well with the experimental value of $\lambda = 7.23a$ (where $a$ denotes the in-plane lattice constant) [8, 9]. Strikingly the canting angle of the rotation plane is numerically found to be 46° for bulk, which is consistent with the corresponding measured value of 55°±10° [8]. Our model therefore reproduces well the correct PS state for bulk, where the spin texture in a single layer will be referred to as $\text{PS}_{\text{cont}}^{(110)}$ state. Note that the parameters from PBE result in the $\langle 110 \rangle$ propagation, as a result of rather strong $J_3/J$. It is also important to know that isotropic Heisenberg terms, by themselves, do not support in-plane $\langle 110 \rangle$ propagation, as $J_2$ and $J$ both favor FM while $J_3$ and $J$ compete against each other (since $J_3 > 0$ and thus favor AFM while $J_3/J = -0.45$). Such isotropic Heisenberg terms lead to an incommensurate state along $\langle 110 \rangle$ ($\text{IC}^{(110)}$), which is consistent with both analytical results [10] and previous models from DFT [11–14]. It therefore indicates that the $\langle 110 \rangle$ propagation is stabilized by mechanisms other than the isotropic Heisenberg terms.

To unravel the puzzling mechanisms that stabilize such $\langle 110 \rangle$ propagation, we built a phase diagram. More precisely, we chose $J = -1$ meV and sweep over $J_3 \geq 0$ and $B \leq 0$ (in this phase diagram, “only” $J$, $J_3$ and $B$ are thus included for now). As shown in Fig. 2, for $B/J = 0$, the chosen negative $J$ stabilizes the FM state when $J_3$ is weak; while the system adopts $\text{IC}^{(110)}$ states when $J_3/J < -0.25$, which is consistent with the analytical results of Ref.[10]. For $B/J > 0$, the negative biquadratic term shifts the $\text{IC}^{(110)}$-FM boundary toward larger magnitude of $J_3/J$, which can be understood by

The Kitaev interaction is therefore now further incorporated into the computations and resulting phase diagram (consequently, $J$, $J_3$, $B$ and $K$ are now included in this new phase diagram). Surprisingly, with $K = 0.1$ meV (resulting thus in $K/J = -0.1$), an incommensurate state propagating along $\langle 110 \rangle$ ($\text{IC}^{(110)}$) emerges at the border of the previous $\text{IC}^{(110)}$-FM transition, as additionally shown in Fig. 2. Such $\text{IC}^{(110)}$ state takes a slim area of the previous FM zone and a relatively large area of the previous $\text{IC}^{(110)}$ state. When increasing the Kitaev interaction even more to $K = 0.2$ meV, the area of $\text{IC}^{(110)}$ state further expands. As a result, the phase points defined by, e.g., $J_3/J = -0.4$ and $B/J = 0$, as well as $J_3/J = -0.5$ and $B/J = 0.2$, transform from the $\text{IC}^{(110)}$ to $\text{IC}^{(110)}$ state. It is thus clear that, for NiI$_2$, the ratios $J_3/J = -0.45$ and $B/J = 0.14$ favor the $\text{IC}^{(110)}$ state, but $K/J = -0.17$ renders the ground state to become the $\text{IC}^{(110)}$ state. Such results therefore demonstrate that the Kitaev interaction (with $K > 0$), along with the frustration between $J$ and $J_3$, tends to stabilize the $\langle 110 \rangle$ propagation.

Moreover, it is found that the aforementioned $\text{IC}^{(110)}$ state resulted from the $J$-$K$-$J_3$(-$B$) model (i.e. a model with only such terms) also exhibits canted rotation plane. This canting angle between the $Y$ axis and out-of-plane

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**TABLE II.** Total energy and relative energies of different PS states, as well as the decomposition of these energies into specific interaction, as calculated with the HSE parameters in Table I. (unit: meV/Ni).

| Para. | $\text{PS}_{\text{cont}}^{(110)}$ | $\text{PS}^{(110)}$ | $\text{PS}^{(110)}$ | $\text{PS}^{(110)}$ | $\text{PS}^{(110)}$ | $\text{PS}^{(110)}$ |
|-------|----------------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $A_{xx}$ | 0.04 | 0.07 | 0.07 | 0.00 | -0.03 | -0.03 |
| $J$ | -11.42 | -11.42 | -11.39 | -0.03 | -0.03 | 0.00 |
| $K$ | 0.56 | 0.61 | 0.61 | 0.00 | -0.05 | -0.05 |
| $B$ | 0.84 | 0.84 | 0.85 | -0.01 | -0.01 | -0.00 |
| $J_2$ | -0.18 | -0.18 | -0.17 | -0.00 | -0.00 | 0.00 |
| $J_3$ | 1.52 | 1.52 | 1.45 | 0.07 | 0.07 | 0.00 |
| Total | -8.64 | -8.56 | -8.59 | 0.03 | -0.05 | -0.08 |
We then develop a model to better understand why Kitaev interaction favors \( \langle 110 \rangle \) propagation, as well as, a canting in rotation plane (see details in SM [21]). Here, we construct \( \text{PS}^{(110)} \) and \( \text{PS}^{(110)} \) states and adopt only the Kitaev interaction. The resulted energies are expressed as

\[
E^{110}/K = c_1(\cos 2\theta_1 - 2\sqrt{2}\sin 2\theta_1) + c_2 \text{ and } E^{110}/K = c_3\cos 2\theta_1 + c_4,
\]

where \( E^{110} \) and \( E^{110} \) are the total energies of the corresponding \( \text{PS} \) states, \( \theta_1 \) is the angle from the \{001\} direction to the normal of the rotation plane, and \( c_n(n = 1 - 4) \) are positive constants. It is found that (i) \( E^{110} \) has its minimum at \( \theta_1 = 54.7^\circ \), which is the angle between the \{001\} direction and the \( Y \) (Z or X, respectively) axis, demonstrating that the Kitaev interaction prefers the rotation plane of the \( \text{PS}^{(110)} \) pattern within the \( XZ \) (\( XY \) or \( YZ \), respectively) plane; (ii) \( E^{110} \) has its minimum at \( \theta_1 = \pm 90^\circ \), indicating an exact \( \text{PS} \) state with rotation plane being perpendicular to the propagation direction; and (iii) \( E^{110}_{\text{min}} < E^{110}_{\text{min}} \), confirming that \( \langle 110 \rangle \) propagation, together with a canting, is energetically more favorable (see Fig. S3 of SM [21]).

The critical role of Kitaev interaction in reproducing the canting in spin rotation plane demonstrates the significance of SOC effects on the spin model of NiI₂. Moreover, our DFT results (see Fig. S7 of SM) show that the strength of electric polarization depends largely on the orientation of the spin rotation plane. It thus indicates that the Kitaev interaction is closely related to the ferroelectricity. Such findings are thus in line with previous work, which demonstrates that the ferroelectric order is controlled by the SOC of iodine [28].

Furthermore, Monte-Carlo simulations, as well as a conjugate gradient (CG) algorithm, are performed on large supercells using the Hamiltonian of Eq. (1). Since bulk only differs from the monolayer only by a longer period of propagation and interlayer AFM alignments, we focus on the monolayer hereafter for simplicity. As shown in Fig. 3(a), these simulations found that canted \( \text{PS} \) states form stripy domains and cover most of the area at low temperatures, which is consistent with the fact that the \( \text{PS}^{(110)} \) states are the ground states of NiI₂ bulk. There are three domains that propagate along \( \langle 110 \rangle \) or the equivalent \( \langle 120 \rangle \) and \( \langle 210 \rangle \) directions, which is also in line with the observed three domains of NiI₂ monolayer [7]. Note that the spin pattern shown in Fig. 3a is only 0.038 eV/Ni higher in energy than the ground state of \( \text{PS}^{(110)} \) monodomain. Interestingly, topological defects are predicted to occur at phase boundaries (see Fig. 3), which is in line with the prediction of skyrmion lattice in monolayer NiI₂ [11].

To conclude, we adopted the symmetry-adapted cluster expansion method and built a realistic spin model for multiferroic NiI₂. Such model can reproduce well the experimental \( \langle 110 \rangle \) propagating proper screw state, as well as the canting in its spin rotation plane. The Kitaev interaction is found to play a key role in NiI₂, and is proved to impose anisotropy on coplanar spin texture. Our work...
thus leads to a better understanding on the magnetism of NiI₂, as well as its type-II multiferroicity.

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