Supporting Information

Ferromagnetism in Magnesium Chloride Monolayer with an Unusual large

Spin-up Gap

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Contents:

Text S1. Computational Details.

Table S1: Summary of formation energy/vacancy (${}^{E_{F}}$) under Mg-rich and Cl-rich environments, magnetic moments/vacancy (μ B), nature of the material and spin-up band gap (eV) for with different Mg-vacancy concentrations.

Figure S1: Spin density distribution (top/side view) [isosurface value 0.0046 e Å⁻³] and partial density of states (PDOS) plot of Mg and Cl atoms in $Mg_{0.89}\delta_{0.11}Cl_2$, $Mg_{0.78}\delta_{0.22}Cl_2$, and $Mg_{0.67}\delta_{0.33}Cl_2$ systems.

Table S2: Bond distance and Bader charge analysis of $MgCl_{2}$, $Mg_{0.67}\delta_{0.33}Cl_{2}$ (MgCl₃) and $Mg_{0.89}\delta_{0.11}Cl_{2}$.

Text S2: Mean Field Theory (MFT).

Text S3: Monte Carlo (MC) Simulation.

Table S3: Summary of Magnetic Anisotropy Energies in μeV /vacancy and the easy axis for $Mg_{0.89}\delta_{0.11}Cl_2$.

Figure S2: (a)-(d) Spin density distribution and TDOS plot of $Mg_{0.89}\delta_{0.11}Cl_2$ under the application of biaxial tensile strain from 1% to 4% along with magnified spin-polarised TDOS around the Fermi showing half-metallic gap [Δ , in the inset figure].

Figure S3: (a)-(d) Spin density distribution and TDOS plot of $Mg_{0.89}\delta_{0.11}Cl_2$ under the application of uniaxial tensile strain from 1% to 4% along with magnified spin-polarised TDOS around the Fermi showing half-metallic gap [Δ , in the inset figure].

Figure S4: (a)-(d) Spin density distribution and TDOS plot of $Mg_{0.89}\delta_{0.11}Cl_2$ under the application of uniaxial compressive strain from 1% to 4% along with magnified spin-polarised TDOS around the Fermi showing half-metallic gap [Δ , in the inset figure].

Figure S5: (a)-(d) Spin density distribution and TDOS plot of $Mg_{0.89}\delta_{0.11}Cl_2$ under the application of biaxial compressive strain from 1% to 4% along with magnified spin-polarised TDOS around the Fermi showing half-metallic gap [Δ , in the inset figure].

Figure S6: (a)-(e) Spin density distribution and TDOS plot of $Mg_{0.89}\delta_{0.11}Cl_2$ under the application of transverse electric field ranging from 0.0 to 1.0 VÅ⁻¹.

Figure S7: Optimized structure and spin-polarized density of states of $Mg_{0.96}\delta_{0.04}Cl_2$ and $Mg_{0.92}\delta_{0.08}Cl_2$ systems.

Text S1. Computational Details

We have performed spin-polarized density functional theory (DFT) calculations for all our structures as implemented in the Vienna Ab initio Simulation Package (VASP).¹ All our calculations have been carried out within the Perdew-Burke-Ernzerhof (PBE) functional using generalized gradient approximation (GGA) ²⁻³ to describe correctly the electron–electron exchange and correlation energies of delocalized *s* and *p* electrons. Projected augmented wave (PAW) method ⁴ is employed using a plane wave cut–off energy of 320 eV to treat interactions between ion cores and valence electrons. Since the van der Waals interactions play a very decisive role for the layered systems, we have adopted van der Waals corrected density functional theory (DFT-D3) proposed by Grimme to overcome the deficiencies of DFT in treating dispersion interactions and correcting potential energy and interatomic forces.⁵ MgCl₂ monolayer and defect induced various phases of MgCl₂ structures are modeled using (3×3×1) hexagonal supercell containing 27 atoms. We have used gamma-centered k-point grid of 9 × 9 × 1 is used to sample the first Brillouin zone of MgCl₂ monolayer for geometry optimization and 15×15×1 is used for spin-polarized

electronic properties (Density of States) calculations. A 20 Å vacuum is employed along the z-direction for avoiding interactions between their periodic images. We have accomplished self-consistency with the convergence tolerance set to 10^{-6} eV and 10^{-3} eV.Å⁻¹ for total energy and force calculations respectively. We have done bader charge analysis⁶⁻⁸ using the Henkelman programme⁹ with a near-grid algorithm refine-edge method to comprehend the charge transfer process. Moreover, we have calculated defect formation (E_F) energies under two different experimental conditions (Mg-rich environment and Cl-rich environment) to estimate the stability of various phases of MgCl₂ systems. Defect formation energy under Mg-rich environment can be calculated from the following equation¹⁰⁻¹¹

$$E_F = E_{def - phase} - \left(E_{MgCl2} - N \times \mu_{Mg - max} \right)$$
(1)

Where $E_{def-phase}$ is total energy of the Mg vacancy induced phases of MgCl₂ monolayer, E_{MgCl2} is the total energy of pure MgCl₂ system, μ_{Mg-max} is the chemical potential of Mg under Mg-rich environment and N is the number vacancy created in the MgCl₂ supercell. Under Mg-rich environment, $\mu_{Mg-max} = E_{Mg(Bulk)}$, where $E_{Mg(Bulk)}$ is the single atom energy of Mg atom from its respective bulk structure.¹² Defect formation energy under Cl-rich environment can be calculated from the following equation ¹⁰⁻¹¹

$$E_F = E_{def - phase} - \left(E_{MgCl2} - N \times \mu_{Mg - min}\right)$$
(2)

Where μ_{Mg-min} is the chemical potential of Mg under Cl-rich environment which can be calculated as

$$\mu_{Mg-min} = \left(E_{MgCl2-unit} - 2 \times \mu_{Cl-max} \right)$$
(3)

Here, $E_{MgCl2-unit}$ is the total energy of the MgCl₂ unit cell containing one Mg and two Cl atoms and μ_{Cl-max} is the chemical potential of Cl, which is single Cl atom energy from gaseous phase.

Furthermore, to predict the magnetic ground state of in defect induced phases of MgCl₂ monolayer, we have calculated the exchange energy¹⁰ ($^{E}_{ex}$) per unit cell and magnetic anisotropic energy¹⁰ of Mg_{0.89} $\delta_{0.11}$ Cl₂. The exchange energy per supercell ($^{E}_{ex}$) is calculated using the following equation where $^{E}_{FM}$ and $^{E}_{AFM}$ denotes the energies of ferromagnetic and antiferromagnetic states.

$$E_{ex} = E_{AFM} - E_{FM} \tag{4}$$

Similarly, magnetic anisotropic energy (MAE)¹³ per unitcell is calculated incorporating spin-orbit coupling (SOC) effect using the following equation where E_{HA} is the energy of the system (along hard axis) with application of magnetic field along magnetizing direction (100), (010), (110), (111) and (001). E_{EA} is the energy of the system in present of a magnetic easy axis, which is an energetically favorable direction for spontaneous magnetization. We have also tried two out of plane direction (001) and (111) magnetizing direction.

$$MAE = E_{HA} - E_{EA} \tag{5}$$

The spin density distribution $(SDD)^{14}$ is plotted to understand the nature of electron spin density on the unpaired electron in Mg vacancy induced phases of MgCl₂ monolayer. The SDD is calculated using the following equation

$$\rho_{SD} = \rho_{up} - \rho_{down} \tag{6}$$

Here, ρ_{up} and ρ_{down} are the up and down electron spin density, respectively. In the SD, the wave functions for different lobes are indicated by yellow colors. The direct mapping of the electron spin density is measured by the neutron diffraction in electron spin resonance (ESR) spectroscopy.^{10,15}

Table S1: Summary of formation energy/vacancy $({}^{E_{F}})$ under Mg-rich and Cl-rich environments, magnetic moments/vacancy (μ B), nature of the material and spin-up band gap (eV) for with different Mg-vacancy concentrations.

Mg Vacancy in MgCl ₂	Formation energy (eV/Vacancy)		Magnetic moment	Nature	Spin-Up Band	Half- Metallic
_	Under Mg-	Under Cl-	/vacancy(µB)		Gap (eV)	Gap
	rich	rich				(eV)
	environment	environment				
$Mg_{0.89}\delta_{0.11}Cl_2$	7.99	2.16	2.00	Half-	6.135	0.242
				Metallic		
$Mg_{0.78}\delta_{0.22}Cl_2$	7.96	2.13	2.00	Half-	6.301	0.157
-				Metallic		



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Table S2: Bond distance and Bader charge analysis of pure $MgCl_{2}$, $Mg_{0.67}\delta_{0.33}Cl_2$ (MgCl₃) and $Mg_{0.89}\delta_{0.11}Cl_2$.

System		Bond-distance	Net effective charge
		(Å)	
MgCl ₂		Mg-Cl ~ 2.52 Å	Mg ~ +1.66, Cl ~ -0.83



Text S2: Mean Field Theory (MFT)

We have taken the MFT approach to calculate the Curie temperature for the two dimensional $Mg_{0.89}\delta_{0.11}Cl_2$ system. This method has been previously used by Li *et al.*¹⁶ for the Curie temperature calculation for Mn-phthalocyanine (MnPc) system. The main idea behind MFT method is to replace all interactions to any one body with an average or effective interaction.¹⁶ It reduces any multi-body problem into an effective one-body problem. The detailed partition function can be written as follows,

$$Z = \sum_{m = -M, -M + 2, \dots, M - 2, M} e^{\gamma J m < M > /K_B T}$$
(7)

Here, the "J" is the exchange parameter, " γ " is the coordination number, "m" is the ensemble average magnetic moment, and "M" is the calculated magnetic moment of Mg-B3 unit.

Thus the average spin of each magnet becomes,

$$Z = \frac{1}{Z} \sum_{m = -M, -M+2, \dots, M-2, M} m \times e^{\gamma J m < M > /K_B T}$$
(8)

Now, we assume that $P = \frac{\gamma J}{K_B T}$

The above equation can be easily deducible when the parameter 'P' varies along with the

static solution <m>. At the critical point,

$$P_c = P = \frac{\gamma J}{K_B T} \tag{9}$$

At this critical point, the phase transition of the system between ferromagnetic to paramagnetic occurs. This critical point is known as Curie temperature.

Text S3: Monte Carlo (MC) Simulation

Monte Carlo simulations involve generating a subset of configurations or samples, chosen using a random algorithm from a configuration space, according to a probability distribution or weight function. Observables are then computed as averages over the samples. ¹⁷ One sample or configuration of the magnet is a particular assignment of spin values, say

$$S_1 = +1; S_2 = -1; S_3 = +1; \dots S_{NS} = +1$$
 (10)

in which each spin is set "up" or "down". According to statistical mechanics, the average value of an observable is got by weighting each configuration with the Boltzmann factor. For example, the average magnetization at some fixed temperature T is given by,

$$\langle M \rangle = \frac{\sum_{config} M e^{-E/K_B T}}{\sum_{config} e^{-E/K_B T}}$$
(11)

Table S3: Summary of magnetic anisotropy energies in $\mu eV/vacancy$ and the easy axis for $Mg_{0.89}\delta_{0.11}Cl_2$

$Mg_{0.89}\delta_{0.11}Cl_2$	Easy Axis	(001)-(100)	(010)-(100)	(110)-(100)	(111)-(100)
	(100)				
	0	452.84 μeV	17.59 μeV	21.01 µeV	160.48 μeV



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