Supporting Information for

High Curie-Temperature Intrinsic Ferromagnetism and Hole Doping-Induced Half-Metallicity in Two-Dimensional Scandium Chlorine Monolayer

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Computational Method

DFT calculations. The structure relaxations were performed using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA), [1]implemented in Vienna ab initio simulation package (VASP) [2]. The projector-augmented plane wave (PAW) [3] approach was used to represent the ion–electron interaction. The energy cutoff of the plane wave was set to 500 eV with a precision energy of 10^{-6} eV and a precision force of 0.01 eV. The addition of on-site Coulomb repulsion (GGA+U) does not influence the band structures much (Figure S8) and thus was not included in the calculations to reduce the computational burden. For the case of hole/electron doping, the carrier density was tuned via removal or addition of electrons in the unit cell using a homogeneous background of opposite charge added.

Phonon calculations and molecular dynamics simulations. Phonon dispersion was calculated by means of density functional perturbation theory (DFPT) as embedded in the PHONOPY program.[4-5] *Ab initio* molecular dynamics (AIMD) simulations were carried out to evaluate the thermal stability of the ScCl monolayer at 300 K with a 4 × 4 supercell. The time step was 1.0 fs and the total simulation time was up to 5.0 ps. The temperature was controlled by using the Nosé– Hoover method.[6]

Monte Carlo Simulations. Based on the Heisenberg model, the T_c of ScCl monolayer can be estimated by using Monte Carlo (MC) simulation:

$$H = -J_1 \sum_{i,j} S_i \cdot S_j - J_2 \sum_{i,l} S_i \cdot S_l - A(S_i^z)^2,$$

Where J_1 and J_2 are the first and second nearest neighboring exchange parameters (Figure S3), respectively. S_i is the spin vector of each atom, S_i^Z is the spin component along the z direction, and A is anisotropy energy parameter (-86 μeV). Based on the calculated total energies of different magnetic configurations, the exchange parameters J_1 and J_2 can be derived by following equations:

$$E_{FM} = E_0 - (3J_1 + 6J_2)|S|^2 - A|S|^2 \quad (1)$$

$$E_{AFM1} = E_0 - (-3J_1 + 6J_2)|S|^2 - A|S|^2 \quad (2)$$

$$E_{AFM2} = E_0 - (-J_1 - 2J_2)|S|^2 - A|S|^2 \quad (3)$$

E_0 is the total energy excluding the magnetic coupling (not sensitive to different magnetic states). For, anisotropy energy parameter A, spin−orbital coupling (SOC) calculations are performed on 2D ScCl crystal to obtain the relative stability along three magnetization directions in plane, that is (100), (010), and (001) direction. A is calculated to be -86 μeV by using the magnetic anisotropy energies as below:

$$A = \frac{E(100) - E(001)}{|S|^2}$$

Table S1. Optimized lattice constant (a, Å), TM-Cl Bond Length ($d_{\text{TM-Cl}}$, Å), TM-TM Bond Length (d_1, Å) between atoms in different planes, TM-TM Bond Length (d_2, Å) between atoms within xy plane, Magnetic Moment (M, μ_B) in unit cell, and bond-angle of TM−Cl−TM for TMCl monolayer and hole-doped ScCl monolayer at the concentration of 2.26×10^{14} cm^{-2} (0.24 hole per cell).

	a	$d_{TM\text{-}Cl}$	d_1	d_2	M	θ
ScCl	3.50	2.59	3.23	3.49	1.56	85°
ScCl-0.24	3.55	2.58	3.28	3.54	1.77	87°
YCl	3.75	2.77	3.54	3.75	/	85°
ZrCl	3.45	2.63	3.12	3.45	/	82°

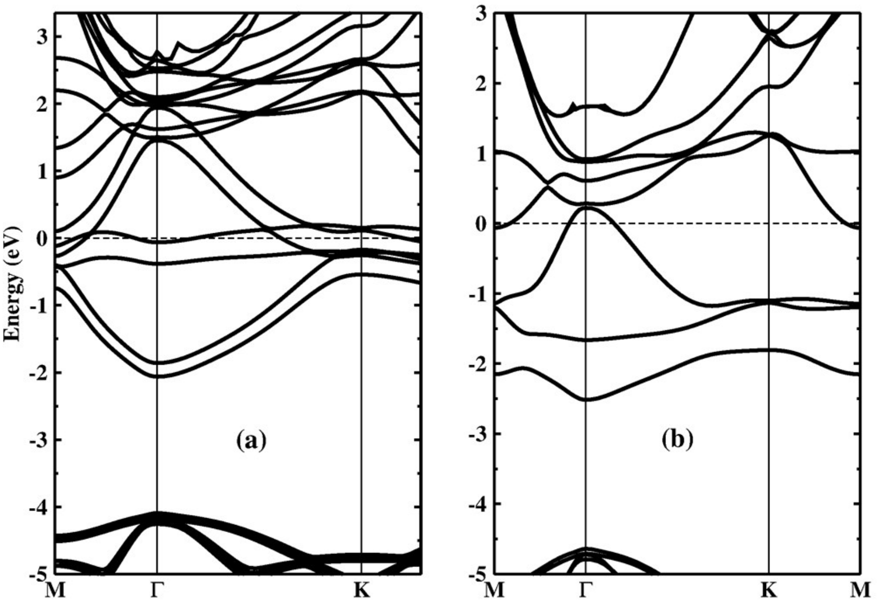

Figure S1. Band structures of YCl and ZrCl monolayer at PBE level.

The layered bulk structures of ScCl, YCl, and ZrCl are isostructure. Their monolayers are exfoliated directly from their bulk phases. The result of various magnetic orders, including nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM), show that ScCl monolayer is FM at its ground state (more details in the main text) and YCl monolayer and ZrCl monolayer are NM. Their optimized structure constants are listed in Table S1. The calculated band structures indicate that YCl monolayer and ZrCl monolayer are metal as shown in Figure S1.

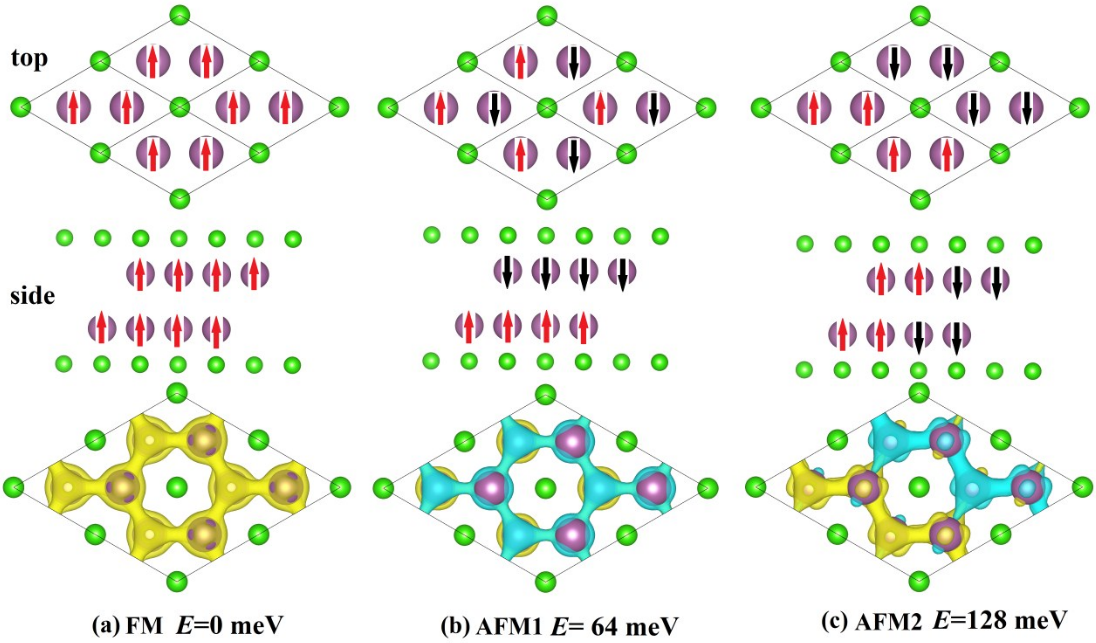

Figure S2. The possible magnetic configurations and the corresponding spin charge density of ScCl monolayer: (a) ferromagnetic (FM) state, and (b, c) antiferromagnetic (AFM1 and AFM2) states. The up-spins and down-spins on the Sc atoms are denoted as red and black arrows, respectively. The relative energies E calculated with respect to the lowest energy configuration (a) are also given.

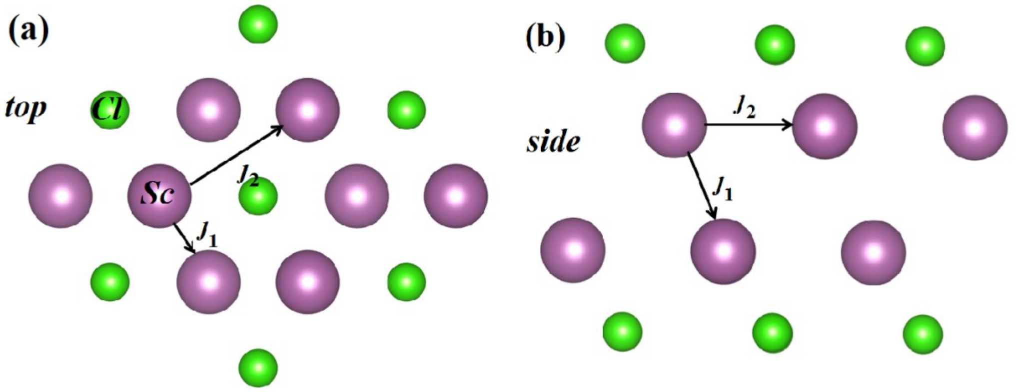

Figure S3. Top view (a) and side view (b) of spin configuration for estimating the exchange-interaction constants. J_1 and J_2 are the first and second nearest-neighboring exchange parameters, respectively.

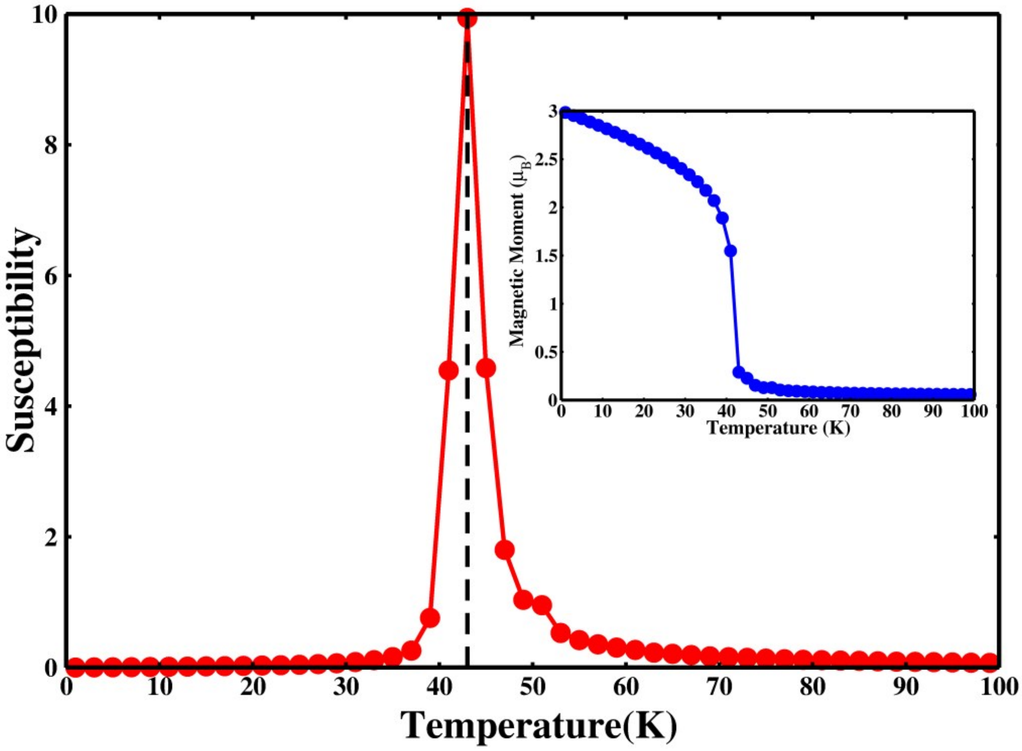

Figure S4. Calculated T_c of CrI_3 monolayer with a J of 2.67 meV.

To assess the reliability of our method for the prediction of Curie temperature, we calculated the T_c for the CrI_3 monolayer using the same methodology, which was used in our work. The value of J is 2.67 meV, which is consistent with the value (2.71 meV) in Ref. 7. Our calculated T_c of CrI_3 monolayer is about 43 K, which is in excellent agreement the experimental measurement of 45 K from Ref. 8. This confirms the reliability of our method.

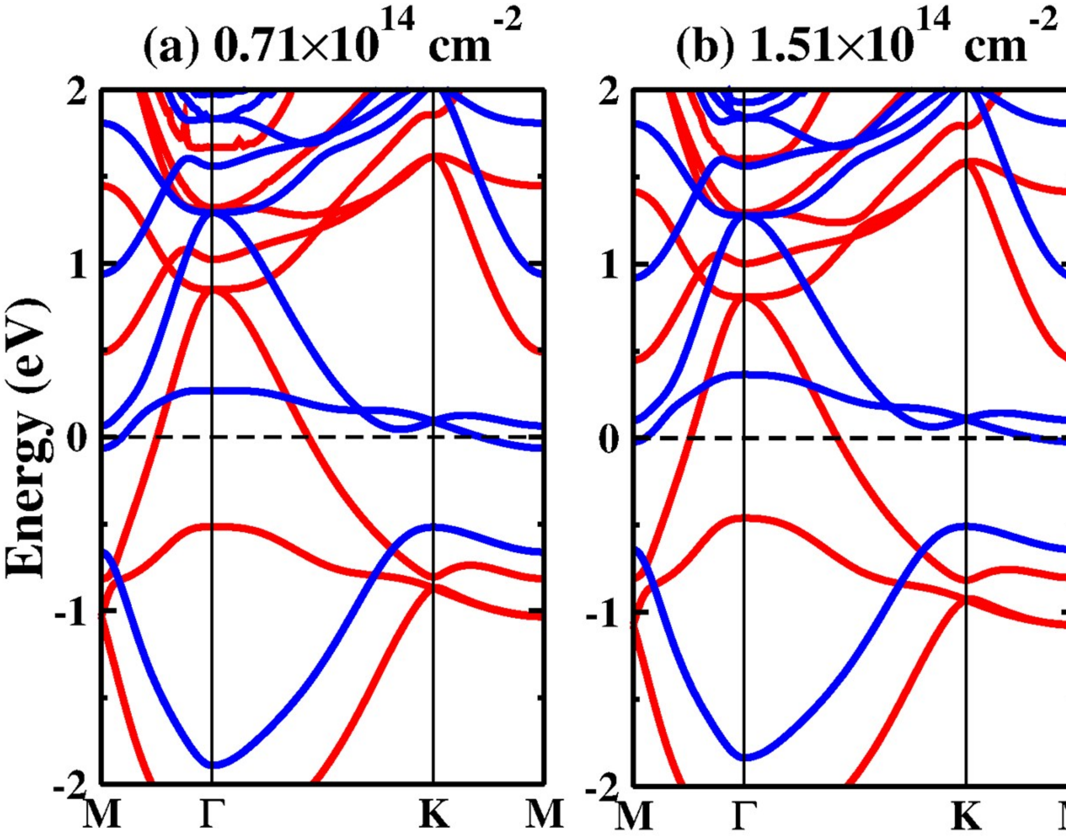

Figure S5. Band structures of ScCl monolayer at the hole doping concentration of 0.71×10^{14} cm^{-2} and 1.51×10^{14} cm^{-2}, respectively.

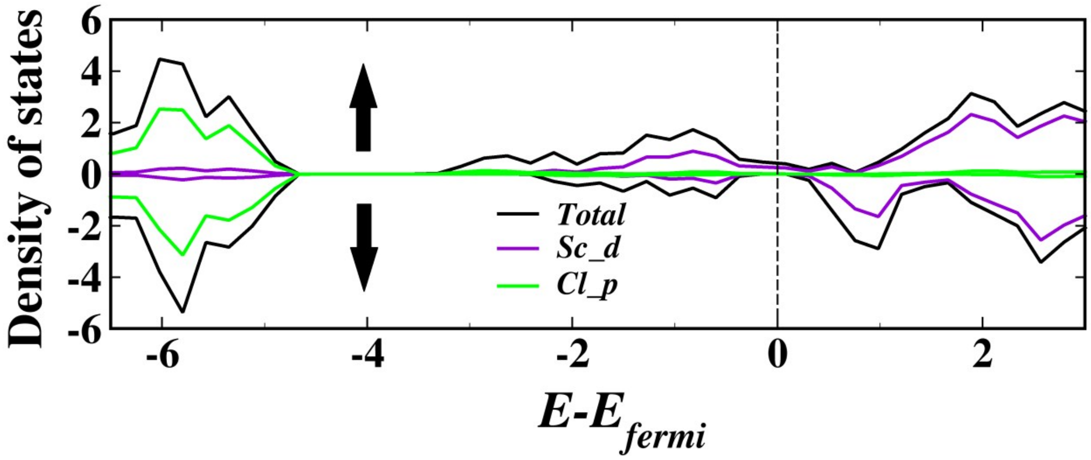

Figure S6. Density of states of ScCl monolayer at the hole concentration of 2.26×10^{14} cm^{-2}. The black arrow donates the spin up and spin down, respectively.

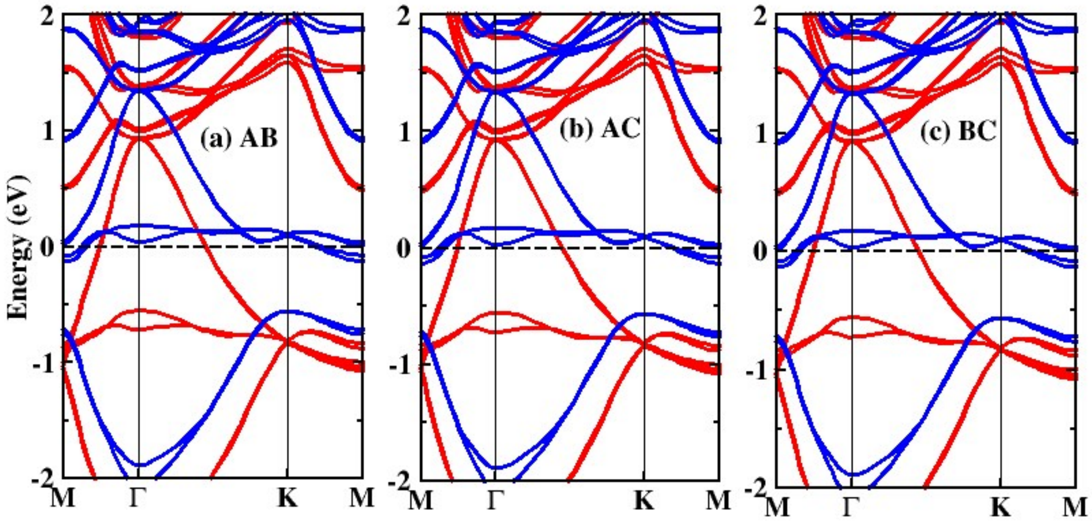

Figure S7 Band structures of ScCl bilayer with AB-stacking (a), AC-staking (b), and BC-staking (c). The red and blue lines represent spin-up and spin-down.

The various magnetic orders of ScCl bilayer were also investigated. Because of the ABC layer stacking of bulk ScCl, AB-stacking, AC-stacking, and BC-stacking were considered for ScCl bilayer. Our total energy calculations show that the considered ScCl bilayers also prefer ferromagnetic (FM) crystals. The FM configuration is found to be 79.2, 79.5, and 80.1 meV lower in energy than their AFM ones per unit cell, respectively. The calculated band structures show that they are also metal as shown in Figure S7.

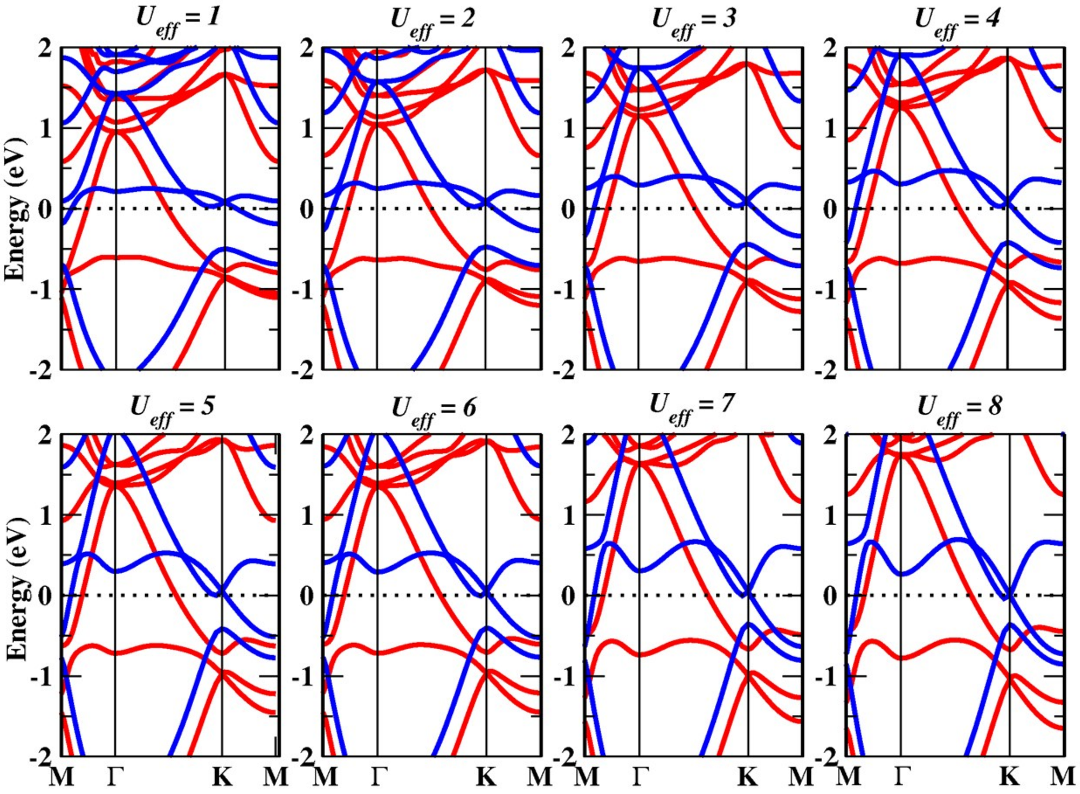

Figure S8. Band structure of ScCl monolayer calculated with different U_{eff} values from 1.0 to 8.0 eV.

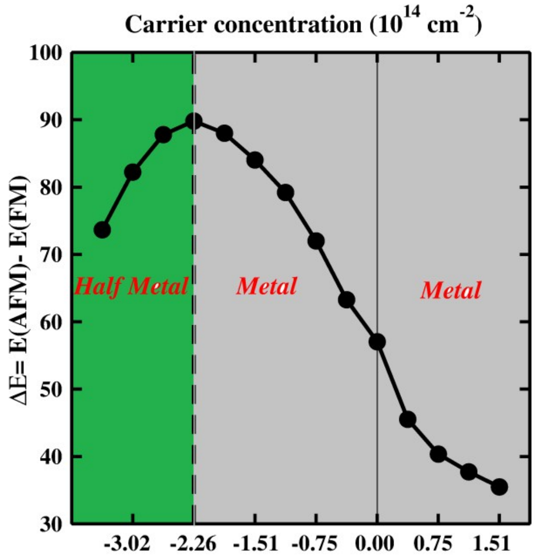

Figure S9. Relative energy of AFM and FM states under the variation of carrier concentration for 2D ScCl. The positive and negative values are for electron and hole doping, respectively.

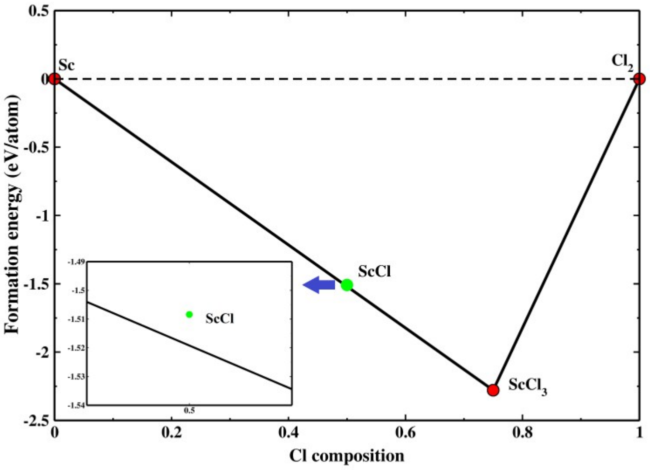

Figure S10. The formation energy of Sc-Cl bulk as a function of Cl composition.

References

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