Ferromagnetic phase of spinel compound MgV$_2$O$_4$ and its spintronics properties

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Spinel compound, MgV$_2$O$_4$, known as a highly frustrated magnet has been extensively studied for its rich magnetic properties, and topological properties. In general, spinel compounds with chemical formula $A_{1-x}B_x(A_2B_2-x)X_4$ are classified into the normal ($\alpha = 0$), inverse ($\alpha = 1$), and complex ($0 < \alpha < 1$), depending on the different cations (A and B) distributions in octahedral and tetrahedral locations. The most widely investigated spinels are normal spinels with chemical formula $AB_2X_4$, where the A and B metal cations are located at the tetrahedral and octahedral sites, respectively. The conventional unit cell is presented in Fig. 1(a), where X ions form the face-centered cubic lattice and cations A and B form diamond and three-dimensional (3D) kagome sublattices, respectively.

For the system to be charge neutral, anion X always accept two electrons while cations A normally donates two or four electrons and cations B donates two or three electrons, leading to the two possible $A^4+\text{B}_2^2\text{X}_4^2$ or $A^2+\text{B}_2^3\text{X}_4^2$ states. Therefore, with combinations of different cations A and B, we are able to selectively populate different sublattices. For example, within vanadium spinels, $V^4+\text{Mg}_2^2\text{O}_4$ shows interesting magnetic Weyl semimetal state due to the diamond lattice constructed by $V^4+$ ions, while $\text{Mg}^{2+}\text{V}_2^{3+}\text{O}_4$ is a well-known highly frustrated magnet that hosts intriguing quantum magnetic states due to the corner-sharing 3D kagome lattice. Both of these spinels, in principle, could be experimentally synthesized by properly controlling the oxygen pressure and stoichiometric ratio between the elements. Nevertheless, the commonly observed phase experimentally is $\text{Mg}^{2+}\text{V}_2^{3+}\text{O}_4$, which is intrinsically an anti-ferromagnetic (AFM) insulator. Studies on other spinel compounds, such as ZnCr$_2$O$_4$ and CaCr$_2$O$_4$, suggest hole doping can stabilize the ferromagnetic (FM) phase. However, the electronic properties of the MgV$_2$O$_4$ in its FM phase is not well understood. Here we reveal that the FM phase can accommodate interesting topological and spintronics properties. This includes large anomalous Hall conductivity, half metallicity, and AFM-FM and metal-insulator transitions. We also explore possible strain and doping approaches where this FM phase might be stabilize, which can motivate its experimental search.

In this work, we revisit the electronic and magnetic properties of MgV$_2$O$_4$ with first-principles calculations based on density functional theory (DFT). A significant point of departure of our work to prior literature is the emphasis on its 3D kagome lattice, and its characteristic flat band (FB). FBs are well studied in the literatures for their interesting physics such as superconductivity[19],[20] and topological state.[21],[22] The FM MgV$_2$O$_4$ shows interesting FB feature and ideal half-metallicity with a large spin gap, which is further analyzed based on tight-binding simulation of the 3D kagome lattice model. We found that intrinsic AFM MgV$_2$O$_4$ could transition into a FM state via experimentally accessible hole doping, such as ionic gel gating. Interestingly, the AFM to FM transition is accompanied with an insulator to metal transition and a giant variation of anomalous Hall effect. Lastly, we demonstrated how lattice and chemically matched interface between MgV$_2$O$_4$ and MgO could help to preserve its half-metallicity. These new predictions could potentially usher in future novel and practical spintronics applications.

FIRST-PRINCIPLES CALCULATION RESULTS

We start by studying the electronic properties of MgV$_2$O$_4$ in the FM state rather than commonly studied AFM phase (Supplemental Material[23]). To treat the strongly localized d electrons of V ions, an on-site Hubbard U term is added. Using the documented value (U=3.0 eV)[24],[25], spin-polarized band structure for FM MgV$_2$O$_4$ is presented in Fig. 1(c), which interestingly shows an ideal half-metallic feature with a large band gap of 4.15 eV for the spin-down channel. The half-metallicity will remain for different U values, which only changes the...
separation between two spin channels. For example, in Fig. 1(c), the minority spin (red) bands are separated from the majority spin (blue) Fermi surface by about 1 eV. Moreover, MgV₂O₄ possesses four nearly FBs right above the Fermi level, with their bandwidths varying from 29 meV (very flat) to 205 meV. Detailed analysis show that there are two three-fold degenerated points formed by two FBs and one dispersive band at the center of Brillouin zone (BZ), (Γ) at energies 16 meV and 196 meV above the Fermi level, respectively.

To reveal the nature of these FBs, we calculated orbital and orbital-projected density of states (PDOS), as shown in Fig. 1(d). Around the Fermi level, there is a sharp peak that corresponds to the FBs. These FBs are mainly contributed by spin up electrons of vanadium atoms, which form the 3D kagome lattice. This agrees with the magnetic moment distribution, which are mainly localized on V atoms. Detailed analysis of PDOS shows that all the twelve bands near the Fermi level (E_F) from 29 meV to 205 meV are contributed by the t₂g orbitals. This can be understood from the crystal field splitting of the V atoms in the octahedron formed by neighboring O ions, which splits the five degenerate d orbitals into two e_g and three t₂g orbitals with relatively lower energy. Due to the slight distortion of the octahedron, three degenerate t₂g orbitals are further split into one lower energy d_xy and two nearly degenerate d_xz and d_yz orbitals, which is further validated by the different O-V bond angle in the octahedron. After donating two s and one d electrons, V³⁺ ions have two d electrons left. Therefore, with the remaining two valence electrons of V³⁺, the d_xy orbitals with the lowest energy will be fully filled while the other two degenerate d_xz and d_yz orbitals will be half-filled.

In forming the band structure, each d orbitals will, in principle, form one set of 3D kagome lattice, and the band filling will be determined by the number of valence electrons of V. These indeed agree perfectly with the band structure from DFT, where the bottom set of 3D kagome bands are fully occupied and the upper eight bands are half filled, which correspond to the two sets of 3D kagome bands. We note that the large difference of the band width between these 3D kagome bands is due to the distortion induced changes of the hopping t for different d orbitals. We also performed maximally localized Wannier functions (MLWFs) calculations using the WANNIER90 package. As shown in Fig. 1(c), the MLWF fitted band structure agrees perfectly with the DFT band structure. The plotted MLWFs further validate the orbital characteristics of vanadium atoms [see Fig. 1(b)].

With the increasing interest in spintronics, materials with ideal half-metallicity and large spin/anomalous Hall effect are extensively studied. However, materials with both of those features are still quite rare. The ideal half-metallicity of the FM MgV₂O₄ has already been demonstrated from the electronic band structure, which shows a spin gap as large as 4.15 eV. Further, we study the anomalous Hall effect by calculating the anomalous Hall conductivity (AHC). First, we recalculate the band structure of MgV₂O₄ by turning on the spin-orbit coupling (SOC) and then fit the results using MLWFs, based on which a tight-binding Hamiltonian is obtained. The AHC can be acquired by integrating the Berry curvature of the occupied bands. We plotted the energy-dependent

![Figure 1](attachment:image.png)
AHC of MgV$_2$O$_4$, as shown in Fig. 1(c). It can be clearly seen a large AHC peak of 670 $\Omega^{-1} \cdot cm^{-1}$ at 0.20 eV above the Fermi energy is observed, which can be traced to the 3D FBs. There is also a large AHC of 450 $\Omega^{-1} \cdot cm^{-1}$ at energy 0.54 eV below the Fermi energy. Note that the three components of AHC have relatively similar values, which is related to the direction of magnetization, that is along (111) direction. The large AHC can arise from the large Berry curvatures and electronic topology of the 3D kagome lattice, which only present in the FM state of MgV$_2$O$_4$. Detailed analysis about the AHC is beyond the scope of this work, which will be discussed in a separate study\textsuperscript{53}.

**TIGHT-BINDING ANALYSIS**

Since the bands of interest are mainly contributed by vanadium $d$ electrons, we can better understand the formation of the FB by analyzing the tight-binding model on a 3D kagome lattice. The primitive unit cell of the 3D kagome lattice contains four atomic states, with one corner-site and three edge-center-site states as presented by green atoms (B) in Fig. 2(a). Here, $\vec{a}$, $\vec{b}$, and $\vec{c}$ are the three primitive vectors pointing between nearest-neighbor (NN) lattice points that form a tetrahedron. It can be seen that the cross section along each of the four faces of the tetrahedron produces one 2D kagome lattice, as shown in Fig. 2(b), and for this we dubbed the system 3D kagome lattice. The first BZ of this lattice with high-symmetry lines is shown in Fig. 2(c). For simplicity, we consider one state per lattice site and only take NN interactions into account in our model. The spinless Hamiltonian is written as

$$H = \sum \epsilon_i c_i^\dagger c_i + \sum_{<ij>} t c_i^\dagger c_j + H.c. , \quad (1)$$

where $\epsilon_i$ is the on-site energy that is set as zero, and $<ij>$ denotes summation over NN sites. $c_i^\dagger$ ($c_i$) creates (annihilates) an electron on the site $\vec{r}_i$ ($\vec{r}_j$), and NN hopping $t$ are set as the same value for all the NNs considering the structural symmetry.

By diagonalizing the Hamiltonian, we obtain the analytical energy bands as $E_{1,2} = -2t(1 \pm \sqrt{1 + A})$ and $E_{3,4} = 2t$. $A$ is given by $A = \cos(2k_x)\cos(2k_y) + \cos(2k_x)\cos(2k_z) + \cos(2k_y)\cos(2k_z)$, where $\vec{k} = (k_x,k_y,k_z)$ is the reciprocal lattice vector. The band structure along high-symmetry k-paths is shown in Fig. 2(d), which shows clearly the completely dispersionless FBs with double degeneracy located on top of two dispersive bands. The FBs touch the dispersive band at the $\Gamma$ point, forming a triple degenerate point, and the two dispersive bands construct the nodal lines along diagonal directions of the square face of BZ (i.e. X-W line). These agree with the calculated band structure of MgV$_2$O$_4$. When considering two $d$ orbitals with slightly different on-site energy, we are able to reproduce the DFT band structure\textsuperscript{52}.

**METAL TO INSULATOR TRANSITION**

However, MgV$_2$O$_4$ is known to have a frustrated AFM ground state, which possesses an insulating state with different electronic properties than the FM case\textsuperscript{33,34,35,36}. In contrast to the FM state, 3D FBs are absent in the AFM ground state of MgV$_2$O$_4$. We seek to engineer the magnetic ground state of MgV$_2$O$_4$ based on DFT calculations. It is worth mentioning that SOC and on-site Coulomb interaction are known to be important for the properties of MgV$_2$O$_4$\textsuperscript{53} and thus all are included in our calculations (see calculation details in Ref\textsuperscript{53}). First, the total energy of the intrinsic MgV$_2$O$_4$ in the FM and AFM states are calculated, which shows that AFM energy, $E_{AFM}$ is about 0.93 eV lower than FM state, $E_{FM}$, in agreement with previous studies\textsuperscript{10,11}. There are several approaches to tuning the magnetic state, e.g., chemical doping, structural engineering, or external magnetic field\textsuperscript{12,13,37,38}. The magnetic field required to change the magnetic state depends on the exchange coupling strength, which is usually hard to manipulate and impractical for devices. Therefore, we focus on the chemical doping and lattice engineering methods.

The strain engineering is accomplished through changing the lattice constant of MgV$_2$O$_4$. We calculated...
the $E_{\text{FM}}$ and $E_{\text{AFM}}$ after applying both isotropic and anisotropic strains. However, within the experimental accessible range, the ground state of MgV$_2$O$_4$ remains to be AFM, as shown in Fig. 3(a). To study the doping effect, we doped the system by changing the total number of electrons of the system while maintaining the charge neutrality with a compensating homogeneous background charge. $E_{\text{FM}}$ and $E_{\text{AFM}}$ for both hole and electron doping scenarios are calculated. As shown in Fig. 3(b), the system remains to be AFM for electron doping while changes to FM with the hole doping of $1 \times 10^{22}$ cm$^{-3}$. We note that this doping concentration is experimentally feasible, which can be achieved through either element substitution or ionic gel gating methods [19,20]. It is also important to mention that apart from a rigid shift of its Fermi level, characteristic band features are preserved after doping, i.e., the 3D kagome band [20]. Therefore, hole doping leads to an insulator-to-half metal transition for MgV$_2$O$_4$, which is consistent with previous experimental observations with Li doping of Li$_x$Mg$_{1-x}$V$_2$O$_4$ [13].

Considering the large variety of the spinel compounds, it should also be possible to find another compounds with FM ground state that host 3D FBs. Such hole doping induced AFM to FM transition has also been reported in chromium (III) spinels [19,21], which could possibly arise due to the breakdown of magnetic frustration, leading to the transition from long-range AFM coupling to short-range FM ordering. Considering the insulating feature of the AFM state without FBs, it is reasonable to expect a negligible AHC in the intrinsic MgV$_2$O$_4$ without hole doping. Therefore, through the hole doping, we actually accomplish a metal to insulator transition with a dramatic change of the AHE simultaneously. We note that due to the limitation of standard DFT in dealing with strong-correlated electrons, exact doping concentration to induce such phase transition from AFM to FM might varies, but the qualitatively phase transition should be valid as already demonstrated by related experiments. Nevertheless, within the standard DFT formalism where electrons correlations are treated in a Hartree-Fock mean field manner, we conclude hole doping to be the most effective and feasible approach to experimentally access the intriguing FM state of MgV$_2$O$_4$.

**HALF-METALLICITY INTERFACE**

Finally, it should be noted that MgV$_2$O$_4$ has a very small lattice mismatch of $\sim 0.7\%$ with MgO, and a similar structure, yielding a smooth interface with MgO. Therefore, it could be used as a spacer layer in magnetic tunnel junction (MTJ) devices, as shown in Fig. 4(a), or as a spin filtering layer [32]. To demonstrate this possibility, we directly simulate the MgO/MgV$_2$O$_4$/MgO heterostructure along (111) direction with three V layers. Interestingly, MgV$_2$O$_4$ remains a half-metal even after integrating with MgO. Figure 4(b) presents total DOS of the heterostructure and PDOS of MgV$_2$O$_4$ layer in the supercell, which shows an almost complete spin polarization for the sandwiched MgV$_2$O$_4$ layer.

**SUMMARY**

In this paper, by using first-principles calculations, we studied the experimentally synthesized MgV$_2$O$_4$ spinel compound and observed interesting 3D FBs in its FM phase. Vanadium atoms reside at the center of octahedrons forms a geometric frustrated 3D kagome lattice, which give rise to the 3D FBs right above the Fermi energy. PDOS calculations revealed that vanadium $t_{2g}$ orbitals contribute to the FBs, which was further confirmed by MLWFs calculations. Through hole doping, MgV$_2$O$_4$ with the insulating AFM ground state can be tuned into FM state, which is an ideal half-metal. Inter-
estingly, the FBs contribute to a giant anomalous Hall effect right above the Fermi level. We believe these findings can greatly enrich the materials that have 3D FB, which could facilitate future experimental validation. Also, the FM-AFM (half-metal-insulator) transition with tunable AHE will also broaden the application of spinel compounds in spintronics.

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See Supplemental Material at [URL will be inserted by publisher] for calculation methods, AFM band structure, band structure with different U, distorted octahedron field-splitting, double pyrochlore bands, energy difference between FM and AFM state under isotropic strain, bands after hole doping, and wannier90 fitted bands.

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