A family of high-temperature ferromagnetic monolayers with locked
spin-dichroism-mobility anisotropy: MnNX and CrCX (X = Cl, Br, I; C = S, Se, Te)

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1. Introduction

In the past decades, a plenty of methods, e.g. magnetic or non-magnetic dopants [1–7], vacancies [8,9] and grain boundaries [10,11], have been attempted to introduce long-range ferromagnetic orders in semiconductors. The long range order is, however, limited by the dopant-host hybridization [2,12] that the highest magnetic orders in semiconductors. The long range order is, however, [10,11], have been attempted to introduce long-range ferromagnetic semiconductors. Recently, the re-discovery of monolayer ferromagnets [32,33] and Fe3GeTe2 [34–36], were experimentally prepared or exfoliated, although with limited air-stability. The lack of interlayer magnetic interactions at the monolayer limit enables a variety of interlayer antiferromagnetic (AFM) or weakly FM coupled materials to be under consideration for FM semiconductors, in which the constraint of strong FM interlayer coupling was eliminated. The CrI3 mono- and bi-layers are exactly the case that they show an in-plane FM order and a weak interlayer antiferromagnetic coupling below 50 K [28].

Two-dimensional magnets have received increasing attention since Cr2Ge2Te6 and CrI3 were experimentally exfoliated and measured in 2017. Although layered ferromagnetic metals were demonstrated at room temperature, a layered ferromagnetic semiconductor with high Curie temperature (Tc) is yet to be unveiled. Here, we theoretically predicted a family of high Tc ferromagnetic monolayers, namely MnNX and CrCX (X = Cl, Br and I; C = S, Se and Te). Their Tc values were predicted from over 100 K to near 500 K with Monte Carlo simulations using an anisotropic Heisenberg model. Eight members among them show semiconducting bandgaps varying from roughly 0.23 to 1.85 eV. These semiconducting monolayers also show extremely large anisotropy, i.e. ~104 for effective masses and ~102 for carrier mobilities, along the two in-plane lattice directions of these layers. Additional orbital anisotropy leads to a spin-locked linear dichroism, in different from previously known circular and linear dichroisms in layered materials. Together with the mobility anisotropy, it offers a spin-, dichroism- and mobility-anisotropy locking. These results manifest the potential of this 2D family for both fundamental research and high performance spin-dependent electronic and optoelectronic devices.

Keywords:
- Two-dimensional materials
- First-principles calculation
- Strong mobility anisotropy
- Spin-locked linear dichroism
- High-temperature ferromagnets
- Direct bandgap semiconductor

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the Janus monolayers and does not have inherently existed unbalanced in-plane strain. This form, different from the hexagonal Janus [37], CrI₃ [28], RuCl₃ [40] Cr₂Ge₂Te₆ [29] and Fe₃GeTe₂ [34] monolayers, has two nearest and four second-nearest neighbors, twice the number of previous candidates in hexagonal lattices. Curie temperatures of these monolayers were predicted using Monte Carlo simulations with a third-nearest anisotropic Heisenberg (AH) model. The maximum \( T_c \) values are over 240 K and near 500 K for semiconducting and metallic monolayers, respectively, which are much more superior to CrOCI [41], a lighter member of CrCXs with our predicted \( T_c \) of 16 K. The bandgaps of these materials are primarily determined by the chalcogen atom, varying from nearly 2 to 0 eV, while eight of them are FM semiconductors and another four of them are FM metals with \( T_c \) up to 492 K. In addition, this MnNX and CrCX family does not show strong structural anisotropy, but the electronic structures, carrier mobility and their resulting optical absorption are highly anisotropic and are locked together. All these results may boost experimental studies on this novel family of 2D magnetic monolayers with extraordinarily high \( T_c \) values.

2. Methods

2.1. DFT calculations

Our density functional theory (DFT) calculations were performed using the generalized gradient approximation for the exchange-correlation potential, the projector augmented wave method [42,43] and a plane-wave basis set as implemented in the Vienna ab-initio simulation package (VASP) [44,45] and Quantum Espresso (QE) [46]. Dispersion correction was made at the van der Waals density functional (vdW-DF) level [47–49], with the optB86b functional for the exchange potential, which was proved to be accurate in describing the structural properties of layered materials [23,50–54] and was adopted for structure related calculations. For energy comparisons among different magnetic configurations, we used either the PBE [55] or hybrid (HSE06) functional [56,57], with the inclusion of spin–orbit coupling (SOC), based on the vdW-DF revealed structures. Density functional perturbation theory [58] was employed to calculate phonon dispersion (QE) and vibrational frequencies at the Gamma point (VASP). In VASP calculations, the kinetic energy cut-off for the plane-wave basis set was set to 700 eV for geometric and 400 eV for electronic structure calculations by the HSE06 functional. A \( \Gamma \)-mesh of \( 10 \times 14 \times 1 \) was adopted to sample the first Brillouin zone of the conventional unit cell of monolayer CrCXs and MnNXs. The phonon dispersion was obtained by Fourier interpolation of the dynamical matrices calculated using an \( 18 \times 20 \times 1 \) \( k \)-mesh and a \( 6 \times 4 \times 1 \) \( q \)-mesh with a plane-wave energy cutoff of 50 Ry. On-site Coulomb interactions to the Cd and Mn d orbitals are considered with \( U \) and \( J \) values ranging from 3.89 – 4.40 eV and 0.80 – 1.25 eV, respectively, as revealed by a linear response method [59] and listed in the Supplementary Table S1. These values are comparable to the values adopted in modeling CrI₃ [60,61] and CrS₂ [37]. The HSE06 functional already considers the exact exchange energy, the \( U \) and \( J \) correction does not apply to HSE06 calculations. The influences of different functionals and \( U, J \) values were also discussed in the Supplementary Figs. S1, S2. More calculation details were provided in the Supplementary Materials.

2.2. Curie temperature prediction

Spin-exchange coupling (SEC) parameters were extracted based on a third-nearest Heisenberg model,

\[
H = H_0 + J_1 \sum \langle S_i \cdot S_j \rangle + J_2 \sum \langle S_i \cdot S_j \rangle + J_3 \sum \langle S_i \cdot S_j \rangle.
\]

Here, \( J_1, J_2 \) and \( J_3 \) represent the first-\( k \)-, second-\( k \)- and third-\( k \)-nearest couplings, respectively, as illustrated in Fig. 1a. We derived the spin exchange parameters by the total energy differences of the four magnetic configurations shown in the Supplementary Fig. S3. The magnetic energy contributions of these magnetic configurations in each magnetic unit cell write as

\[
E_{\text{HM}} = \frac{N^2}{4} \times \frac{1}{2} \{2J_1 + 4J_2 + 2J_3\}.
\]
\[ E_{\text{APM1}} = \frac{N^2}{4} \times \frac{1}{2} (2J_1 - 4J_2 + 2J_3), \]
\[ E_{\text{APM2}} = \frac{N^2}{4} \times \frac{1}{2} (2J_1 - 2J_1), \]
\[ E_{\text{APM3}} = \frac{N^2}{4} \times \frac{1}{2} (-2J_1 + 2J_3), \]

where \( N \) represents the unpaired spins on each Cr atom, which is chosen as 3 in our calculations.

Metropolis Monte Carlo simulations were carried out to predict Curie temperatures. A \( J_1-J_2-J_3 \) model was used to do the Metropolis Monte Carlo simulations, in which two nearest, and two next-nearest Cr (Mn) atoms were considered. This model is more advanced than the one only contains four nearest sites in a square lattice, as used in a previous work [41]. A 50 x 50 lattice was used for all simulations and each lattice point include 2 Cr (Mn) atoms. Simulation results revealed with the Ising model show that the corresponding lattice constant along the transport direction was used for all simulations and each lattice point include 2 Cr atoms. We denote the SEC parameter of this interaction as \( C_{\text{film}} \), which is estimated by

\[ C_{\text{film}} = \frac{\pi e^2}{\sqrt{2} \hbar^2 k_B T} \left[ \frac{1}{2} \sum_{n} \left\{ \frac{\pi^2}{2} [1 - \text{erf}(\Omega(n))] + \Omega(n) e^{-D_{\text{neff}}(n)} \right\} \right] \]

where

\[ \Omega(n) = \frac{\sqrt{n^2 \pi^2 h^2}}{2 m W_{\text{eff}} k_B T} \]

The erf() represents an error function and the summation over integer \( n \) is due to quantum confinement along the \( z \)-direction. Effective thickness of the film (\( W_{\text{eff}} \)) is expressed by

\[ W_{\text{eff}} = \int_{-\infty}^{+\infty} P(z) dz = \sum_{n} \frac{\rho^2(z)}{N \Delta z} + \frac{\rho(z)}{N \Delta z}. \]

Here, \( P(z) \) is the electron probability density along the \( z \)-direction. We divided the space along the \( x \) direction into \( n \) parts by \( \Delta z \). Variable \( \rho^2(z) \) is the sum of the number of electrons \( n^2 \) region along the \( z \)-direction. Here, \( N \) is the total number of valence electrons in the film, \( j \) and \( f \) represent equilibrium and deformed films, respectively. The electronic structures in carrier mobility elimination are all calculated with the HSE06 functional. We implemented these carrier mobility estimation methods in a computer package, “Remmin Mobility Calculator” (ReMoC). Please visit http://sim.phys.ruc.edu.cn/tools/ for details.

2.4. Optical absorption spectra and conductivity calculation

The absorption spectra were calculated from the dielectric function using expression [23,51] \( A(\omega) = \sigma(\omega) \Delta \omega \), where \( \sigma(\omega) = \text{Im} \epsilon_{\omega} / \text{Re} \epsilon_{\omega} \) is the absorption coefficient, \( n = \sqrt{\text{Re} \epsilon_{\omega}^2 + \text{Im} \epsilon_{\omega}^2} \) is the index of refraction, \( \text{Re} \epsilon_{\omega} \) and \( \text{Im} \epsilon_{\omega} \) are the real and imaginary parts of the dielectric function [64], respectively. \( \omega \) is the light frequency, \( c \) is the speed of light in vacuum and \( \Delta \omega \) represents the unit-cell size in the \( z \) direction. The conductivity tensor was calculated from the imaginary parts of the dielectric function as well, \( \sigma_{ij} = \frac{e^2}{4 \pi} \text{Im} \epsilon_{\omega} \), where \( i, j \) represent the directions \( x, y \) and \( z \). The electronic structures were obtained from the results unveiled using the PBE functional and the \( k \)-mesh was increased to \( 28 \times 32 \times 1 \) in calculating dielectric functions. Enough conduction bands were considered and exciton effects were not considered in the optical properties calculations. Because the dielectric function is a tensor, the absorption spectra along the \( x, y \) and \( z \) directions were obtained separately. The energies of incident light of the horizontal axis in absorption spectra were shifted by the differences of bandgaps between the PBE + U-J (-SOC) and HSE06 (-SOC) results.

3. Results and discussion

Figs. 1a and 1b show a top- and a perspective-views of the fully relaxed atomic structure of CrSCI in the CrCXs form while its other less stable forms, e.g. JT-Janus, are available in the Supplementary Fig. S5 and Table S2. Phonon dispersion spectra are also available in the Supplementary Fig. S6 indicating the stability of the CrCXs form. We used CrSCI as an example that it is comprised of perpendicularly oriented Cr-S/Cl rhomboid chains along \( y \) and distorted Cr-S rectangular chains along \( x \). The shortest Cr-Cr distance of 3.44 Å was found in the rhomboid chains, being bridged by an S and a Cl atoms. We denote the SEC parameter of this interaction as \( J_1 \) (red arrow). The second-nearest Cr-Cr interaction is bridged by two S atoms with a distance of 3.61 Å and a Cr-S-Cr angle of 91.5°, the SEC parameter of which is denoted as \( J_2 \) (green arrow). In addition, SEC parameter \( J_3 \) represents a nearly linear Cr-S-Cr
interaction (black arrow). Detailed structural information of CrXs and MnNXs can be found in the Supplementary Table S3. The derivation details of these three parameters are available in the Section 2.

The FM state in all CrXs and MnNXs is energetically more stable than other magnetic configurations regardless which functional is used and whether \( U \) or \( J \) is added, as shown in the Supplementary Fig. S3. By comparing their total energies, we derived \( J_1 = 0.90 \text{ meV}, J_2 = 2.98 \text{ meV} \) and \( J_3 = 1.26 \text{ meV} \) for CrSCl. Exact SE parameters and predicted Curie temperatures are listed in Table 1. Here, we used a classical magnetic moment \( S = 3/2 \) according to the DFT value of roughly \( 3 \mu_B \) per Cr atom. Although \( J_2 \) represents a 0.17 A longer distance than \( J_1 \), the coupling strength of \( J_2 \) is triple that of \( J_1 \). Replacement of Cl with Br or I substantially enlarges \( J_1 \) and slightly enlarges \( J_2 \) and \( J_3 \) in the S/Se-series, leading to nearly comparable \( J_1 \) and \( J_2 \) for the \( \ell \)-series monolayers. The Series is fairly different from the S/Se-series that the comparable or nearly comparable coupling between two adjacent Cr cations, which is reinforced by kinetic energy gains [65]. Therefore, the line \( J_1 \) gives rise to FM coupling in the CrS/Se- and MnN-series. In the Te-series, the \( \ell_2 \) orbitals become partially occupied and dominate the bandstructures around the Fermi level thus leading to a strong itinerant FM in the monolayer limit; this explains the fairly large FM \( J_1 \) in CrTeCl. The occupation of the antibonding conduction bands gradually reduces from CrTeCl to CrTeI (the Supplementary Figs. S9g–S9h). Therefore, the super-exchange FM coupling is eventually overcome the FM coupling, leading to a small AFM \( J_2 \) for CrTeCl.

Monte Carlo simulations were performed with an anisotropic Heisenberg (AH) model and a three-nearest Ising model (see the Supplementary Fig. S4 and Methods for details). Here, the AH model considers both on-site and spin-spin anisotropies, which play a key role when the thickness of a layered materials reduces to its 2D limit. The on-site anisotropy is primarily a result of spin–orbit coupling (SOC). For spin-spin interactions, we used a simplified model where the interactions along two hard magnetization axes were averaged. Table 1 shows the single-ion magnetic anisotropy energies (MAEs) of all considered CrXs/MnNXs. The easy axes of CrSCl, CrTeBr, CrTeI, MnNCl and MnNBr were found parallel to the z direction. This group contains direct and indirect bandgap semiconductor and metals with both highly dispersive and nearly flat bands around the Fermi Level. Table 1 also shows the RSWT predicted \( T_c \) values. The RSWT simulations give nearly identical \( T_c \) values to the MC results for CrBr and CrSe. For other layers, the RSWT results show substantially higher \( T_c \) values compared with MC calculations, except for CrTeI where RSWT predicts a value of 86 K while MC gives a value of 139 K. We found the use of HSE leads to larger FM exchange parameters and reinforced virtual hopping for the spin up electrons of the Cr \( \ell_2 \) orbitals; this strongly favors FM coupling and is consistent with the Hund’s rule. This picture also explains the always slightly stronger \( J_2 \) than \( J_1 \) that the Cr-S-Cr coupling (Fig. 1g and h), having a 2/3 \( \ell \) reduced number of filling electrons, offers an additional partial channel for FM coupling to the Cr-Cl-Cr coupling. It also suggests that a reduced number of the filling spin-down electrons of the bridging atoms may open more hopping channels and thus enlarge the value of \( T_c \), which was elucidated by the 492 K \( T_c \) of the MnNI monolayer (see Table 1).

In a local moment picture, the linear Cr-S-Cr coupling (\( J_2 \)) usually favors AFM. Here, the hybridization of chalcogen \( p_z \) with Cr \( d_{3z} \) orbitals form delocalized bonding and antibonding states (see Fig. 2 and Supplementary Fig. S8). The bonding state is occupied and itinerant electrons of this state dominate and mediate a FM coupling between two adjacent Cr cations, which is reinforced by kinetic energy gains [65]. Therefore, the line \( J_1 \) gives rise to FM coupling in the CrS/Se- and MnN-series. In the Te-series, the Cr \( \ell_2 \) orbitals become partially occupied and dominate the bandstructures around the Fermi level thus leading to a strong itinerant FM in the monolayer limit; this explains the fairly large FM \( J_1 \) in CrTeCl. The occupation of the antibonding conduction bands gradually reduces from CrTeCl to CrTeI (the Supplementary Figs. S9g–S9h). Therefore, the super-exchange FM coupling is eventually overcome the FM coupling, leading to a small AFM \( J_2 \) for CrTeCl.

The magnetic properties of the 12 monolayers, including the intralayer spin-exchange coupling parameters \( J_1, J_2, J_3 \), anisotropic spin–spin exchange parameter \( \lambda \) and easy axis single ion anisotropy \( D \), easy axis direction, Curie temperatures predicted using Ising model, anisotropic Heisenberg (AH) model and RSWT, bandgaps without on site Coulomb \( U \) and exchange \( J \) (w/o \( U/J \)) are summarized in Table 1. The on-site anisotropy is primarily a result of spin–orbit coupling (SOC). For spin-spin interactions, we used a simplified model where the interactions along two hard magnetization axes were averaged. Table 1 shows the single-ion magnetic anisotropy energies (MAEs) of all considered CrXs/MnNXs. The easy axes of CrSCl, CrTeBr, CrTeI, MnNCl and MnNBr were found parallel to the z direction. This group contains direct and indirect bandgap semiconductor and metals with both highly dispersive and nearly flat bands around the Fermi Level. Table 1 also shows the RSWT predicted \( T_c \) values. The RSWT simulations give nearly identical \( T_c \) values to the MC results for CrBr and CrSe. For other layers, the RSWT results show substantially higher \( T_c \) values compared with MC calculations, except for CrTeI where RSWT predicts a value of 86 K while MC gives a value of 139 K. We found the use of HSE leads to larger FM exchange parameters and reinforced virtual hopping for the spin up electrons of the Cr \( \ell_2 \) orbitals; this strongly favors FM coupling and is consistent with the Hund’s rule. This picture also explains the always slightly stronger \( J_2 \) than \( J_1 \) that the Cr-S-Cr coupling (Fig. 1g and h), having a 2/3 \( \ell \) reduced number of filling electrons, offers an additional partial channel for FM coupling to the Cr-Cl-Cr coupling. It also suggests that a reduced number of the filling spin-down electrons of the bridging atoms may open more hopping channels and thus enlarge the value of \( T_c \), which was elucidated by the 492 K \( T_c \) of the MnNI monolayer (see Table 1).

Table 1

| CrScI | J1 (meV) | J2 (meV) | J3 (meV) | Easy axis (K) | Tc (K) | Bandgap (eV) |
|-------|----------|----------|----------|--------------|--------|-------------|
| CrSBr | 1.66     | 3.09     | 1.52     | Ising        | 2.98   | 1.26        |
| CrSI  | 2.49     | 3.07     | 1.69     | RSWT         | 1.01   | 6.00        |
| CrSeCl| 1.34     | 3.52     | 0.76     | HSE/SOC      | 0.02   | 0.01        |
| CrSeBr| 2.09     | 3.52     | 0.76     | PBE+U/J       | 0.01   | 0.02        |
| CrSel | 3.12     | 3.67     | 1.18     | N/A          | 0.01   | 0.01        |
| CrTecI| 1.45     | 3.67     | 1.18     | N/A          | 0.01   | 0.01        |
| CrTecI| 2.91     | 3.67     | 1.18     | N/A          | 0.01   | 0.01        |
| CrTel | 4.56     | 4.13     | 1.90     | N/A          | 0.01   | 0.01        |
| MnNCl | 5.53     | 4.13     | 3.35     | N/A          | 0.01   | 0.01        |
| MnNBr | 5.66     | 3.68     | 5.41     | N/A          | 0.01   | 0.01        |
| MnI  | 14.15   | 3.71     | 8.39     | N/A          | 0.01   | 0.01        |
| CrCl  | 1.62     | 3.68     | 5.41     | N/A          | 0.01   | 0.01        |
| CrOCI| -0.02    | 0.07     | 1.46     | N/A          | 0.01   | 0.01        |

* Stands for metal.
spin–spin and on-site FM couplings for magnetic anisotropy (the Supplementary Table S4); this thus results in higher transition temperatures. In light of this, our predicted transition temperatures using MC are rather conservative and the measured \( T_c \) values might be even larger than our predicted values.

In terms of metallic layers, MnNI has the highest \( T_c \) of 492 K and the lowest one of 139 K was found in CrTeBr. The bandgap of MnNbR is less conclusive that the HSE and PBE + U-J calculations suggest different results. These metallic FM monolayers, serving as FM metals in transitional magnetic devices, offer flexibility and largely reduced thickness in 2D magnetic devices. The \( T_c \) values of semiconducting monolayers were lower than those of metallic layers. In particular, the highest \( T_c \) of 238 K (600 K with the Ising Model and 376 K with RSWT) was found in MnNCl (Table 1) with the easy axis along \( z \) while the lowest \( T_c \) is 108 K for CrSeCl (AH model value) or 124 K for CrSeBr (RSWT value). These values are roughly five times and twice the measured value of 45 K [28] and this-work predicted value of 43 K for CrI\(_3\). Here, a \( T_c \) over 200 K approaches the room temperature and is subject to further substrate induced enhancement, as found in the MnSe\(_2\) [38,39] and Cr\(_2\)Ge\(_2\)Te\(_6\) [29] cases, and the doping enhancement as realized in Fe\(_x\)GeTe\(_2\) [34–36].

Table 1 suggests that the S- and Se-series, MnNCl and MnNbR (inconclusive) are semiconductors with varying bandgaps from 1.85 to 0.23 eV (HSE–SOC)/1.52 to 0.33 (PBE + U-J–SOC), among which CrSeCl is of a near direct-bandgap (direct- and indirect-bandgaps differ by 0.5 meV) and CrSeBr also offers a small difference of 6 meV. According to a private communication with Yu Ye from Peking University, PBE + U-J–SOC result, with our linear–response derived \( U \) and \( J \) values, for the bandgap of CrOCl layers appears to be closer to the experimental value than that of HSE. In light of this, our \( U \) and \( J \) values should be very close to the set fitted using bandgaps. However, we cannot rule out the role of defects in the bandgap measurements, we thus used the HSE values in our following discussion on electronic and optical properties, which are independent from \( U \) and/or \( J \) values and were found comparable with experimental values in 2D layers. Fig. 2a depicts the bandstructure of CrSeBr because of its moderate bandgap (0.89 eV, in the infrared range), high predicted \( T_c \) and a representative bandstructure of CrCXs. Bandstructures of other monolayers calculated with different functionals were shown in the Supplementary Figs. S9–S12.

Strong anisotropy, nearly linear dispersion and a roughly flat band are more clearly shown in a simplified bandstructure of CrSeBr (Fig. 2b), which contains two spin-up CBs, two spin-down CBs, and two spin-down VBs, respectively. The spin-up CB2 (pink) is comprised of \( \text{Cr}d_{x^2-r^2} \) and \( \text{Se/Br}p_z \) orbitals (Supplementary Fig. S7b–d), which exceptionally form extended Cr-Se-Cr channel states along the \( x \) direction (Fig. 3c) but highly localized along the \( y \) direction (Fig. 3d), giving rise to a quasi-1D electronic state in a 2D orthogonal lattice. Note that we define the \( d_p \) or \( p_x \) direction along the \( x \) direction and \( p_x, p_y \) and \( d_{x^2-y^2} \) along the Cr–X (\( X = \text{Cl}, \text{Br} \) and I) bonding directions (see Supplementary Fig. S7a). This quasi-1D state offers a small effective mass of 0.06 me\(_0\) along G–X but a rather large effective mass of 1.18 me\(_0\) along G–Y, leading to the mobility \((6.10 \times 10^3 \, \text{cm}^2/\text{V} \cdot \text{s})\) for spin-up CB2 along \( x \) 68 times that along \( y \) \((0.09 \times 10^3 \, \text{cm}^2/\text{V} \cdot \text{s})\) (Supplementary Table S5). State spin-up CB1 (red) shares the same feature but its wavefunction is more localized along either \( x \) or \( y \) (Supplementary Fig. S8f and 8h), consistent with the larger effective masses of 0.40me\(_0\) and 7.1me\(_0\) respectively. The position of the spin-down component of CB sites over 1 eV higher than the spin-up CBM, while it also slightly depends on \( U \) values in PBE + U-J calculations (see the Supplementary Fig. S1). Spin-up VBs are rather interesting that the anisotropy of effective masses was found in either spin-up–VB1 (red) and -VB2 (pink), both of which are composed of Se/Br \( p_z \) and Cr \( d_{x^2} \) orbitals (Supplementary Fig. S7e–g). The spin-up–VB1 appears a nearly mirror analogue to that of spin-up–CB1 with respect to the gap around the G point, namely \( m_x = 0.06 \, m_0 \) and \( m_y = 1.30 \, m_0 \) (Supplementary Table S5), which shares the same mechanism of the CB case (Fig. 2e and f). The mass anisotropy of spin-up–VB2, i.e. 0.53me\(_0\) (\( y \)) and 2.66me\(_0\) (\( x \)), is reversal to spin-up–VB1 along the \( x \) and \( y \) directions. A similar behavior was found for those two spin-down VBs (blue and green) with less pronounced anisotropy (Supplementary Fig. S8 and Table S5). In CrSeBr, spin-down–VB1 serves as the highest VB, which may change in other CrCXs, e.g. in CrSeCl, where the monolayer becomes a nearly direct-bandgap half–semiconductor (Fig. 3 and Supplementary Fig. S9).

The giant effective masses found along either direction for these bands imply likely strong correlation of VBs or doped CBs, which is, most likely, more pronounced in CrTeBr (Fig. 2g). It shows a nearly flat-band along G–Y near \( E_F \), which is even flatter and closer to \( E_F \) with the inclusion of SOC (Supplementary Fig. S10i). Such a flat band mixed with two spin components might suggest emerging physical phenomena with strong correlation. In terms of MnNXs, they contain band crossings along G–Y with likely band inversions. The semiconducting MnNCl is a result of interaction induced gap–opening (Supplementary Fig. S10e). Other semiconducting layers, except MnNbR, show similar anisotropic features and share the same mechanism of anisotropy (Supplementary Fig. S9). This general spin–dependent mobility anisotropy suggests spin-up electron carriers moving much faster along the \( x \) direction than along the \( y \) direction and the reversal for hole carriers. If an off-axis in-plane electric field is established, spin accumulation might be observed in the more localized \( y \) direction, which may potentially be used in transferring spin torques. All band structures and detailed energy levels of VBM and CBM of CrCXs and MnNXs are available in Fig. 3 and Supplementary Fig. S9.
Figs. 3 a and b plot the positions of CBMs and VBMs calculated without and with SOC, respectively. The energy levels of CBM at G and Y have tiny differences below 0.15 eV and an 1% in-plane strain can induce a transition between indirect and direct bandgap. It is exceptional that the energy positions of the CBMs for all semi-conducting CrCXs and MnNCl monolayers are rather deep, from −5.17 to −6.57 eV, suggesting the anisotropy of CBs could be feasibly utilized in practical devices. The band alignments indicate the possibility of constructing type-I (e.g. CrSeI/CrSI), type-II (e.g. CrSeCl/CrSeI) and type-III (e.g. CrSel/MnNCl) heterostructures. The type-III heterostructures are of particular interest that they may be employed to build Dirac-source devices with the sub-threshold swing smaller than 60 meV/decade [66].

Fig. 4 a shows a sketch-map of the bands around the G point of the CrSeBr monolayer. The CB energies at G and Y are nearly degenerated. Since the halogen atoms strongly affect the interactions along the y direction, heavier halogen atoms lead to more extended wavefunctions and thus show stronger band dispersions; this gives rise to flatter CBs and large splitting of spin-up-CB1 and -CB2 in CrSeC than those in CrSI (Supplementary Figs. S9 and S11). An exchange-induced enhancement of CB splitting at G was found when comparing results using the hybrid HSE06 functional with those of PBE + U-J (Supplementary Figs. S9 and S11). In addition, the inclusion of spin-spin exchange J or on-site U term in HSE calculations, as a result of overestimated FM exchange, enlarges the splitting of the two CB at the G point (Supplementary Fig. S2), resulting in a lower energy of CB at G than Y, which, we believe, is an artefact in the groundstate but might be valid under certain external fields. These results highlight the importance of exchange interactions in obtaining direct bandgap at the G point in CrCXs.

The optical conductivity [67] (Fig. 4 c) and the light absorbance [51,64] (Fig. 4d), explicitly show a spin-selective linear dichroism. In particular, only the up-spin component has absorbance in an energy range from 1.05 eV (transition from spin-up-VB1 to -CB1) to 2.27 eV while the down-spin component becomes excitable by light with even higher energies; this allows to generate pure spin-polarized photo-current using light linearly polarized in certain directions. In this range, light linearly polarized along the x direction has much higher absorbance (4.26% per layer at 2.00 eV) than that along the y direction (0.31% per layer at 2.00 eV), showing a spin-dichroism locking. This spin-locked linear dichroism is thus substantially different common spin-dependent optical excitations by left- or right-hand circularly polarized light in magnetic semiconductors and the circular dichroism led by valley physics in transitional metal dichalcogenides (TMDs) [68–74], as well as the linear dichroism induced by wavefunction asymmetry [20].

Although the absorption of CrSeBr initializes in the infrared range, this energy range is tunable to lower or higher energy range by substituting S or Cl with Se, Br or I atoms since it is highly relevant with the bandgaps. In the presence of Se, Br and I atoms, strong SOC eliminates symmetry forbidden rules of different spin
components, which shifts the absorption edge of CrSeBr from 1.05 to 0.89 eV (Fig. 4d) since the both spin channels could be excited to the CB states. Therefore, we infer CrSel (with a gap of 0.55 eV, equivalently 2.255 nm) may have better absorbance among these CrCXs. In addition, this dichroism suggests CrCX monolayers may be used to construct spin-optical selectors. In particular, pure spin-up photo-electrons, moving much faster in the $x$ direction, were excitable only by linearly polarized lights along the same direction while the excitations of spin down electrons are forbidden; this might shed light on generating pure spin-polarized photo-current by only linear polarized incident light.

### 4. Conclusion

In summary, we discovered a family of ferromagnetic semiconducting and metallic monolayers, namely CrCXs and MnNXs, which share the same structure. Their $T_c, values are predicted up to 492 K with strong intra-layer and weak inter-layer magnetic couplings. Both localized and itinerant electrons contribute to the formation of the FM ordering. The strengths of these two competing coupling mechanisms are tunable by element substitutions. A reduced number of filling electrons to the chalcogen and halogen atoms was found a key factor for stronger FM couplings, which enlightens a strategy for searching other high $T_c$ FM monolayers. Given over 100 K $T_c$ for CrSCI, it turns out the strong SOC is not paramount in obtaining high $T_c$ in 2D layers [75] while spin-spin interaction or orbital anisotropy does offer magnetic anisotropy, which opens an avenue for searching magnetic monolayers. Additional high $T_c$ indicators include greater local magnetic moment (usually three $t_{2g}$ electrons) and larger neighboring numbers.

Strong anisotropy is a key characteristic of this monolayer family. The spin-up VBs and CBs of semiconducting CrCXs show highly anisotropic electron and hole effective masses and mobilities that the mass ratio is up to 22 and the mobility ratios are near 670 between the $x$ and $y$ directions. Strongly dispersive S/Se $p_z$ and Cr $d_{z^2}$ states along $x$ and nearly flat-band Cr $d_{xy}$ states along $y$ were exceptionally found in CrCXs, resulting in the coexistence of nearly free-electron and highly correlated states. Here, the chalcogen atoms do not include O since the O-Cr polarization is much stronger than those in other bonds leading to more localized states. In addition to the previously revealed purely circular and linear dichroisms found in MoS$_2$ [68,69], BP [23,76,77] and other 2D materials [70–74], we found a spin-selective (locked) linear dichroism in 2D CrCX layers, showing a spin-dichroism–mobility locking effect. Only the spin-up component could be excited with linearly polarized light along the $x$ direction and the excited spin-up electrons moving much faster along the same direction. Note that the energy difference between interlayer FM and AFM configurations for each CrCX or MnNX is roughly 1 meV/\text{Cr} or 1 meV/Mn (not shown here) and the bulk form of CrSBr was experimentally synthesized [78]. These facts suggest the feasibility of experimental investigations and manipulations of the CrCXs and MnNXs monolayers. All these results compellingly indicate that the CrCXs/MnNXs family is a novel interesting category of FM monolayers for either spintronics or optoelectronics, which is experimentally accessible and of high potential in applications.

### Conflict of interest

The authors declare that they have no conflict of interest.

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### Author contributions

Wei Ji designed the research. Cong Wang performed the calculations of the geometry structures, electronic structures and magnetic coupling parameters. Xieyu Zhou performed Metropolis Monte Carlo simulations and the calculations of the optical properties. Linwei Zhou coded program “Renmin Mobility Calculator” (ReMoC) for carrier mobility calculations. Ning-Hua Tong carried out the renormalized spin wave theory (RSWT) study of two-dimensional anisotropic Heisenberg model (2DAHM) on square lattice and on honeycomb lattice. Cong Wang, Xieyu Zhou, Ning-Hua Tong, Zhong-Yi Lu and Wei Ji analyzed the results and wrote the manuscript. All authors commented on the manuscript.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.02.011.

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