

Supplementary Information:

Auxetic two-dimensional transition metal selenides and halides

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Supplementary Methods

Computational methods for mechanical properties. We use the formula $E_S = a_1 \varepsilon_x^2 + a_2 \varepsilon_y^2 + a_3 \varepsilon_x \varepsilon_y$ to calculate the elastic properties of our studied compounds under small strain (< 2% strain). Here E_S , ε_x , and ε_y are the energy deviation from the equilibrium state, strains along x -direction and y -direction, respectively. The 2D and 3D elastic modulus are calculated by $Y_{2D} = [2a_1 - a_3^2/2a_1]/A_0$, and $Y_{3D} = Y_{2D}/h$, where A_0 and h are the area of the unit cell, and the height of 2D sheet, respectively. For simplicity we adopt a similar method that was used in a recent work to calculate the height, $h = h_0 + 0.8 \text{ \AA}$, where h_0 is the distance between the top and bottom X atoms, and $0.8 \text{ \AA}$ is the estimated effective decay length of electron density into the vacuum¹.

We adopt the following equation to fit the curve of energy under strain:

$$E_S = a_1(\varepsilon_x - \Delta_x)^2 + a_2(\varepsilon_y - \Delta_y)^2 + a_3(\varepsilon_x - \Delta_x)(\varepsilon_y - \Delta_y). \quad (1)$$

where Δ_x and Δ_y are used to consider the uncertainty in our optimized lattice constants. Note that $\Delta_x = \Delta_y$ due to the 4-fold rotational symmetry.

Under an isotropic strain:

$$E_{iso} - E_0 = (a_1 + a_2 + a_3)(\varepsilon_x - \Delta_x)^2 \quad (2)$$

$$\begin{aligned} E_{iso} &= (a_1 + a_2 + a_3)(\varepsilon_x - \Delta_x)^2 + E_0 \\ &= (2a_1 + a_3)(\varepsilon_x - \Delta_x)^2 + E_0 \\ &= (2a_1 + a_3)\varepsilon_x^2 - (4a_1 + 2a_3)\Delta_x \varepsilon_x + const \end{aligned} \quad (3)$$

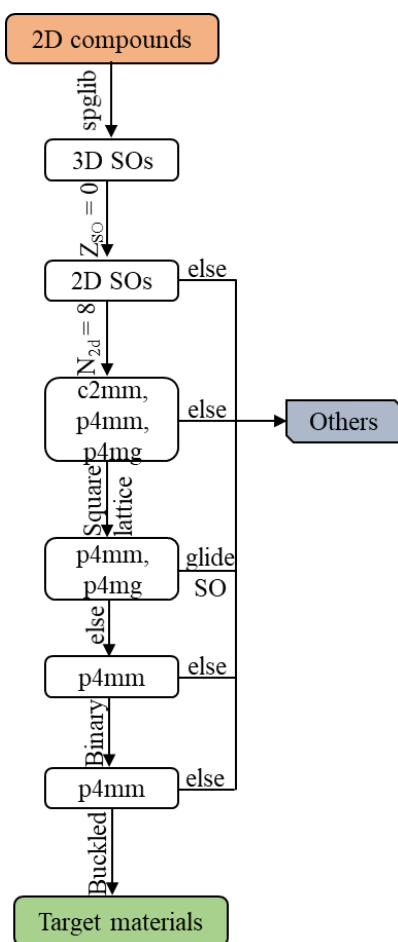
Under a uniaxial strain along x -direction:

$$E_{aniso} - E_0 = a_1(\varepsilon_x - \Delta_x)^2 + a_2(0 - \Delta_x)^2 + a_3(\varepsilon_x - \Delta_x)(0 - \Delta_x) \quad (4)$$

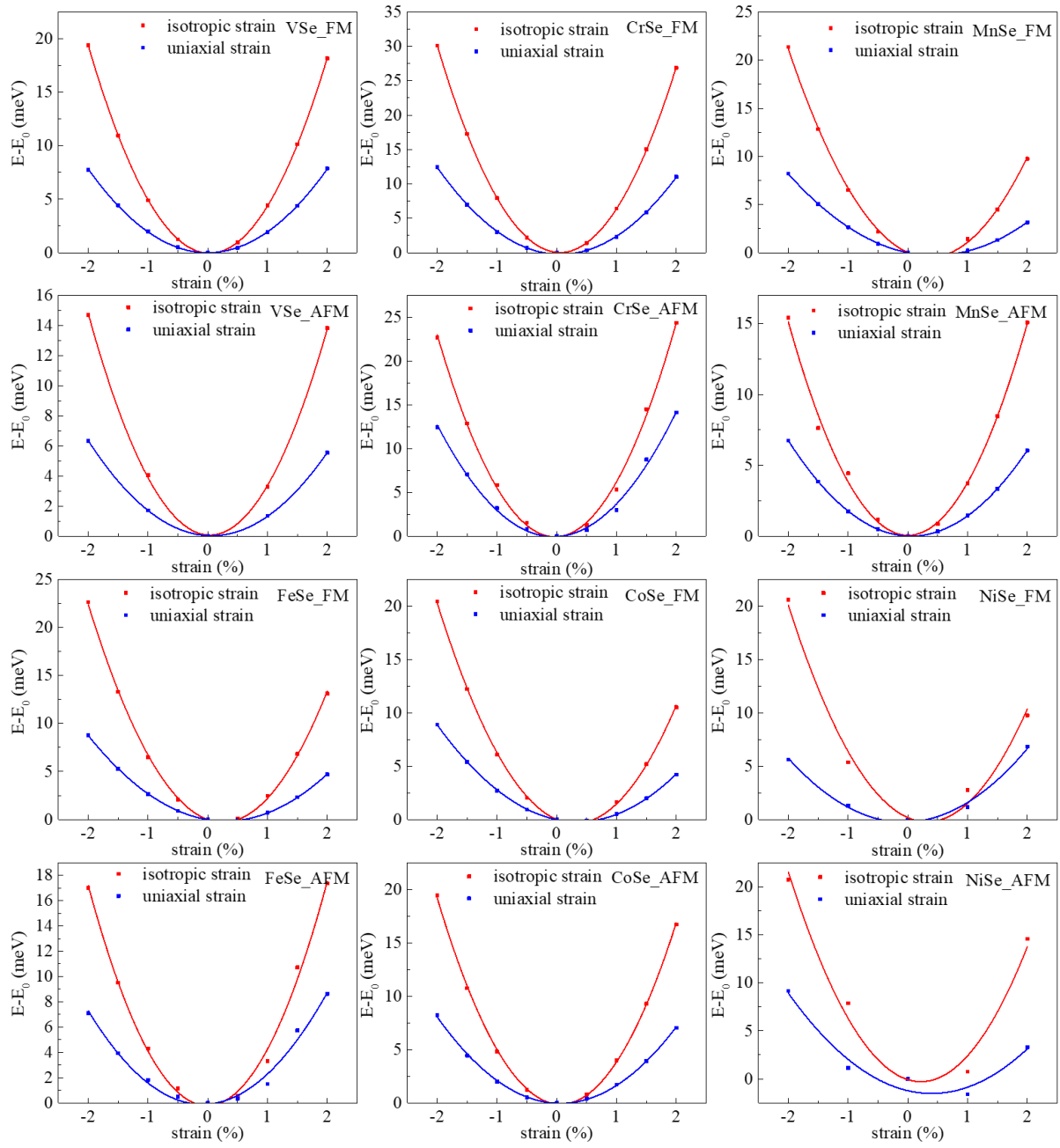
$$E_{aniso} = a_1 \varepsilon_x^2 - (2a_1 + a_3)\Delta_x \varepsilon_x + const \quad (5)$$

Computational methods for material stability. To verify the dynamical stability of monolayer transition metal selenides and halides, phonon dispersion analysis was performed by using the density functional perturbation theory method as implemented in the Phonopy code², interfaced with VASP. In phonon calculations, GGA+U³ along with the projector-augmented wave (PAW) potentials were employed, with a convergence criterion of 10^{-8} eV for energy. The U values of transition metal atoms are outlined in Wang et al.'s work⁴. The energy cutoff, k-point mesh, and

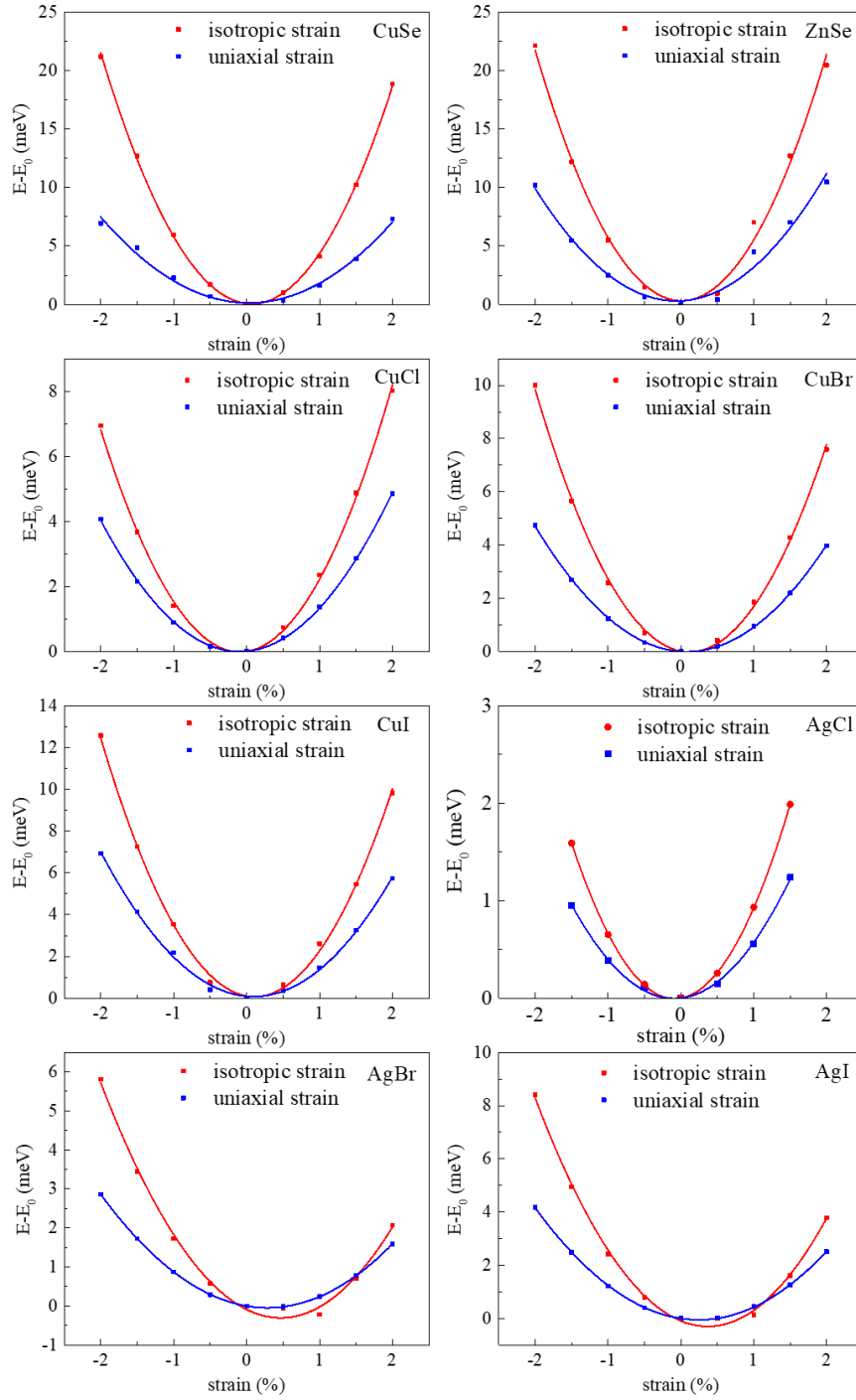
vacuum length are all the same as those in mechanical properties calculations. For the *ab initio* molecular dynamics (MD) simulations^{5, 6}, a canonical (NVT) ensemble was used. Time interval between each step is 0.25 fs.



Supplementary Figure 1. Plane group symmetry screening pipeline that generates the studied MX compounds in this work. SO means symmetry operation, Z_{2d} is the matrix element of symmetry operation along z-direction, N_{2d} is the total number of 2D symmetry operations. The symmetry operations are obtained by using the open-source spglib code⁷. The representations of 2D plane groups are described in the Bilbao Crystallographic Server⁸. The plane group symmetry based material screening pipeline used in this work is represented in the above figure. By using this screening workflow, 70 compounds in $p4mm$ plane group are identified from our 2D material database, therein 24 out of them are binary compounds with buckled structures and can be classified into four families according to geometric structures. To investigate the general correlations among geometric structures, electronic structures, and mechanical properties, we chose the largest MX family which contains most of our studied compounds. Additional d^9 - d^{10} compounds in the family, including CuSe, CuCl, AgCl, and AgBr, are created by elemental substitution.



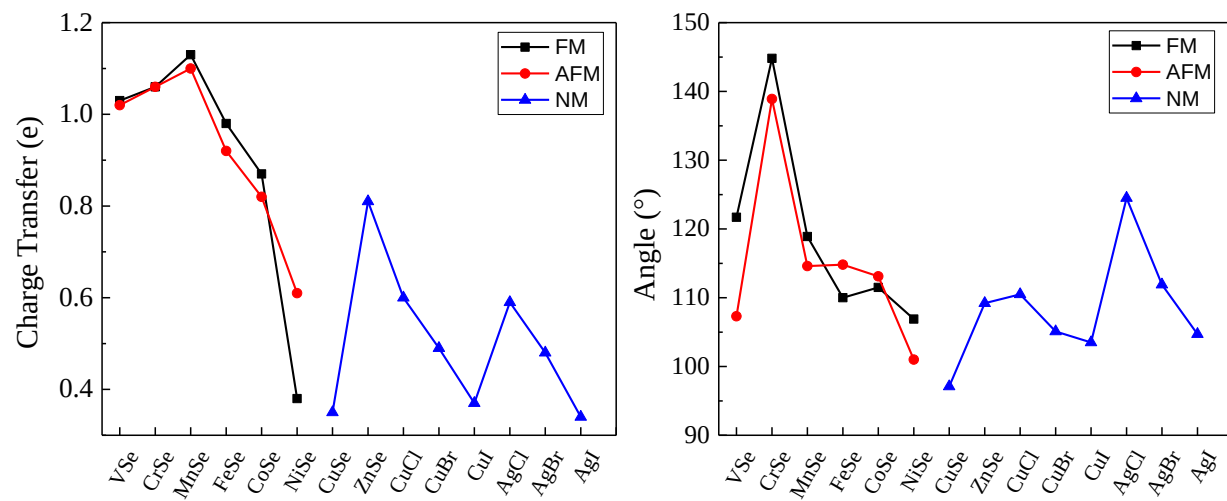
Supplementary Figure 2. Evolution of E_s ($E-E_0$) for magnetic compounds under isotropic and uniaxial strain along the x-direction.



Supplementary Figure 3. Evolution of $E_s (E-E_0)$ for non-magnetic compounds under isotropic and uniaxial strain along the x -direction.

Supplementary Table 1. Lattice constant (L), magnetic ordering (MO), HSE band gap (E_g), a_i (parameter in least-squares formula), h (height), 3D (Y_{3D}) and 2D (Y_{2D}) in-plane stiffness of MX compounds. FM, AFM, NM are ferromagnetic state, anti-ferromagnetic state, and non-magnetic state, respectively.

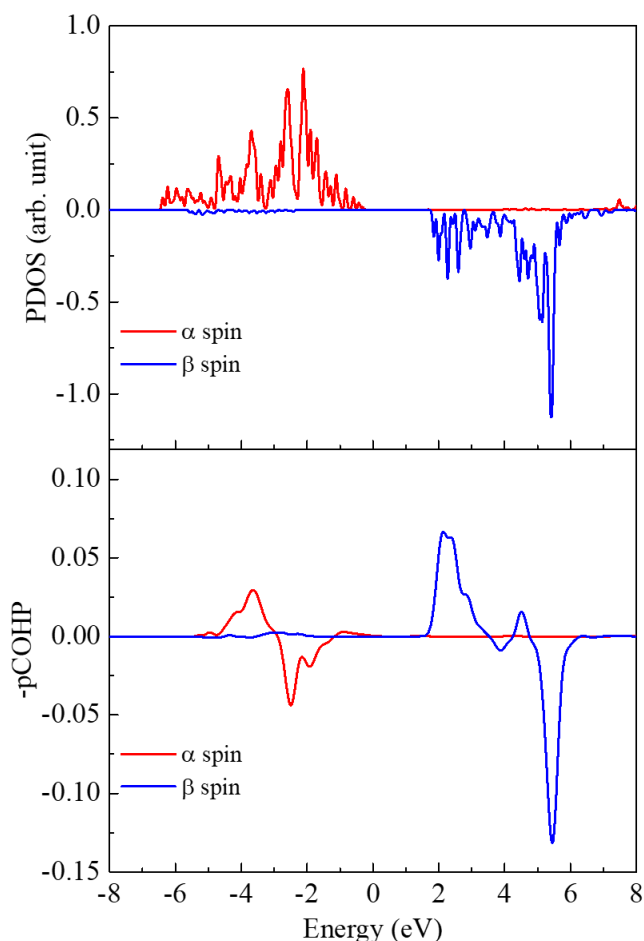
Formula	L(Å)	MO	E_g (eV)	a_1, a_2	a_3	h (Å)	Y_{3D} (GPa)	Y_{2D} (N/m)
VSe	4.37	FM	0.46	19.53	8.01	3.24	96.75	31.38
VSe	3.97	AFM	1.21	14.78	5.94	3.37	85.62	28.89
CrSe	4.84	FM	0.0	29.72	11.79	2.35	166.59	39.12
CrSe	4.72	AFM	1.77	33.72	-8.10	2.57	185.85	47.75
MnSe	4.49	FM	2.21	14.19	10.41	3.47	56.22	19.51
MnSe	4.32	AFM	3.53	15.99	5.58	3.57	74.36	26.58
FeSe	4.16	FM	1.35	16.85	10.94	3.73	74.94	27.92
FeSe	4.22	AFM	0.0	20.22	3.45	3.50	103.24	36.13
CoSe	4.13	FM	1.13	16.39	5.90	3.63	81.98	29.79
CoSe	4.13	AFM	2.06	19.03	7.25	3.53	97.39	34.40
NiSe	3.77	FM	0.0	16.05	5.45	3.62	97.14	35.19
NiSe	3.79	AFM	0.0	18.12	8.02	3.94	97.38	38.35
CuSe	3.64	NM	0	15.90	15.91	4.02	71.55	28.74
ZnSe	4.11	NM	3.49	25.58	1.87	3.72	130.58	48.55
CuCl	3.88	NM	3.45	11.72	-2.68	3.60	68.52	24.68
CuBr	3.99	NM	3.32	10.88	0.24	3.86	56.60	21.85
CuI	4.19	NM	3.64	15.75	-3.69	4.11	69.05	28.34
AgCl	4.73	NM	3.71	4.84	-1.72	3.24	20.68	6.70
AgBr	4.59	NM	3.38	5.57	-1.23	3.90	21.41	8.35
AgI	4.60	NM	3.45	8.35	-1.41	4.35	28.95	12.58



Supplementary Figure 4. Correlation between the charge transfer from cation M to anion X (estimated by Bader charge analysis) (left) and the M-X-M bond angle (right).

Supplementary Note 1

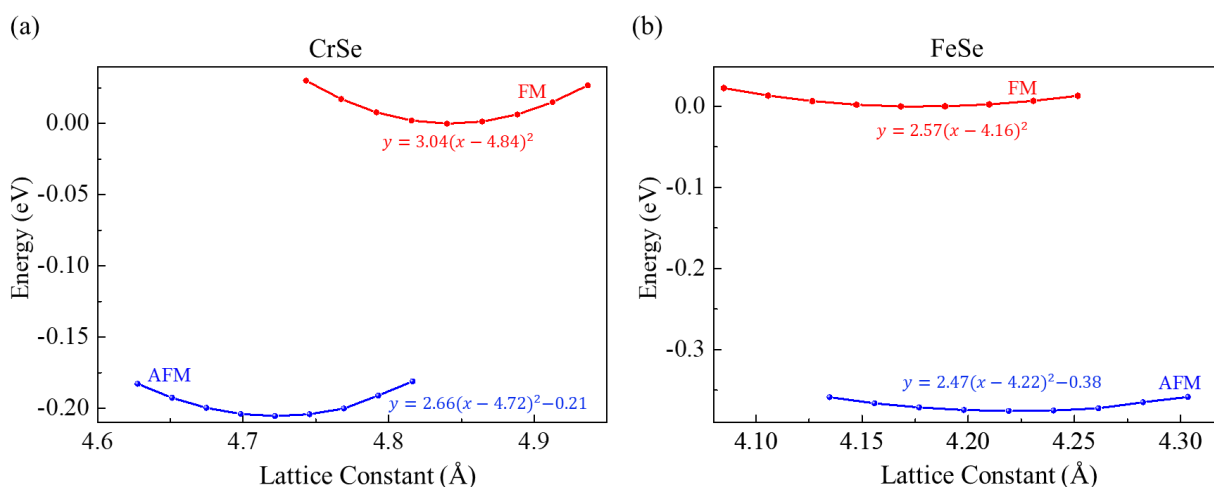
Bonding/antibonding interactions in FM CrSe. As shown in the Fig. 2, 2D CrSe is an outlier with a much larger M-X-M angle than other selenides, indicating a much weaker metal-metal interaction at the equilibrium lattice constant. The weaker metal-metal interaction can be traced back to the electronic structure of 2D CrSe and the occupation of antibonding d_{xy} orbitals. To further clarify this picture, we carried out the Crystal Hamiltonian Orbital Population (COHP)⁹ analysis for ferromagnetic CrSe. As shown in the figure below, the comparison between the projected density of states on d_{xy} orbitals and the COHP analysis reveals that both bonding and antibonding d_{xy} orbitals are fully occupied and located below the Fermi level in one of the spin channels in FM CrSe, indicating a weaker metal-metal interaction.



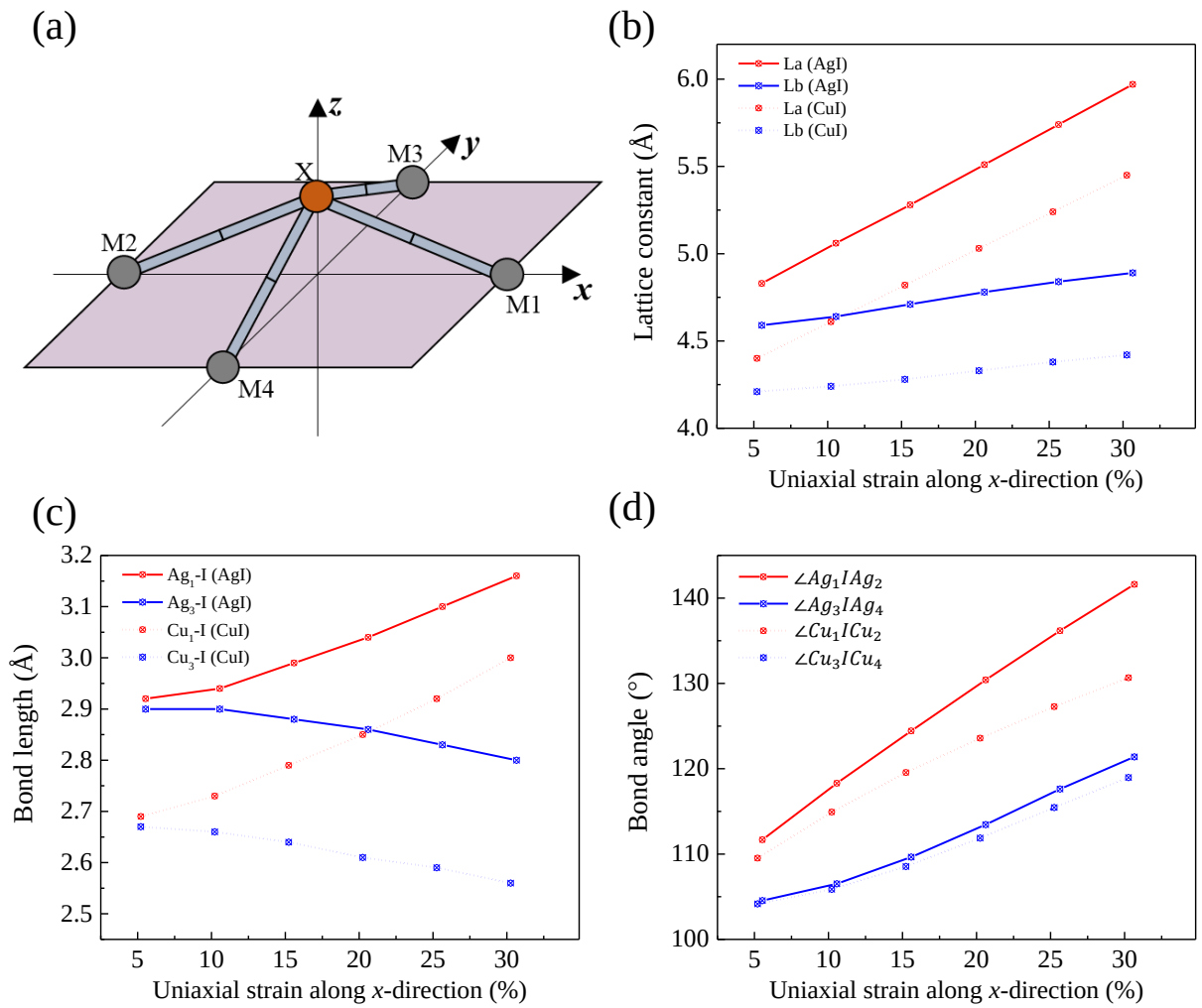
Supplementary Figure 5. Projected density of states (top) of d_{xy} orbitals and the COHP analysis of bonding/antibonding interactions between d_{xy} orbitals (bottom) in ferromagnetic CrSe.

Supplementary Note 2

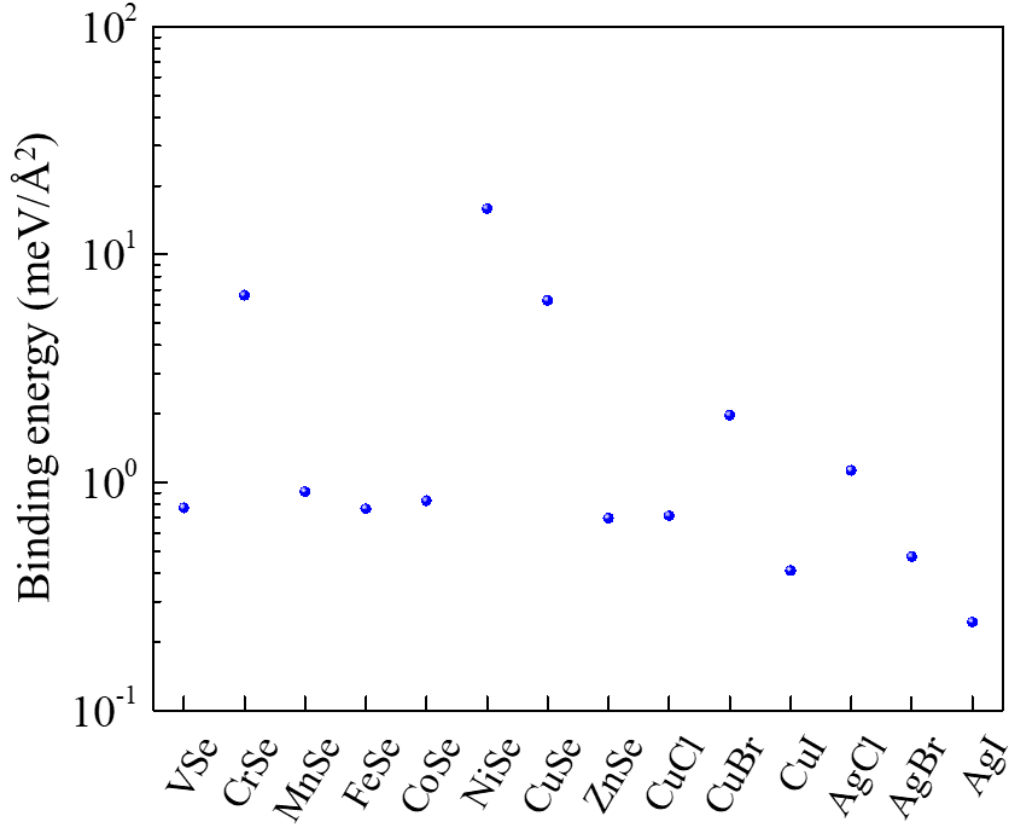
Magnetic properties of MX selenides under strain. Evaluated by magnetic calculations using the primitive cell, CrSe, MnSe, FeSe, CoSe are more stable in their AFM phases and the FM-AFM energy differences are ranging from 0.2 eV to 0.4 eV per primitive cell. VSe and NiSe are more stable in the FM phase (by 0.12 eV and 0.01 eV, respectively). Since it is possible that the primitive cell is not large enough to find the most stable AFM phases, the magnetic ground states of VSe and NiSe need further exploration, which is beyond the scope of our current work.



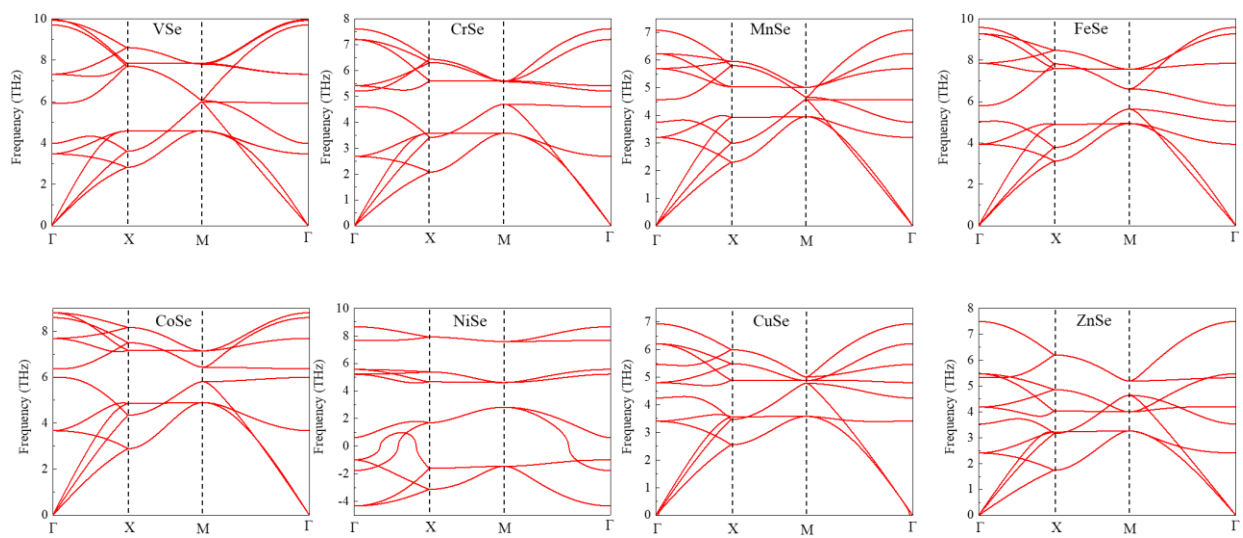
Supplementary Figure 6. Relations between lattice constants and total energies of CrSe and FeSe in FM and AFM phases. The total energies of these two compounds in FM phases without strain are set to zero. Under a small tensile strain (less than 2%), the change in total energy per primitive cell is only several tens of meV for CrSe and FeSe, one order of magnitude smaller than the total energy difference under different magnetic ordering. Therefore, a reasonably large tensile strain does not induce a FM-AFM magnetic phase transition in most MX systems. However, this kind of study indeed provides a good platform to study the magnetostriction effect in 2D systems.



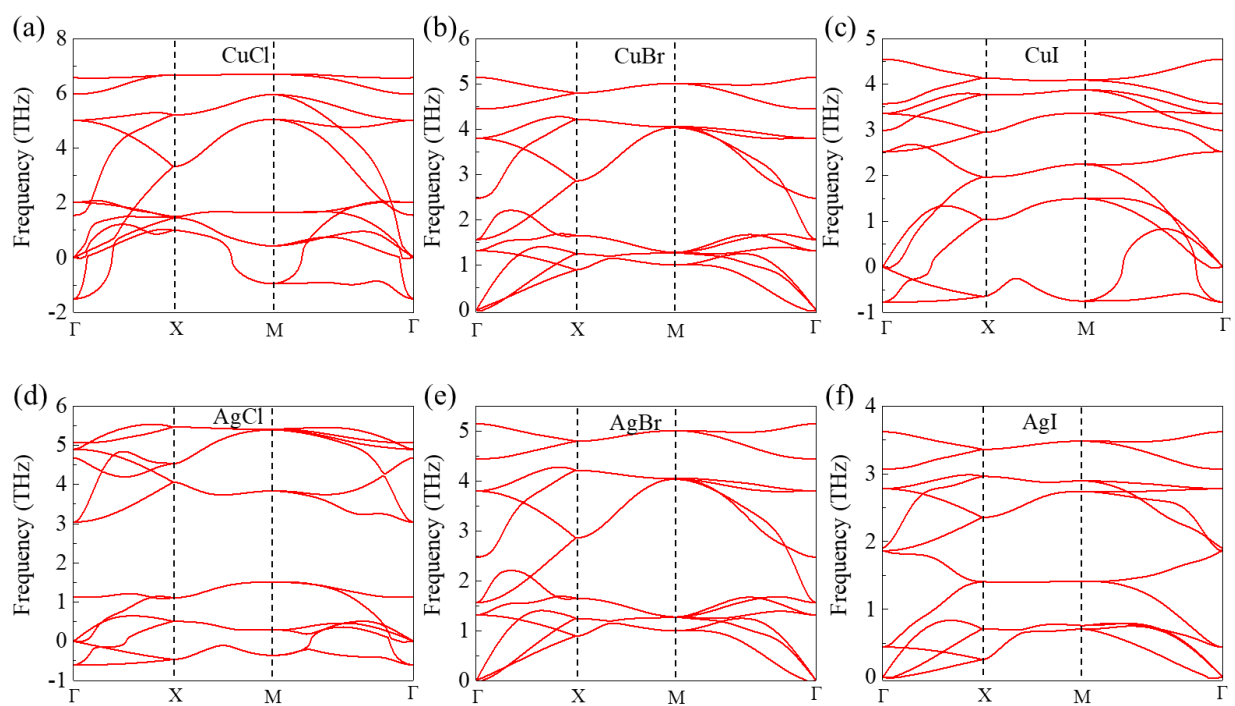
Supplementary Figure 7. Geometric structure evolution of AgI and CuI under large uniaxial strain along x-direction.



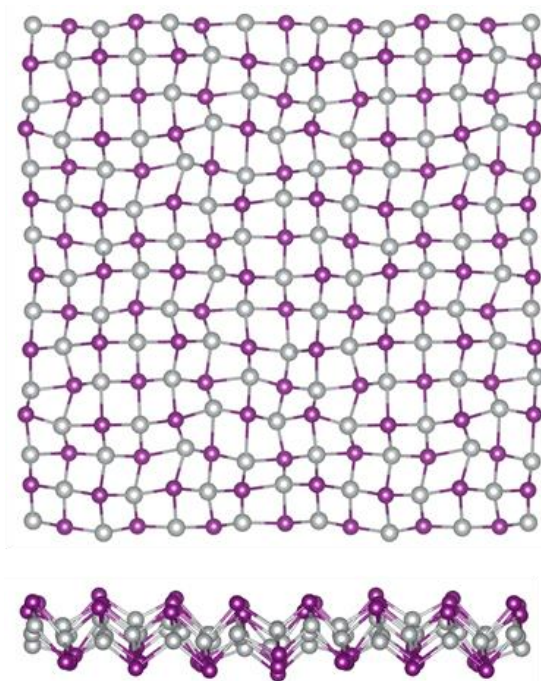
Supplementary Figure 8. Binding energies of 14 MX compounds. Following the work by N. Mounet *et al.*¹⁰, we use the rVV10 method to consider the van der Waals interlayer interactions between two neighboring layers in bilayer MX systems. The normalized binding energies are calculated by $E_b = (2E_{monolayer} - E_{bilayer})/S$, where $E_{monolayer}$ and $E_{bilayer}$ are total energies of monolayer and bilayer MX compounds, and S is the area. The computed binding energies vary from only 0.2 meV/Å² to 20 meV/Å², which are all very small as compared to those of existing and exfoliable monolayer 2D materials¹⁰, indicating high possibilities of monolayer exfoliation.



Supplementary Figure 9. Phonon spectra of MX transition metal selenides.



Supplementary Figure 10. Phonon spectra of MX transition metal halides.



Supplementary Figure 11. Snapshots from *ab initio* MD simulations of AgI monolayer at 300 K (after 5.0 ps).

Supplementary Reference:

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