Inducing Magnetic Phase Transitions in Monolayer CrI$_3$ via Lattice Deformations

Michele Pizzochero$^{1,2}$ and Oleg V. Yazyev$^{1,2}$

$^1$Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
$^2$National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

(Dated: May 23, 2022)

Atomically thin films of layered chromium triiodide (CrI$_3$) have recently been regarded as suitable candidates to a wide spectrum of technologically relevant applications, mainly owing to the opportunity they offer to achieve a reversible transition between coexisting in-plane ferro- and out-of-plane antiferromagnetic orders. However, no routes for inducing such a transition have been designed down to the single-layer limit. Here, we address the magnetic response of monolayer CrI$_3$ to in-plane lattice deformations through a combination of isotropic Heisenberg spin Hamiltonians and first-principles calculations. Depending on the magnitude and orientation of the lattice strain exerted, we unveil a series of direction-dependent parallel-to-antiparallel spins crossovers, which yield the emergence of ferromagnetic, Néel antiferromagnetic, zigzag and stripy antiferromagnetic ground states. Additionally, we identify a critical point in the magnetic phase diagram whereby the exchange couplings vanish and the magnetism is quenched. Our work establishes guidelines for extensively tailoring the spin interactions in monolayer CrI$_3$ via strain engineering, and further expands the magnetically ordered phases which can be hosted in a two-dimensional crystal.

Introduction. Over a decade after the first isolation of graphene [1], the class of two-dimensional materials currently encompasses a broad range of diverse properties [2–8]. Among them, the emergence of correlated electron phases, including superconductivity, Mott-insulating phases, or charge density waves [9–13], has culminated in the discovery of intrinsic magnetism in certain atomically thin crystals [14, 15]. In these systems, the pivotal role played by the single-ion anisotropies serves magnetic order in low dimensions [16], as unambiguously demonstrated by the groundbreaking exfoliation of the bulk ferromagnet CrI$_3$ down to the monolayer limit [17], rapidly followed by the appearance of many other ultrathin magnets, e.g. Fe$_2$GeTe$_2$, Cr$_2$Ge$_2$Te$_6$, FePSe$_3$ [14, 15, 18–20].

Within the constantly expanding family of two-dimensional magnets, semiconducting thin films of CrI$_3$ are arguably the most prototypical members. They exhibit a layered crystal structure, in which Cr atoms are located at the corners of in-plane honeycomb networks and reside in edge-sharing octahedra formed by I atoms [21]. As far as the magnetism is concerned, each Cr$^{3+}$ ion features effective spin 3/2 [22], which interacts with neighboring sites through intra-layer (inter-layer) ferromagnetic (antiferromagnetic) exchange couplings, as pinpointed by the evolution of the thickness-dependent hysteretic features reported in recent MOKE experiments [17]. The competition between ferro- and antiferro-magnetic couplings in bi- and few-layer CrI$_3$ allows one to switch between these two phases, thereby tailoring the nature of the magnetic ground state. This has been experimentally accomplished through a broad variety of different techniques, including electrostatic gating [23], doping [24], applied external pressure [25, 26], off-plane lattice deformations [27], or adjusting the stacking patterns of the layers [28, 29]. Such an extensive control over the magnetism in atomically thin CrI$_3$ holds promise for the realization of novel ultrathin magnetoelectronic devices [30, 32].

Down to the single-layer limit, however, the lack of antiferromagnetic interactions across the crystal hinders the realization of any magnetic order other than the ferromagnetic one. In this Letter, we theoretically investigate the effect of in-plane lattice deformations on the magnetism of monolayer CrI$_3$. We unveil a series of magnetic phase transitions arising from the competition between symmetry inequivalent Heisenberg exchange couplings in the distorted lattice, which gives rise to both antiferromagnetic and ferrimagnetic orders, along with a non-magnetic phase. Overall, our findings provide useful guidelines for modulating the magnetic properties of CrI$_3$ down to the ultimate limit of atomic thickness through strain engineering.

Methodology. Our first-principles calculations are performed within the spin-polarized Density Functional Theory (DFT) framework, as implemented in VASP [33, 34]. We adopt the generalized gradient approximation devised by Perdew, Burke and Ernzerhof [35], and further include a Hubbard correction $U = 1.5$ eV on the $d$ orbitals of Cr atoms [36]. Such an exchange-correlation density functional ensures an excellent description of magnetic properties of monolayer CrI$_3$ when compared to benchmark multireference wavefunction results [37] and available experimental data [17, 38]. The cutoff on the kinetic energy is set to 400 eV and the Brillouin zone is sampled with a $12 \times 12$ k-mesh. We determine the exchange couplings between a pair of magnetic Cr$^{3+}$ sites through the well-established four-state method for energy mapping analysis detailed in Refs. [39, 40]. This approach allows one to determine the exchange cou-
neighbors sites, respectively. We determine $J$-plings between nearest, second-nearest, and third-nearest with earlier calculations [38], we note that the inter-site to be equivalent exchange couplings tively. The $2 \times 3$ grey circles representing chromium and iodine atoms, respectively.

FIG. 1: Atomic structure of monolayer CrI$_3$, with white and grey circles representing chromium and iodine atoms, respectively. The $2 \times 2$ supercell considered in our calculations is indicated with black dashed lines. The three symmetry inequivalent exchange couplings $J_1$, $J_2$, and $J_3$ between Cr$^{3+}$ ions are indicated with blue, red, and green solid lines, respectively.

...ppling between a pair of sites without introducing any arbitrary choice on the magnetic configurations of the supercells. For each spin configuration, we optimized the atomic coordinates until the residual Hellmann-Feynman forces acting on each atom converge to 0.005 meV/Å. In order to properly account for all the relevant exchange couplings between the nearest neighbors in the distorted lattice, we consider an atomic model of monolayer CrI$_3$ consisting of a $2 \times 2$ hexagonal supercell containing 32 atoms. For the calculation of the exchange couplings between the second- and third-nearest neighbors, on the other hand, we adopt a $3 \times 3$ hexagonal supercell containing 72 atoms.

Results and Discussion. We start by describing magnetic interactions in unstrained monolayer CrI$_3$. According to our previous quantum chemistry investigation [37], the isotropic exchange coupling exceeds inter-site anisotropies in CrI$_3$ by several orders of magnitude. This indicates that the isotropic Heisenberg Hamiltonian $\mathcal{H}$ which couples the $i$-th and $j$-th sites carrying $S_i$ and $S_j$ spins, respectively, is a suitable spin model for the description of the magnetic exchange interactions in monolayer CrI$_3$ [22, 37]. Such a Hamiltonian reads as

$$\mathcal{H} = \frac{J}{2} \sum_{\langle i,j \rangle} \hat{S}_i \cdot \hat{S}_j + \frac{J'}{2} \sum_{\langle\langle i,j \rangle\rangle} \hat{S}_i \cdot \hat{S}_j + \frac{J''}{2} \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} \hat{S}_i \cdot \hat{S}_j$$

(1)

with $J$, $J'$ and $J''$ being the Heisenberg exchange couplings between nearest, second-nearest, and third-nearest neighbors sites, respectively. We determine $J$, $J'$ and $J''$ to be $-1.53$ meV, $-0.38$ meV, and $-0.01$ meV. In line with earlier calculations [38], we note that the inter-site interactions are primarily dictated by the nearest neighbor exchange coupling $J$, as the next-nearest neighbors couplings $J'$ and $J''$ are substantially weaker and further feature the same sign, thereby ruling out any possible competition between $J$, $J'$, and $J''$ in determining the magnetic ground state. Hence, in the following we restrict our description to nearest neighbors couplings only ($J' = J'' = 0$ meV), according to which Eqn. (1) boils down to

$$\mathcal{H} = \frac{J}{2} \sum_{\langle i,j \rangle} \hat{S}_i \cdot \hat{S}_j$$

(2)

We systematically investigate the effect of lattice deformations on single-layer CrI$_3$ by introducing in-plane lattice strain along both the $a$ and $b$ directions shown in Fig. 1. We quantify the relative amount of strain along each direction as $\epsilon_a = (a - a_0)/a_0$ and $\epsilon_b = (b - b_0)/b_0$, with $a_0 = b_0$ being the experimental equilibrium lattice constant of 13.734 Å in the adopted $2 \times 2$ supercell. We span an interval of lattice strain $\epsilon_a = [-8\%, 0]$ and $\epsilon_b = [-8\%, 8\%]$ through a $9 \times 17$ grid. Upon the introduction of an anisotropic strain (that is, $\epsilon_a \neq \epsilon_b$), the honeycomb lattice on which the Cr$^{3+}$ ions reside is subjected to a non-symmetric distortion, which gives rise to the formation of the three inequivalent bonds between the nearest spin-3/2 centers. Such a symmetry breaking, in turn, requires the introduction of three distinct Heisenberg exchange couplings $J_1$, $J_2$, and $J_3$ (see Fig. 1) in order to establish the nature of the magnetic ground state. It is clear that these bond-dependent couplings
FIG. 3: Magnetic phase diagram of monolayer CrI$_3$ under in-plane lattice deformations. The spin configurations emerging in the honeycomb network are also shown, with white and black circles representing Cr$^{3+}$ ions carrying opposite magnetic moments. Bonds between Cr$^{3+}$ ions are color-coded according to Fig. 1. Dashed lines indicate the unit cell.

become equivalent by symmetry ($J_1 = J_2 = J_3$) in either the unstrained ($\epsilon_a = \epsilon_b = 0$) or biaxially strained ($\epsilon_a = \epsilon_b \neq 0$) lattice. Overall, the determination of $J_1$, $J_2$, and $J_3$ within the strain grid mentioned above requires over 1800 calculations.

The response of $J_1$, $J_2$, and $J_3$ to lattice deformations is presented in Fig. 2. While the strain exerted does not affect the of the local magnetic moments carried by the Cr$^{3+}$ ions, it is found to have a strong influence on the magnitude and sign of the exchange couplings. On the one hand, tensile strain lowers all of them, hence further strengthening the ferromagnetic phase. On the other hand, lattice compressions are found to increase $J_1$, $J_2$, and $J_3$ and eventually revert their signs, thereby promoting a bond-dependent parallel-to-antiparallel spins transition. Indeed, the amount and direction of the lattice strain which is necessary to promote such a transition largely differ for the three couplings. Specifically, our calculations indicate that an antiparallel orientation of the spins along each pair of Cr$^{3+}$ ions occurs at ($\epsilon_a \lesssim -1.5\%$; $\epsilon_b \lesssim -1.5\%$), ($\epsilon_a \lesssim -5\%$, and ($\epsilon_a \lesssim -4.5\%$) for $J_1$, $J_2$, and $J_3$, respectively.

Such a pronounced competition between the three Heisenberg exchange couplings induces the emergence of a strain-dependent magnetic ground state in monolayer CrI$_3$. Indeed, six distinct domains can be distinguished in the space spanned by the lattice strains, depending on the (relative) signs of $J_1$, $J_2$, and $J_3$. The magnetic phase diagram of strained CrI$_3$, along with the spin configurations which are realized upon lattice deformations, are shown Fig. 3. In Domains 1, and 4, all the exchange couplings feature the same sign, yielding a ferromagnetic or Néel antiferromagnetic ground state, respectively, whereas the other regions exhibit a ferrimagnetic ground state whereby the equality $\text{sgn}(J_1) = \text{sgn}(J_2) = \text{sgn}(J_3)$ does not hold. Specifically, Domains 2 and 6 enclose the zigzag antiferromagnetic state, where two exchange couplings are positive and one is negative. An opposite situation, in which two couplings are negative and only one is positive, is observed in Domains (3) and (5), therefore giving rise to a stripy antiferromagnetic state. It is worth noting that these magnetic phases can be realized within a relatively narrow interval of lattice strain of $\sim 5\%$ in magnitude – provided that the direction along which the deformation occurs is carefully controlled – thereby highlighting a marked interplay between lattice deformations and magnetic exchange couplings in monolayer CrI$_3$. Indeed, the six strain-induced magnetic transitions encompass all the possible magnetically ordered phases which can be realized on a honeycomb lattice.

Importantly, we remark that the phase diagram shown in Fig. 3 displays a singularity located at $\epsilon_a \approx \epsilon_b \approx -5\%$. This corresponds to the point in which the domain boundaries intersect, leading to $J_1 \approx J_2 \approx J_3 \approx 0$. According to the adopted isotropic Heisenberg spin Hamiltonian, such a critical point signals the absence of any magnetic order. The strain-induced quenching of the isotropic exchange couplings may be exploited to single out the otherwise negligible anisotropic exchange couplings in monolayer CrI$_3$ [37]. This is of particular interest in the context of Kitaev physics [11], which emerges when a large Kitaev-to-Heisenberg coupling ratio is achieved. In our previous work [37], we have quantified the Kitaev parameter $K$ in unstrained monolayer CrI$_3$ to be $-0.08$ meV, resulting in a practically negligible $K/J$ ratio of 0.06. Under appropriate strain conditions ($\epsilon_a \approx \epsilon_b \approx -5\%$), however, we suggest that the $K/J$ ratio can be enhanced to a great extent, hence driving monolayer CrI$_3$ in the Kitaev spin-liquid phase, provided that $K$ remains non-vanishing. Indeed, a recent quantum chemistry investigation has demonstrated that compressive biaxial strain substantially increases the magnitude of the ferromagnetic Kitaev coupling in several honeycomb lattices [42].

Finally, we briefly comment on the dependence of the exchange couplings on the crystal structure. According to the rule proposed by Goodenough [43] and Kanamori [44], the sign of the exchange coupling in superexchange-dominated magnetic lattices is mainly governed by the metal-ligand-metal angle. Specifically, depending on whether such an angle is close to either 90° or 180°, a parallel or antiparallel spin orientation has to be expected, respectively. Unstrained CrI$_3$ complies with this rule [22], as the bond angle $\angle \text{Cr-I-Cr} \approx 90^\circ$ is accompanied by $J < 0$. In Fig. 4 we present the dependence of the 459 isotropic exchange couplings calculated in this work on the $\angle \text{Cr-I-Cr}$. We observe that a ferro-
metal-ligand-metal bond angle (\(\angle\text{Cr-I-Cr}\)) in monolayer CrI\(_3\). Dashed lines mark the equilibrium values in unstrained CrI\(_3\). Background shaded in red and blue colors marks positive and negative values of \(J\), respectively, indicating a ferromagnetic and antiferromagnetic interaction between nearest-neighbors Cr\(^{3+}\) ions, respectively.

antiferro-magnetic crossover occurs when the bond angle takes values which are lower than 88\(^\circ\). This is at odds with the Goodenough-Kanamori rule, according to which such a crossover should instead take place when approaching the 180\(^\circ\) limit. Overall, our results indicate that the Goodenough-Kanamori rule is not an appropriate guideline to rationalize the magnetism of monolayer CrI\(_3\) subjected to lattice deformations.

Conclusion. In summary, we have combined model spin Hamiltonians with DFT+U calculations to address the magnetic response of monolayer CrI\(_3\) to in-plane lattice deformations. We revealed that, depending on the magnitude and the direction along which the applied strain is exerted, the ferromagnetic ground state can be driven into either the Néel antiferromagnetic or ferrimagnetic phases, these latter including both stripy and zigzag spin configurations. We identified a critical point emerging at the intersection between the magnetic phase boundaries in the strain space whereby the isotropic Heisenberg exchange couplings vanish, hence quenching any magnetically ordered phase. To conclude, our findings open new viable routes for extensively engineering the magnetism of CrI\(_3\) through lattice strain down to the ultimate limit of thickness miniaturization.

Acknowledgments. M.P. acknowledges Ravi Yadav for fruitful interactions. This work was financially supported by the Swiss National Science Foundation (Grant No. 172543). First-principles calculations were performed at the Swiss National Supercomputing Center (CSCS) under the project s832.

* Electronic address: michele.pizzochero@epfl.ch

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
[2] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proceedings of the National Academy of Sciences of the United States of America 102, 10451 (2005).
[3] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, and J. N. Coleman, Science 340, 1226149 (2013).
[4] N. Mounet, M. Gibertini, P. Schwaller, D. Campi, A. Merkys, A. Marruzzo, T. Solier, I. E. Castelli, A. Cepellotti, G. Pizzi, et al., Nature Nanotechnology 13, 246 (2018).
[5] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Review of Modern Physics 81, 109 (2009).
[6] O. V. Yazyev and A. Kis, Materials Today 18, 20 (2015).
[7] M.-W. Chen, H. Kim, C. Bernard, M. Pizzochero, J. Zaldivar, J. I. Pascual, M. M. Ugeda, O. V. Yazyev, T. Greber, J. Osterwalder, et al., ACS Nano 12, 11161 (2018).
[8] Z. Pedramrazi, C. Herbig, A. Pulkin, S. Tang, M. Phillips, D. Wong, H. Ryu, M. Pizzochero, Y. Chen, F. Wang, et al., Nano Letters 19, 5634 (2019).
[9] A. H. Castro Neto, Physical Review Letters 86, 4382 (2001).
[10] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero, Nature 556, 43 (2018).
[11] Y. Cao, V. Fatemi, A. Demir, S. Fang, S. L. Tomarken, J. Y. Luo, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, E. Kaxiras, et al., Nature 556, 80 (2018).
[12] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, Nature Reviews Materials 2, 17033 (2017).
[13] M. Pizzochero, M. Bonfanti, and R. Martinazzo, Physical Chemistry Chemical Physics 21, 26342 (2019).
[14] K. S. Burch, D. Mandrus, and J.-G. Park, Nature 563, 47 (2018).
[15] C. Gong and X. Zhang, Science 363, 706 (2019).
[16] N. D. Mermin and H. Wagner, Physical Review Letters 17, 1133 (1966).
[17] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, et al., Nature 546, 270 (2017).
[18] M. Gibertini, M. Koperski, A. F. Morpurgo, and K. S. Novoselov, Nature Nanotechnology 14, 408 (2019).
[19] D. Torelli, K. S. Thygesen, and T. Olsen, 2D Materials 6, 045018 (2019).
[20] A. Avsar, A. Ciarrocchi, M. Pizzochero, D. Umucak, O. V. Yazyev, and A. Kis, Nature Nanotechnology 14, 674 (2019).
[21] M. A. McGuire, H. Dixit, V. R. Cooper, and B. C. Sales, Chemistry of Materials 27, 612 (2015).
[22] J. L. Lado and J. Fernández-Rossier, 2D Materials 4, 035002 (2017).
[23] B. Huang, G. Clark, D. R. Klein, D. MacNeill, E. Navarro-Moratalla, K. L. Seyler, N. Wilson, M. A. McGuire, D. H. Cobden, D. Xiao, et al., Nature Nanotechnology 13, 544 (2018).
[24] S. Jiang, L. Li, Z. Wang, K. F. Mak, and J. Shan, Nature Nanotechnology 13, 549 (2018).
[25] T. Song, Z. Fei, M. Yankowitz, Z. Lin, Q. Jiang, K. Hwangbo, Q. Zhang, B. Sun, T. Taniguchi, K. Watanabe, et al., arXiv:1905.10860 (2019).

[26] T. Li, S. Jiang, N. Sivadas, Z. Wang, Y. Xu, D. Weber, J. E. Goldberger, K. Watanabe, T. Taniguchi, C. J. Fennie, et al., arXiv:1905.10905 (2019).

[27] L. Thiel, Z. Wang, M. A. Tschudin, D. Rohner, I. Gutiérrez-Lezama, N. Ubrig, M. Gibertini, E. Gianinni, A. F. Morpurgo, and P. Maletinsky, Science 364, 973 (2019).

[28] N. Sivadas, S. Okamoto, X. Xu, C. J. Fennie, and D. Xiao, Nano Letters 18, 7658 (2018).

[29] N. Ubrig, Z. Wang, J. Teyssier, T. Taniguchi, K. Watanabe, E. Giannini, A. F. Morpurgo, and M. Gibertini, 2D Materials 7, 015007 (2019).

[30] Z. Wang, I. Gutiérrez-Lezama, N. Ubrig, M. Kroner, M. Gibertini, T. Taniguchi, K. Watanabe, A. Imamoglu, E. Giannini, and A. F. Morpurgo, Nature Communications 9, 2516 (2018).

[31] T. Song, X. Cai, M. W.-Y. Tu, X. Zhang, B. Huang, N. P. Wilson, K. L. Seyler, L. Zhu, T. Taniguchi, K. Watanabe, et al., Science 360, 1214 (2018).

[32] D. R. Klein, D. MacNeill, J. L. Lado, D. Soriano, E. Navarro-Moratalla, K. Watanabe, T. Taniguchi, S. Manni, P. Canfield, J. Fernández Rossier, et al., Science 360, 1218 (2018).

[33] G. Kresse and J. Hafner, Physical Review B 47, 558 (1993).

[34] G. Kresse and J. Furthmüller, Physical Review B 54, 11169 (1996).

[35] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters 77, 3865 (1996).

[36] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Physical Review B 57, 1505 (1998).

[37] M. Pizzochero, R. Yadav, and O. V. Yazyev, arXiv:1911.12150 (2019).

[38] D. Torelli and T. Olsen, 2D Materials 6, 015028 (2018).

[39] H. J. Xiang, E. J. Kan, S.-H. Wei, M.-H. Whangbo, and X. G. Gong, Physical Review B 84, 224429 (2011).

[40] H. Xiang, C. Lee, H.-J. Koo, X. Gong, and M.-H. Whangbo, Dalton Transactions 42, 823 (2013).

[41] A. Kitaev, Annals of Physics 321, 2 (2006).

[42] R. Yadav, S. Rachel, L. Hozoi, J. van den Brink, and G. Jackeli, Physical Review B 98, 121107 (2018).

[43] J. B. Goodenough, Journal of Physics and Chemistry of Solids 6, 287 (1958).

[44] J. Kanamori, Journal of Physics and Chemistry of Solids 10, 87 (1959).