

Pseudo-easy-axis anisotropy in antiferromagnetic $S=1$ diamond-lattice systems

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We investigate the magnetic properties of $S=1$ antiferromagnetic diamond-lattice, $\text{Ni}X_2(\text{pyrimidine})_2$ ($X=\text{Cl}, \text{Br}$), hosting a single-ion anisotropy (SIA) orientation which alternates between neighboring sites. Through neutron diffraction measurements of the $X=\text{Cl}$ compound, the ordered state spins are found to align collinearly along a pseudo-easy axis, a unique direction created by the intersection of two easy planes. Similarities in the magnetization, exhibiting spin-flop transitions, and the magnetic susceptibility in the two compounds imply that the same magnetic structure and a pseudo-easy axis is also present for $X=\text{Br}$. We estimate the Hamiltonian parameters by combining analytical calculations and Monte Carlo (MC) simulations of the spin-flop and saturation field. The MC simulations also reveal that the spin-flop transition occurs when the applied field is parallel to the pseudo-easy axis. Contrary to conventional easy-axis systems, there exist field directions perpendicular to the pseudo-easy axis for which the magnetic saturation is approached asymptotically and no symmetry-breaking phase transition is observed at finite fields.

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I. INTRODUCTION

A fundamental goal in condensed matter physics has been the control of dominant energy scales in magnetic systems, allowing experimental exploration of various emergent phases and quantum phenomena. To this end, molecule-based magnets, where molecular ligands link magnetic metal ions, have proven particularly effective [1–5]. The wide choices of ligands available provide a high level of control over the final crystal structure and thus control over various aspects of the magnetic properties [6–8]. For example, a mix of bridging and nonbridging ligands can be used to create quasilow-dimensional magnetic structures [9–11]. The control over the magnetic properties has been achieved through various means, including the substitution of ligands [12–17], metal-ions [10,18] and counter-ions [19,20], and by applying

hydrostatic pressure [21–24]. Moreover, organic ligands such as pyrimidine (pym = C₄H₄N₂) provide the flexibility to create structurally nontrivial systems such as staggered and chiral antiferromagnetic (AFM) $S = 1/2$ spin chains [25–28]. In these systems, the alternating orientation of the spin octahedra between nearest neighbors leads to magnetic properties that differ significantly from conventional spin-half chains. Such properties were explained by the application of the sine-Gordon model of quantum field theory [29,30].

In the present study, we explore the effects of halide substitution and alternating local octahedra orientation in the context of $S = 1$ three-dimensional diamond-lattice systems NiX₂(pym)₂, where X = Cl, Br. The zero-field-splitting in these systems presents the possibility of single-ion-anisotropy (SIA), with energy D , which follows the local spin octahedra and alternates in orientation on neighboring spin sites. Previous studies on the isostructural $S = 2$ system FeCl₂(pym)₂, showed that an alternating easy-axis SIA direction results in a large canting angle of 14° and weak ferromagnetism significantly larger than that which is conventionally caused by the Dzyaloshinskii-Moriya (DM) interaction alone [31]. A subsequent study on NiCl₂(pym)₂ under applied hydrostatic pressure observed temperature-dependent magnetic susceptibility, $\chi(T)$, curves that exhibited similarities to the $\chi(T)$ of FeCl₂(pym)₂. This led to the assumption that the Ni system hosted a similar spin-canted ground state [32]. However,

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neutron diffraction or magnetic hysteresis measurements showing a zero-field remanent magnetization were not available to support this claim. The application of pressure was reported to increase the magnetic ordering temperature, T_N , due to increasing orbital overlap in the Ni–N (N from the pym) bond. Quantitative modeling of the pressure-dependent T_N found that $J \approx 7$ K but an estimation for the size of the SIA was not possible. More recently, studies on a family of metalorganic magnets $M\text{Cl}_2L$, where $M = \text{Ni}$ and Fe , $L = (\text{pym})$ and 2,1,3-benzothiadiazole (btd) also find that an alternating easy axis induces a canted magnetic structure [33]. In contrast, in the frustrated chain-like material, Cs_2CoBr_4 , easy-plane anisotropy, alternating between weakly coupled chains, led to the formation of collinear magnetic order [34,35].

Our neutron diffraction measurements reveals a collinear magnetic structure in NiCl₂(pym)₂, which is attributed to an *easy-plane* SIA that alternates in orientation. The intersection of these alternating planes coupled with the nearest-neighbor antiferromagnetic exchange interaction creates a unique pseudo-easy axis along which the moments align. Given the similarities in the crystal structures (determined using electron diffraction), magnetometry, and muon-spin rotation ($\mu^+\text{SR}$) data, we propose that a pseudo-easy axis is also present in the

$X = \text{Br}$ case. The magnetic order present in these systems is consistent with the negligible zero-field remanent magnetization in measurements of the field-dependent magnetization, $M(H)$. Additionally, we find that the pseudo-easy axis, similar to a real easy axis, results in a spin-flop transition seen in the $M(H)$ data. Monte Carlo (MC) simulations of $M(H)$ and mean-field calculations of the spin-flop and saturation field, H_{SF} and H_{C1} , respectively, are used to determine J and D for $X = \text{Cl}$ and Br . For $X = \text{Br}$, we find that D is reduced while a secondary AFM interaction mediated by the $X \cdots X$ exchange bonds is increased. This is in keeping with the trends established in the magnetic chain compounds NiX₂(3,5-lut)₄ ($X = \text{HF}_2$, Cl, Br, or I) [17] and NiX₂(pyz)₂ (pyz = pyrazine C₄H₄N₂; $X = \text{Cl}$, Br, I, NCS) [15]. Finally, MC simulations of single-crystal $M(H)$ curves reveal that a magnetic saturation phase transition only occurs for fields applied along certain directions.

II. RESULTS AND DISCUSSION

A. Crystal structure

The crystal structures of both $X = \text{Cl}$ and Br compound are solved using single-crystal electron diffraction (3D ED) at $T =$

120 K with lattice parameters obtained from powder x-ray diffraction (PXRD) measurements collected at the I11 beamline of the Diamond Light Source at the same temperature. The details of these measurements and the structural refinement can be found in the Supplemental Material [36]. The resulting crystal structure of $\text{NiX}_2(\text{pym})_2$ is illustrated in Fig. 1 and Table I provides the lattice parameters.

The $X = \text{Cl}$ and $X = \text{Br}$ materials are isostructural and both crystallize in the $I4_122$ space group. These materials consist of three-dimensional diamond-like networks of Ni(II) ions connected by the pym ligand. The Ni(II) ions sit at the center of axially distorted octahedra consisting of four equatorial bonds to the N atoms of the pym rings and two longer axial coordination bonds to the halides.

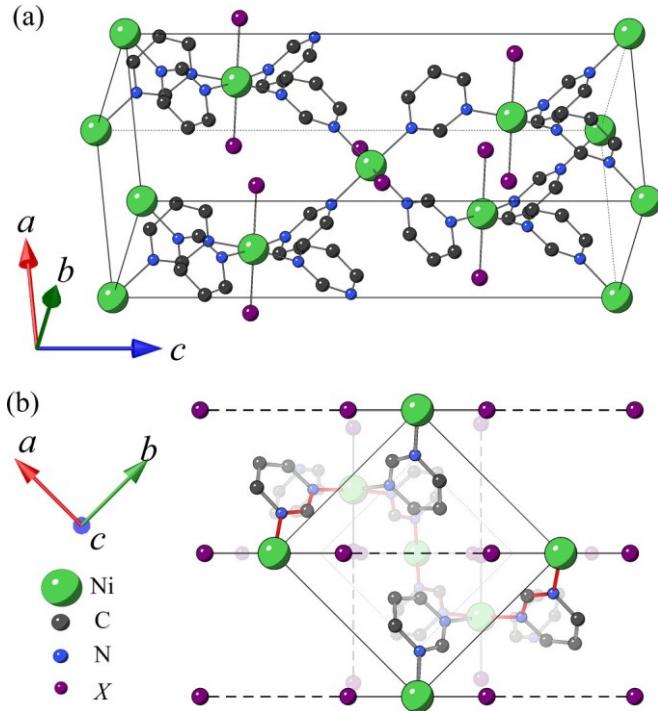


FIG. 1. (a) The $I4_122$ crystal structure of $\text{NiX}_2(\text{pym})_2$ where $X = \text{Cl}$ or Br and pym = pyrimidine. (b) Displays the view down the c -axis. In this structure, the pym ligands bridge neighboring Ni ions and mediate the primary exchange interaction, forming a three-dimensional diamond network. Between neighboring Ni ions connected by pym, the Ni– X axial bond direction rotates by 90°. The black-dashed lines highlight the weak $X \cdots X$ exchange bonds that mediate the secondary exchange interaction along the Ni– $X \cdots X$ –Ni chains. The red bond highlights the exchange pathway, in the Ni–pym network, between two Ni(II) ions connected by the $X \cdots X$ exchange bond.

Within the unit cell Ni(II) ions reside in planes perpendicular to c at heights of $z = 0, c/4, c/2$, and $3c/4$. For Ni(II) ions in the $z = 0$ and $z = c/2$ planes, the axial direction of the local octahedra is orientated along the $[110]^-$ direction. Owing to the 4_1 screw symmetry, this axial direction is rotated

by 90° to align along $[110]$ for Ni(II) ions in the $z = c/4$ and $z = 3c/4$ planes. This rotation ensures if a SIA anisotropy is present in these systems it will be rotated by 90° between neighboring spins connected by pym.

Pym ligands have been shown to be an effective mediator of exchange interactions of the order of 10 K [33]. Secondary interactions are mediated through the halide-halide exchange bond, shown as dashed lines in Figs. 1(a) and 1(b). Such exchange paths depend strongly on the halide ions, but are known to carry exchange of the order of 1 K [17]. This

TABLE I. Lattice parameters for the $I4_122$ structure of $\text{NiX}_2(\text{pym})_2$, $X = \text{Cl}$ and $X = \text{Br}$, determined using powder x-ray diffraction at $T = 120$ K.

| | a, b (Å) | c (Å) |
|-------------------------------|------------|------------|
| $\text{NiCl}_2(\text{pym})_2$ | 7.3576(2) | 19.4956(5) |
| $\text{NiBr}_2(\text{pym})_2$ | 7.50690(6) | 19.5378(2) |

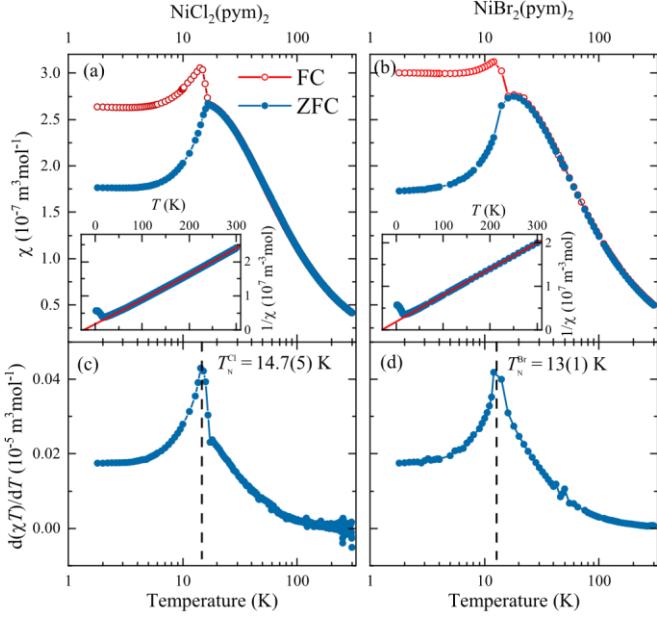


FIG. 2. Temperature-dependent magnetic susceptibility $\chi(T)$ for powder samples of $\text{Ni}X_2(\text{pym})_2$, where (a) $X = \text{Cl}$ and (b) $X = \text{Br}$. For both a field of $\mu_0 H = 0.1$ T was applied, the field-cooled data are depicted as red circles and zero-field-cooled (ZFC) data are blue circles. The insets present the Curie-Weiss fit to the ZFC χ^{-1} . (c), (d) Peak in the ZFC $d(\chi T)/dT$ marks the onset of magnetic long-range order at $T_N = 14.7(5)$ K for $X = \text{Cl}$ and $T_N = 13(1)$ K for $X = \text{Br}$.

results in weakly interacting $\text{Ni}-X \cdots X-\text{Ni}$ chains propagating along the $[110]^-$ direction for ions in the $z = 0$ and $z = c/2$ planes and along $[110]$ for ion in the $z = c/4$ and $z = 3c/4$ planes. In the cases where there is AFM coupling through both the pym ligands and the halide-halide exchange bonds, the two interactions will be in competition, resulting in a reduced net effective interaction.

The spin Hamiltonian of $\text{Ni}X_2(\text{pym})_2$, written in terms of the two spin sites i and j is

$$\mathcal{H} = J \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\langle i, j \rangle} g\mu_B\mu_0 \mathbf{H} \cdot \mathbf{S}_{ij} \left[\sum_i (\hat{\mathbf{D}}_i \cdot \mathbf{S}_i)^2 + \sum_j (\hat{\mathbf{D}}_j \cdot \mathbf{S}_j)^2 + D\mathbf{S}_j \right] \quad (1)$$

Here, \mathbf{S}_{ij} is the spin of each ion, $\langle i, j \rangle$ denotes the sum over unique pairs of neighboring spins with exchange interaction

strength J , D is the size of the SIA, $\hat{\mathbf{D}}_i = [110]^-/\sqrt{2}$, and

$\hat{\mathbf{D}}_j = [110]/2$ are the hard-axis unit vectors for sites i and j , and $g\mu_B\mu_0 \mathbf{H} \cdot \mathbf{S}_{ij}$ is the Zeeman energy term assuming an isotropic g -factor. Although the symmetry permits the DM

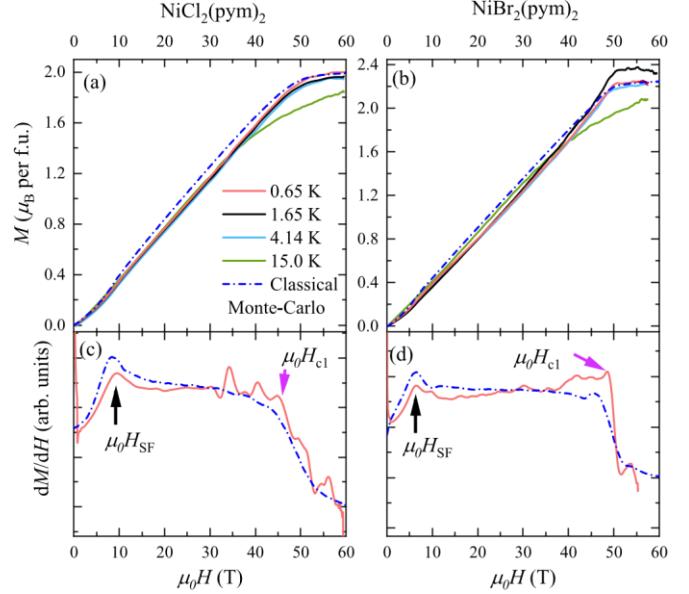


FIG. 3. Powder-averaged magnetization, $M(H)$, data for interaction, its magnitude is expected to be small compared to the terms in Hamiltonian given in Eq. (1). As we will show in the following sections, all data presented here can be accounted for by this minimal Hamiltonian.

B. Magnetometry

Powder $\chi(T)$ data for $X = \text{Cl}$ are presented in Fig. 2(a). On cooling from 300 K, both the field-cooled (FC) and zero- $\text{Ni}X_2(\text{pym})_2$, where (a) $X = \text{Cl}$ and (b) $X = \text{Br}$ at various temperatures. The $T = 0.65$ K differential susceptibility, dM/dH , below ordering temperature for (c) $X = \text{Cl}$ and (d) $X = \text{Br}$. The black arrows mark the spin-flop field in both and the blue dash-dotted lines show the results of the classical Monte Carlo simulation discussed in Sec. II E of the text.

field-cooled (ZFC) data exhibit a smooth rise to a sharp cusp and a bifurcation of the two curves at $T \approx 15$ K. Plotting the ZFC data as $d(\chi T)/dT$ in Fig. 2(d) reveals a lambda-like peak, close to the bifurcation, which is suggestive of a transition to long-range magnetic order below $T_N = 14.7(5)$ K [37]. Further cooling results in plateaus in the FC and ZFC curves below 4.6 K. In the inset to Fig. 2(a), a Curie-Weiss (CW) fit to the inverse susceptibility, $\chi(T)^{-1}$, for 50 K $\leq T \leq 300$ K, yields $g = 2.14(1)$, CW temperature $\theta_{\text{CW}} = -26.1(2)$ K, and a temperature-independent constant $\chi_0 = -2.62(5) \times 10^{-9} \text{ m}^3\text{mol}^{-1}$. The negative θ_{CW} here indicates an AFM coupling of the Ni ions.

The $\chi(T)$ curves for $X = \text{Br}$ in Fig. 2(b) display a similar behavior to $X = \text{Cl}$. However, the bifurcation and the lambda peak in ZFC $d(\chi T)/dT$ [see Fig. 2(d)] are suppressed to a lower

$T_N = 13(1)$ K, revealing a rounded local maximum prior to the bifurcation of the ZFC and FC curves. CW fit to the $\chi(T)^{-1}$ [see inset to Fig. 2(b)], results in $g = 2.27(1)$, $\theta_{\text{CW}} = -31.7(2)$ K, and $\chi_0 = 1.09(9) \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$.

Figures 3(a) and 3(b) present the pulsed-field $M(H)$ data for $X = \text{Cl}$ and Br , respectively. In both materials, at low fields and temperatures below T_N , there is an upturn in the magnetization observed as a peak in the differential susceptibility, dM/dH , shown in Figs. 3(c) and 3(d). These features, reminiscent of the spin-flop transition found in easyaxis systems, are observed at $\mu_0 H_{\text{SF}} = 9.5(8)$ T and $6.6(8)$ T for $X = \text{Cl}$ and Br , respectively. In the $X = \text{Cl}$ sample, further increase in field results in a near linear rise in $M(H)$, up to the first saturation field $H_{\text{c1}} = 46(3)$ T. H_{c1} is defined as the point where $M(H)$ deviates from a linear field dependence (point where dM/dH starts to decrease). The 0.65 K $M(H)$ data for

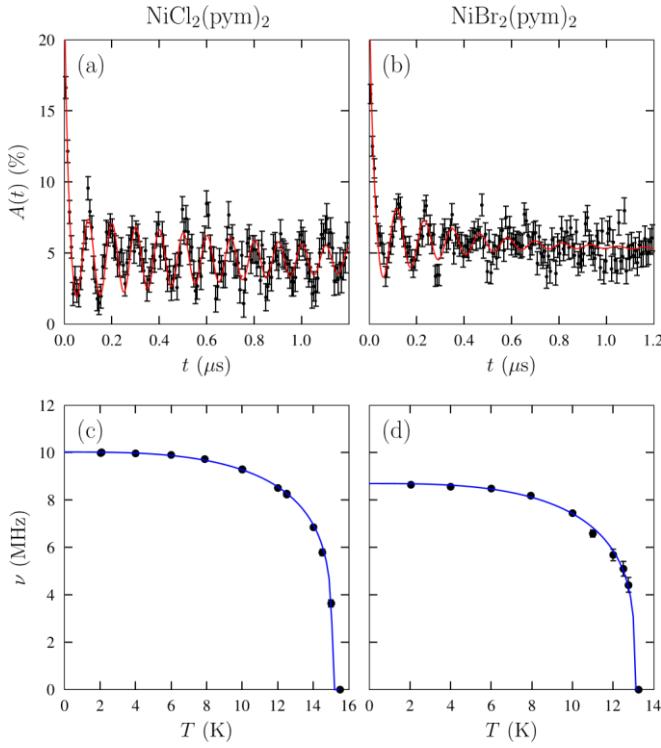


FIG. 4. The zero-field μ^+ SR spectra data (black circles) collected at $T = 4$ K for $\text{Ni}X_2(\text{pym})_2$, where (a) $X = \text{Cl}$ and (b) $X = \text{Br}$. The temperature dependence of the oscillation frequency ν for (c) $X = \text{Cl}$ and (d) $X = \text{Br}$. The solid lines represent fits to the data.

$X = \text{Br}$ display a slightly concave approach to the first saturation field, resulting in a peak in dM/dH at $H_{\text{c1}} = 48(1)$ T. As we will show in Sec. III E, H_{c1} corresponds to magnetic saturation for grains in which the field aligns along the [001] axis. For $H > H_{\text{c1}}$, the projected value of the saturation magnetization suggests a low-temperature g factor of $g = 2.06$

for $X = \text{Cl}$ and $g = 2.25$ for $X = \text{Br}$. The g for $X = \text{Cl}$ is slightly lower than predicted by the CW fit at high temperatures while the values for $X = \text{Br}$ are in good agreement. For a spin-canted magnetic structure, similar to $\text{FeCl}_2(\text{pym})_2$, a remanent $M(H)$ at zero-field is expected. However, in both $X = \text{Cl}$ and Br , very small remanent $M(0)$ of $0.001 \mu_B$ and $0.00016 \mu_B$ per $\text{Ni}(\text{II})$ ion, respectively, are observed [36]. These small $M(0)$ are readily explained by the presence of a small amount of $\text{Ni}X_2(\text{pym})$ impurity phases (as seen in the crystallographic data for the $X = \text{Cl}$ sample in the Supplemental material [36]) which are known to exhibit a $M(0) = 0.127 \mu_B$ per $\text{Ni}(\text{II})$ [33].

C. Muon-spin rotation

Zero-field μ^+ SR measurements were carried out at the Swiss Muon Source, Paul Scherrer Institut. Data were collected at temperatures $2 \leq T \leq 16$ K and example spectra at 4 K for $X = \text{Cl}$ and $X = \text{Br}$ are shown in Figs. 4(a) and 4(b), respectively. For both materials, the time-dependent asymmetry function exhibits clear oscillations, indicative of long-range magnetic order throughout the bulk of the material. The quasistatic local field, arising in the presence of longrange magnetic order, causes a coherent precession of the spin of those muons for which a component of their spin polarization lies perpendicular to this local field (expected to be $2/3$ of the total spin polarization for a polycrystalline sample). The frequency of the oscillation is given by $\nu_i = \gamma_\mu |B_i|/2\pi$, where $\gamma_\mu = 2\pi \times 135.5$ MHz T $^{-1}$ is the muon gyromagnetic ratio and B_i is the average magnitude of the local magnetic field at the i^{th} muon site. As such, ν_i is an effective order parameter and indicative of the total ordered moment within each sample.

To describe the temperature evolution of the asymmetry function and hence $\nu_i(T)$, fits were produced to a function of the form

$$A(t) = A_1 e^{-\lambda_1 t} \cos(2\pi\nu t) + A_2 e^{-\lambda_2 t} + A_b, \quad (2)$$

where λ_i are relaxation rates and A_b is a background contribution from muons stopping outside the sample. The first term in Eq. (2) accounts for the oscillatory signal and the second term accounts for the muon polarization initially parallel to the local magnetic field. The presence of a single frequency for both materials implies that a single muon site gives rise to the oscillatory components of the spectra. The resulting temperature-dependent $\nu(T)$, shown in Figs. 4(c) and 4(d), is described using the phenomenological function [38]

$$\nu(T) = \left[1 - \left(\frac{T}{T_N} \right)^\alpha \right]^\beta. \quad (3)$$

For $X = \text{Cl}$, we obtain $v(0) = 10.0(1)$ MHz (corresponding to a local field of 74 mT), $T_N = 15.05(1)$, and $\beta = 0.22(1)$ for a fixed $\alpha = 3$. The ordering temperature extracted here is in excellent agreement with the analysis of the $\chi(T)$ data. The rapid drop in $v(T)$ with increasing temperature along with the fitted value of β implies the existence of fluctuations, close to the phase transition, that are intermediate between a two- and three-dimensional character. For $X = \text{Br}$, the fit yields $v(0) = 8.70(3)$ MHz (corresponding to a local field of 64 mT), $T_N = 13.1(1)$, and $\beta = 0.27(1)$. The ordering temperature is again in excellent agreement with the $\chi(T)$ data. Compared to $X = \text{Cl}$, an increased β in $X = \text{Br}$ implies the fluctuations here are more three-dimensional. This is in keeping with the expectation that there are nonzero exchange interactions through the halides in the $X = \text{Br}$ system, while in $X = \text{Cl}$ this interaction is expected to be much smaller [17].

D. Elastic neutron scattering

Elastic neutron diffraction measurements on powder samples of $\text{NiCl}_2(\text{pym})_2$ were performed on the WISH instrument at the ISIS, UK Neutron and Muon Source [39], at temperatures above ($T = 20$ K) and below ($T = 1.4$ K) the magnetic ordering transition. Rietveld refinement of the nuclear structure was performed on the data collected at $T = 20$ K, across four separate detector banks, using the FULLPROF software package [40]. Figure 5(a) present the structural fit with $R_{\text{Bragg}} = 3.361\%$ to data from one such detector bank at average $2\theta = 58.330^\circ$. The resulting lattice parameters, $a = 7.3425(2)\text{\AA}$ and $c = 19.4841(9)\text{\AA}$, and nuclear structure are in good agreement with the values determined from the 3D ED and PXRD measurements at 120 K and accounted for all observed peaks at 20 K.

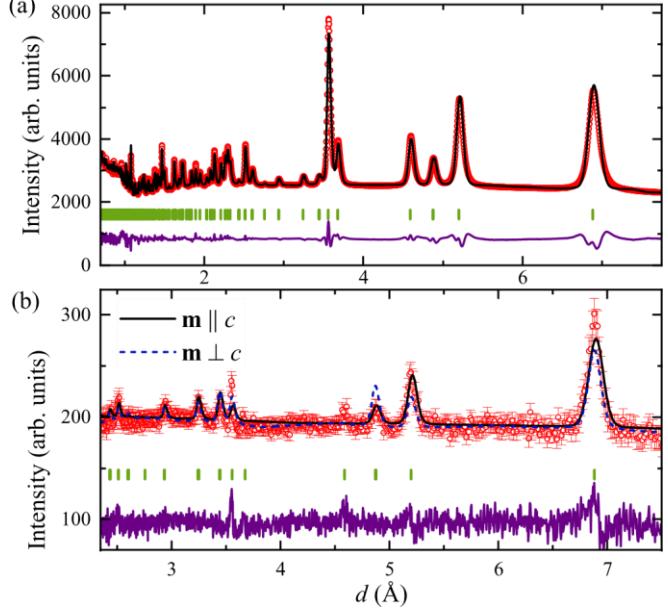


FIG. 5. (a) Rietveld refinement of the $I4_122$ the nuclear structure of $\text{NiCl}_2(\text{pym})_2$ to powder neutron diffraction data collected at $T = 20$ K. The data points are shown as red circles, fitting curve in black, Bragg positions are marked by green ticks, and the difference between the data and the calculated pattern is shown in purple. (b) Magnetic diffraction pattern obtained by subtracting data collected at 20 K from the 1.4 K data. The fitted pattern (black) has magnetic moments parallel to the c -axis compared to the pattern with moments perpendicular to c (blue dashed line).

The difference between the data collected at $T = 1.4$ K and $T = 20$ K reveals magnetic Bragg peaks residing on top of the nuclear peak positions, indicating magnetic order with propagation vector $\mathbf{k} = (0,0,0)$. Symmetry analysis in ISODISTORT [41,42] reveals three candidate symmetries (irreps m_2 , m_3 , and m_5) for the magnetic structure. Among these, m_3 corresponds to ferromagnetic (FM) order and is ruled out from the $\chi(T)$ measurements. The magnetic moments in the magnetic structure described by the m_2 irrep are constrained to point parallel to the c -axis with nearest-neighbors antiferromagnetically coupled through pym. Consequently, the ordered moment size is the only refinable parameter in this irrep. The structure associated with m_5 irrep decomposes into a linear combination of perpendicular FM and AFM modes within the ab -plane and hence encompasses the canted structure observed in the $\text{FeCl}_2(\text{pym})_2$ system [31].

The diffraction pattern resulting from the refinement of both AFM models is shown in Fig. 5(b). The magnetic structure associated with irrep m_2 is found to best fit the data with $R_{\text{mag}} = 4.16\%$ compared to $R_{\text{mag}} = 34.89\%$ of irrep m_5 . The resulting ordered moment size is $1.99(3)$ μ_B per Ni(II) ion, which is in excellent agreement with the low-temperature magnetic saturation value. The resulting collinear magnetic

structure is depicted in Fig. 6 and is consistent with an easyplane SIA. While the local easy plane, defined by the local Ni–pym equatorial plane and shown as blue circles in Fig. 6, rotates by 90° between each neighboring Ni(II) ion, the intersection of these planes defines a pseudo-easy axis along the

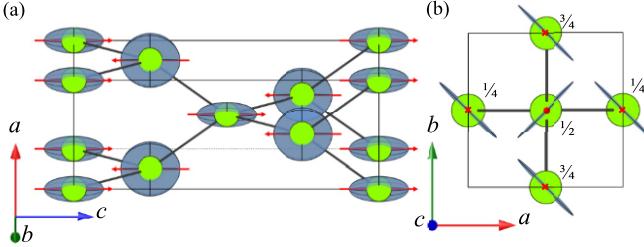


FIG. 6. (a) Zero-field magnetic structure of $\text{NiCl}_2(\text{pym})_2$ determined through powder neutron diffraction. The red arrows indicate the magnetic moment direction of Ni(II) ions (green spheres). The blue circles show the local single-ion easy plane of Ni(II) ions and the black lines show the nearest neighbors' exchange interactions. (b) View down the c -axis illustrates 90° rotation of the easy plane between nearest neighbours. Ni(II) ions at $[x,y,0]$ and $[x,y,1]$ are omitted for clarity.

c direction. Moments aligning along this axis satisfy both the exchange interaction through pym and the SIA. The collinear structure observed here indicates the absence of any significant DM interaction, which would result in spin-canting. Additionally, the $\mathbf{k} = (0,0,0)$ vector and the magnetic structure is only possible when the exchange through the pym is dominant and AFM.

Our bulk magnetic characterisation suggests $X = \text{Cl}$ and $X = \text{Br}$ are described by the same magnetic Hamiltonians but with differing values of J and D . Since the magnetic ground state determined for $X = \text{Cl}$ is independent of the values of AFM J and easy-plane D , we expect $\text{NiBr}_2(\text{pym})_2$ will adopt the same magnetic structure.

E. Calculations and simulations

1. Critical fields

In a similar manner to ordinary easy-axis systems, applying the field parallel to the pseudo-easy axis will cause a spin-flop and magnetic saturation transitions which are seen in the $M(H)$ data in Fig. 3. Mean-field calculations, under the assumption that $D \ll J$, presented in the Supplemental Material [36], predict that these transitions occur at

$$\mu_0 H_{\text{cl}} = \frac{2nJ - D}{g\mu_B}, \quad (4)$$

$$\mu_0 H_{\text{SF}} = \frac{\sqrt{2nJD - D_2}}{g\mu_B} \quad (5)$$

$g\mu_B$

Here $n = 4$ is the number of nearest neighbors. Taking the isotropic low-temperature g -factors and the critical field from the $M(H)$ data, we determine that $J = 8.1(5)$ K, $D = 2.6(5)$ K for $X = \text{Cl}$ and $J = 9.2(2)$ K, $D = 1.2(3)$ K for $X = \text{Br}$. The phase diagram of D/J ratio against the ratio of Zeeman energy and exchange energy, $g\mu_B\mu_0H/J$, is shown in Fig. 7. While the phase diagram extends up to $D/J = 1.50$ in Fig. 7, the zero-field collinear AFM order induced by the pseudo-easy-axis anisotropy may be expected to extend up to larger values of D/J . Indeed, in Cs_2CoBr_4 , the collinear AFM ground state is present for $D/J \sim 8$ [34]. The D/J ratios for both $X = \text{Cl}$ and Br materials are marked in the phase diagram and are summarized in Table II.

FIG. 7. Phase diagram for $\text{NiX}_2(\text{pym})_2$, for $\mathbf{H} \parallel c$ and calculated using a classical mean-field model described in the text. The x -axis is the ratio of easy-plane single-ion anisotropy and the exchange energies. The y -axis is the ratio of the Zeeman and the exchange energy. The red line represents the calculated spin-flop transition taking the systems from an antiferromagnetic state to a spin-canted state. The blue line is the boundary between the spin canted to the spin-polarized state. The black and purple dashed lines mark the D/J ratio of the $X = \text{Cl}$ and Br materials, respectively, and the shaded regions indicate the experimental uncertainty in these values.

2. Monte Carlo simulations

To confirm the values of J and D , determined using Eqs. (4) and (5) and reported in Table II, classical MC simulations of the powder-averaged $M(H)$ were carried out. $M(H)$ curves were calculated for 100 different field directions evenly spaced on a unit sphere and averaged to calculate the powder averaged $M(H)$. The resulting simulated $M(H)$ curves for $X = \text{Cl}$ and Br are shown in Figs. 3(a) and 3(b), respectively, and the differential susceptibilities are shown in Figs. 3(c) and 3(d).

In both $X = \text{Cl}$ and Br , there is a good agreement between the experimental and the simulated $M(H)$ curves. The simulations show a small overestimation of the $M(H)$ due to the slight concavity in the measured $M(H)$ curves. In $[\text{Ni}(\text{HF}_2)(\text{pym})_2]\text{SbF}_6$, a similar discrepancy was attributed to the development of quantum fluctuations resulting from the quasi-one-dimensional nature of the magnetic exchange [4]. Here the discrepancy may also arise from quantum fluctuations in these $S = 1$ systems.

For $X = \text{Br}$, there is a good agreement between simulated and observed $\mu_0 H_{\text{SF}}$ and $\mu_0 H_{\text{cl}}$. For $X = \text{Cl}$, the larger D/nJ results in a slight underestimation of D when calculated using Eq. (5), which is derived under the approximation that

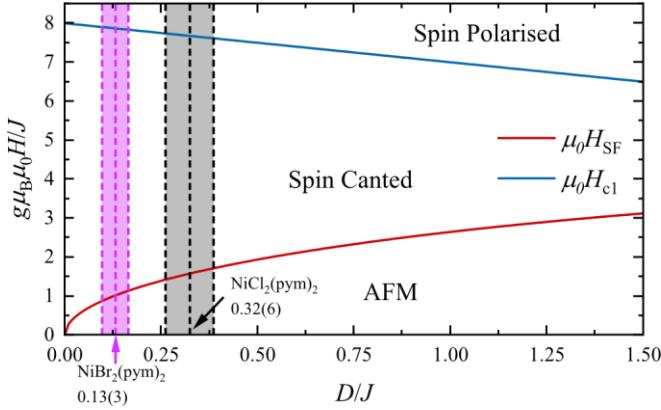


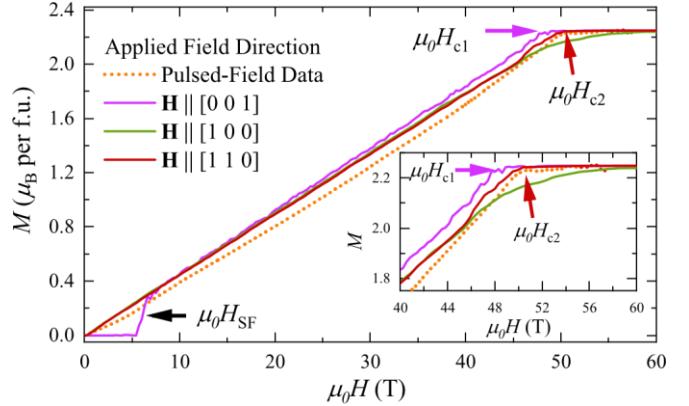
TABLE II. The AFM exchange energy J and the easy-plane single-ion anisotropy parameter D , derived using mean-field calculations of the observed critical fields in the magnetization $M(H)$ data. The g -factors are the low-temperature values determined experimentally through the $M(H)$ saturation value.

| | J (K) | D (K) | g | D/J |
|-------------------------------|---------|---------|------|---------|
| $\text{NiCl}_2(\text{pym})_2$ | 8.1(5) | 2.6(5) | 2.06 | 0.32(6) |
| $\text{NiBr}_2(\text{pym})_2$ | 9.2(2) | 1.2(3) | 2.25 | 0.13(3) |

FIG. 8. Monte Carlo simulation of the magnetization $M(H)$ for $\text{NiBr}_2(\text{pym})_2$ with the field along various crystallographic directions along with the measured pulsed field $M(H)$ data. The inset is zoomed into the $40 \mu_0H$ – 60 T range. The black arrow highlights the spin-flop field and the purple arrow points toward the saturation field for $\mathbf{H} \parallel [001]$ (field parallel to pseudo-easy axis). The red arrow indicates the saturation field for $\mathbf{H} \parallel [110]$ (perpendicular to the pseudo-easy axis but in the easy plane of a sublattice). There is no magnetic saturation in the $M(H)$ for fields that are not aligned within the easy plane of either sublattice in the systems (green line).

D nJ . Consequently, MC simulations using the calculated J and D values (as reported in Table II) results in a slightly smaller simulated μ_0H_{SF} than the observed value for $X = \text{Cl}$. However, as seen in Figs. 3(a) and 3(c), the deviation in μ_0H_{SF} is small and the derived value of D is expected to be correct within the experimental error.

It is often the case that for anisotropic magnets, a symmetry-breaking phase transition occurs at saturation when a sufficiently large magnetic field is applied along the principle anisotropy axes. In our systems, the rotational symmetry around the SIA axis is broken by the alternation of the Ni(II) octahedra. As a result, field directions perpendicular to the pseudo-easy axis exist for which a phase transition is absent at finite fields. Here, the SIA can always save energy by canting spins away from the applied field and a spin-polarized phase is only reached in the limit of infinite field. This is illustrated by the MC simulation of $M(H)$ for $\mathbf{H} \parallel [100]$ presented in Fig. 8, in which $M(H)$ asymptotically approaches the saturation value. When the applied field is parallel to the pseudo-easy axis, the field-polarized phase



minimizes the SIA energy for spin in both i and j sites resulting in the first saturation phase transition at $\mu_0H_{\text{c}1}$. A second saturation field is expected to occur for $\mathbf{H} \parallel [110]$ or $[110]^-$, corresponding to direction in which the field aligns parallel to the hard axis of one site and also within the easy plane of the other site [43]. In a powder-averaged $M(H)$ experiment, the second saturation field is hard to define in the data.

III. CONCLUSION

In summary, we thoroughly characterized the magnetic properties of the $S = 1$ diamond-lattice systems, $\text{Ni}X_2(\text{pym})_2$ ($X = \text{Cl}$ or Br). The octahedral orientation and the SIA axis of neighboring Ni(II) ions connected by AFM exchange mediating pym ligands alternate by a 90° rotation about the $[001]$ direction. While an alternating easy axis induces a spin-canted magnetic order, as seen in $\text{FeCl}_2(\text{pym})_2$ [31], $\text{NiCl}_2(\text{pym})$, and $\text{NiCl}_2(\text{btd})$ [33], an alternating easy-plane anisotropy is expected to result in collinear order along the unique direction created by the intersection of the two easy planes. Here we denote this direction as the pseudo-easy axis. Recent studies on $\text{FeCl}_2(\text{pym})$ and $\text{FeCl}_2(\text{btd})$ found that while hosting an alternating easy-plane anisotropy, significant spin-canting arose due to rhombic anisotropy, DM or higher-order interaction [32]. In contrast, our neutron diffraction measurements revealed that the magnetic moments in $\text{NiCl}_2(\text{pym})_2$ align collinearly along $[001]$, the pseudo-easy axis.

Similar $\chi(T)$ and a low-field feature in $M(H)$, which is ascribed to a spin-flop transition, was observed in both $X = \text{Cl}$ and Br compounds, implying that $X = \text{Br}$ also hosted a pseudo-easy-axis anisotropy and adopts the same collinear order. Mean-field calculations of the spin-flop and the magnetization saturation field were used to determine that $J =$

8.1(5) K, $D = 2.6(5)$ K for $X = \text{Cl}$ and $J = 9.2(2)$ K, $D = 1.2(3)$ K for $X = \text{Br}$. The values of J calculated here are comparable to $J = 7$ K reported in Ref. [32] and MC simulations of the powder-average $M(H)$ simulations were

performed to verify these Hamiltonian parameters. Moreover, MC simulations of single-crystal $M(H)$ curves indicate that when the applied field is parallel to the pseudo-easy axis, characteristic spin-flop and a magnetic saturation phase-transition, akin to conventional easy-axis systems, occur. However, due to the broken rotational symmetry around the pseudo-easy axis, there are field directions perpendicular to the pseudo-easy axis where the $M(H)$ exhibits an asymptotic approach to magnetic saturation rather than a saturation phase transition at finite fields.

The reduction in D and an increase in secondary exchange through the halide-halide bond in $X = \text{Br}$ is in keeping with the magnetostructural correlations established for halides of different radii in $\text{Ni}X_2(3,5\text{-lut})_4$ [17]. Similar to $\text{NiI}_2(3,5\text{lut})_4$, we expect $\text{NiI}_2(\text{pym})_2$ to exhibit a small easy-axis D accompanied by a larger halide-halide exchange interaction. This would lead to the observation of a SIA-induced spincanted magnetic order, similar to that observed in isostructural $\text{FeCl}_2(\text{pym})_2$ [31].

Data presented in this paper will be made available at [49].

ACKNOWLEDGMENTS

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Correction: Support information was incomplete and has been fixed.