Large spin gaps in half metals \( MN_4 \) (M=Mn, Fe, Co) with \( N_2 \) dimers

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We predict that cubic \( MN_4 \) (M=Mn, Fe, Co) are all half metals with the largest spin gap up to \( \sim 5 \) eV. They possess robust ferromagnetic ground states with the highest Curie temperature up to \( \sim 10^5 \) K. Our calculations indicate these compounds are energetically favored, dynamically and mechanically stable. It is proposed that self-doping of these 3\( d\) transition metals occurs in \( MN_4 \) due to the reduction in electronegativity of \( N_2 \) dimers. This model can well explain the calculated integer magnetic moments, large spin gaps of \( MN_4 \) and semiconducting behavior for \( NiN_4 \) as well. Our results highlight the difference in electronegativity between transition metal ions and non-metal entities in forming half metals and the role of \( N_2 \) dimer in enlarging the spin gaps for nitride half metals.

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I. INTRODUCTION

Half metals are a class of materials that behave as metals by electrons of one spin orientation and as semiconductors by electrons of the other spin orientation.\(^1\) They are promising candidates for spintronics applications from magnetic tunneling junctions to giant magnetoresistance devices and injecting spin-polarized currents into semiconductors.\(^2\)–\(^4\). For practical applications, ideal half metals should be magnets having high Curie temperatures \( (T_c) \) and large enough half-metallic gaps. Previous studies identified a number of half metals with varying \( T_c \) \((\sim 1100\text{K})\) and gap \((0.5 \text{eV} \sim 2 \text{eV})\), including full heusler \( \text{Co}_2\text{FeSi} \), half heusler \( \text{NiMnSb} \), oxides \( \text{CrO}_2 \) and \( \text{Fe}_3\text{O}_4 \), perovskites \( \text{Sr}_2\text{FeMoO}_6 \), and so on, which have been intensively investigated over the last decades. The search and prediction of new half metal with better performance, however, are still tough tasks.

So far, all known half-metallic candidates lie in a limited structural types and chemical species. They can be basically categorized into two groups: one being high-valence transition metal oxides, the other low-valence transition metal silicides or antimonides. Both groups of half metals contain one or two transition metals centered either in tetrahedra or octahedra in their structures. Ferromagnetism is realized through double-exchange or super-exchange interactions of spins affected by the effects of Hund’s rule, crystal field and orbital hybridization. Two channels of band structure, metallic and non-metallic characteristics, form in terms of spin direction as the most striking feature for half metals. In the non-metallic channel, the valence bands (VB) are always composed of half-filled five \( d \) or three \( p \) orbitals, resulting in full occupation of the bands in one spin direction. These \( d \) electrons come from a single magnetic \( \text{Fe} \) ion in \( \text{Sr}_2\text{MoFeO}_6 \) or two magnetic ions as \( \text{Ni} \) and \( \text{Mn} \) in Heusler \( \text{NiMnSb} \). The \( p \) orbitals usually come from oxygen in the case for \( \text{CrO}_2 \) or \( \text{Fe}_3\text{O}_4 \). Their conduction bands (CB) are, therefore, empty. In the metallic channel, the energy bands composed of hybrid orbitals of \( d \) metals or/and non-metal elements cross the Fermi energy.

From an electronegative point of view, these half-metals can be regarded as formation from high valence transition metal ions and a non-metallic element with large electronegativity, or from low-valence transition metal ions and non-metallic elements with relative low electronegativity. High-valence transition metals in oxides are difficult further to transfer electrons to oxygen or via versa because of metals’ high ionization energy for remaining electrons and large electronegativity for oxygen. So do for the second group half metals with low-valence transition metals where the hopping of electrons are forbidden due to the weak bonding of transition metals and low-electronegative \( \text{Si} \) and \( \text{Sb} \). If a transition metal has a proper number of electrons in its \( d \) subshell to guarantee a full occupation of VB half-metallicity will ensue. \( N_2 \) dimer has a lower electronegativity in comparison with atomic \( N \) as it meets the octet electron rule. Moreover, the \( \pi \) and \( \pi^* \) orbitals in the dimer can serve as the VB and CB with a large gap in the non-metallic channel, helpful in widening the spin gaps for half metals. This proposition deserves a test for there is no known half metals with a dimer as its non-metallic component up to now.

Recently, a new cubic compound \( \text{SiN}_4 \) was predicted to be both thermodynamically and lattice-dynamically stable. Its structure consists of \( \text{SiN}_4 \) tetrahedra connected by \( N_2 \) dimers.\(^26\) In this study, by first principles calculations, we examined the above-mentioned proposition and half-metallicity for \( MN_4 \) (M=Mn, Fe, Co, and Ni). Our results indicate that they are all half metals with
largest spin gap up to $\sim 5$ eV and highest $T_c \sim 10^3$ K except for Ni. We propose that the transition metals are self-doped with their $4s$ electrons due to the relatively low electronegativity of the N$_2$ dimer and the ferromagnetism arises by their spin-parallel $3d$ electrons in the metallic channel. In the non-metallic channel, the large spin gaps can be attributed to the big energy difference between the bonding and antibonding states of N$_2$ dimers.

## II. COMPUTATIONAL METHODS

Geometry optimizations, phonon spectra, band structures were performed using the density functional theory with the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) [27] exchange-correlation potential implemented in CASTEP [28]. Mechanical properties, orbital resolved band structures were calculated by using Vienna $ab$ initio simulation Package (VASP) [29]. The Hubbard repulsion term $U$ was introduced to account for the correlated effects of $3d$ electrons. In calculation of band gaps, the HSE06 hybrid functional was adopted to enhance the accuracy. The detailed calculation methods can be found at the Supplemental Material [30].

### III. RESULTS AND DISCUSSION

As described in Ref. [26], we build MN$_4$ with a diamond-structure (space group $Fd\bar{3}m$) shown in Fig. 1(a), where M is Mn, Fe and Co. In each unit cell, there are eight MN$_4$ tetrahedral units that are connected by N-N bonds. The M ions occupy the Wyckoff 8(a) site, N 32(e) site. After optimization, the M-N and N-N bondlengths are slightly shortened compared with the known compounds [12, 31, 32] and diazenides [33, 34]. Their structural parameters are summarized in Table S1 [30].

The stability of these compounds were examined by phonon spectra, in which no negative frequencies appear, suggesting these compounds are lattice-dynamically stable, see Fig. 2(a), 2(b) and 2(c). Then we evaluate the cohesive energies $E_c$ for MN$_4$, FeN$_4$, and CoN$_4$ along with other Mn, Fe, and Co nitrides for comparison. $E_c$ is defined as $E_c = (E_{M,N_4} - xE_M - yE_N)/(x+y)$, where $E_M$, $E_N$, and $E_{M,N_4}$ are the total energy of a single M atom, a single N atom, and $M_4N_4$ compound. The results are listed in Table I. MnN$_4$, FeN$_4$, CoN$_4$ are either more negative or close to $E_c$ of the known binary compounds, indicating they are energetically stable in terms of cohesive energy. On the other hand, a convex hull analysis based on formation energy is performed. The formation energy

| Compounds | $E_c$ (eV/atom) | Compounds | $E_c$ (eV/atom) | Compounds | $E_c$ (eV/atom) |
|-----------|---------------|-----------|---------------|-----------|---------------|
| FeN$_4$ ($Fd\bar{3}m$) | -5.079        | CoN$_4$ ($Fd\bar{3}m$) | -5.182        | MnN$_4$ ($Fd\bar{3}m$) | -4.867        |
| Fe($F\bar{4}3m$) [12] | -5.188        | CoN($F\bar{4}3m$) [13] | -5.297        | MnN($I4/mmm$) [13] | -4.737        |
| Fe$_2$N ($Pbcn$) [15] | -4.991        | Co$_2$N ($Pnmm$) [16] | -5.393        | Mn$_3$N$_2$ ($I4/mmm$) [17] | -4.703        |
| Fe$_2$N ($P3m1$) [19] | -4.930        | Co$_2$N ($P6_322$) [19] | -5.416        | Mn$_4$N ($Pm\bar{3}m$) [20] | -4.009        |
| Fe$_2$N ($P312$) [21] | -5.050        | Co$_4$N ($Pm\bar{3}m$) [19] | -5.423        |                     |               |
| Fe$_2$N ($P31m$) [22] | -5.050        |                     |               |                     |               |
| Fe$_2$N ($P6_322$) [23] | -5.063        |                     |               |                     |               |
| Fe$_2$N ($P312$) [24] | -5.063        |                     |               |                     |               |
| Fe$_2$N ($Pm\bar{3}m$) [24] | -5.015        |                     |               |                     |               |
| Fe$_2$N ($I4/mmm$) [25] | -4.981        |                     |               |                     |               |

TABLE I. Computed cohesive energies for MN$_4$ and known M-N compounds (M=Fe, Co, Mn).
is defined as $E_T = (E_{M,N} - x\mu_M - y\mu_N)/(x + y)$, where $\mu_M$, $\mu_N$, and $E_{M,N}$ are the total energy of stable bulk crystal A, crystal B, and $A_xB_y$ compound. Fig. 3 along with Table S2 [30] shows that these MN are also stable. Furthermore, for a stable cubic structure, the elastic matrix should satisfy the Born stability criteria [35]:

$$\mu_{AB} > 0, C_{11}C_{12} > 0, C_{11}+2C_{12} > 0, C_{44} > 0.$$  

The structural stability of FeN4 is determined by calculating the total energies of ferromagnetic (FM), antiferromagnetic (AFM), and non-magnetic (NM) states. The FM state is obtained from collinear spin-polarized optimization of identical spin directions of the M atoms (see Fig. S2(a) [30]). The AFM state is just reversing the nearest M spin directions in the lattice (see Fig. S2(b) [30]) and the NM state a non-spin-polarized optimization. Whether or not considering the Hubbard U term, the FM is found to be the ground state with local magnetic moments of 1.99 μB, 1.97 μB, 1.95 μB per formula unit for MnN4, FeN4, CoN4, respectively. The FM coupling strength, or the FM coupling constant $C_{FM}$, can be estimated by the mean-field approximation (MFA) through $E_{FM} = 2\Delta E/3N$, where $E_{FM}$ is the Boltzmann constant, $N$ is the number of magnetic atoms in the unit cell and $\Delta E$ the energy difference between AFM and FM states. This formula, however, usually overestimates $C_{FM}$. By using empirical relationship $T_C/T_{FM} = 0.8162$, we correct the $T_C$ list them in Table II. All $T_C$s are well above room temperature, especially for FeN4 with $T_C = 2.70 \times 10^3$ K, much higher than that for known ferromagnets.

Fig. 4 (a-c) show the spin resolved band structures of MN4 (M=Mn, Fe, Co) calculated by PBE exchange functional, where the Fermi level is set to be zero. In the spin-down sub-band, a metallic feature shows up. While in the spin-up sub-band, a semiconducting feature with varying gap emerges. The calculated $T_C$s and gaps of MN4 and known half metals are summarized in Table II. Among them, FeN4 owns the largest spin gap $\sim 2.65$ eV. The effect of the on-site Hubbard $U$ of 3d metals should be taken into account. If we adopt $U=3.8$ eV for Fe, a modest value as in Ref. [48], this yields a gap $\sim 3.63$ eV, see Fig. S3(b) [30]. To get a more accurate half-metallic gap for FeN4, we performed the calculation using the HSE06 hybrid functional (see Fig. 5(a) and 5(b)) and got a spin gap $\Delta = 5.39$ eV. It is noted that the energy spans, labeled $\Delta$ and $\Delta'$ in Fig. 4(f), are 3.29 eV and 2.10 eV, respectively, which are wide enough to prevent spin-flip transitions by thermal excitations.

Apart from MnN4, FeN4, CoN4, extension to other isostructural 3d transition metals VN4, CrN4, and NiN4 is tried. Again, no any negative frequencies are present in their phonon spectra for CrN4 and NiN4 (see Fig. S4 [30]). For VN4, a small negative value $\sim 0.3$ THz is present near point L, which can be neglected in comparison with its large positive frequencies. In contrast, considerably negative frequencies exist for ScN4, TiN4, CuN4 and ZnN4. Among the lattice-dynamically stable
structures, none is magnetic and VN4, CrN4 are normal metals (Fig. S5 [30]). Of particular interest, NiN4 is a semiconductor, see Fig. 3(d). Their lattice parameters and properties are summarized in Table S1 [30].

Now, we try to understand the origin of the half-metallicity of MnN4. Fig. 5(a) and 5(b) show the orbital resolved band structure of non-metallic and metallic channels for FeN4, respectively. The 3d orbitals of Fe atoms are split into two groups, t2g orbitals \((d_{xz}, d_{yz}, d_{z^2})\) and e orbitals \((d_{x^2−y^2}, d_{z^2})\), which is consistent with the situation under a tetrahedral crystal field. Apart from the sp hybrid orbitals, \(\pi\) and \(\pi^*\) orbitals are expected to form in N2 dimers since electron density accumulations in between N-N dimers can be clearly seen in Fig. 5(d). In the non-metallic channel, the VB are composed mainly of the Fe t2g orbitals and the CB of the N \(\pi^*\) orbitals. It is noted that the energy is weakly dispersed in the VB, suggesting Fe 3d are not strongly bonded with the N2 dimers. A similar situation occurs in the bands just above the Fermi energy in the other channel. The \(\pi\) bands (not shown) in both channels are far below the Fermi energy due to the wide energy separation of the \(\pi\) and \(\pi^*\) orbitals in the N2 dimers.

Here we propose a model showing the bonding states between an Fe atom and four N2 dimers sketched in Fig. 5(c). As the Fe atom is coordinated by four N2 dimers, four \(\sigma\) bonds might form from Fe-4sp\(^3\) orbitals and N-2sp orbitals. Since Fe-4sp\(^3\) is much higher than N-2sp in energy, these electrons in the \(\sigma\) bonds can be totally contributed by the latter. A similar hybridization of Co-Si bond in Heusler Co2MnSi [49] was observed. If this is true for the Fe-N \(\sigma\) bonds, then Fe 4s electrons can only flow into its d orbitals. That is the so-called self-doping, resulting in an Fe 3d electron configuration \(↑↑↑↑↑↑↑↑↓↓↓↓\), in good agreement with the calculated magnetic moment \(2\mu_B\) per FeN4 formula unit. More importantly, in the non-metallic channel, the Fe 3d orbitals are fully occupied by five electrons, giving rise to a completely filled VB and an empty CB as the \(\pi^*\) orbitals are far higher in energy. In this way a large gap appears as labeled \(\Delta\) in Fig. 5(c). The charge density shown in Fig. 5(e) confirms that the main occupancy of the Fe 3d electrons in the VB and the empty of N-N antibonding states in the CB. On the contrary, in the metallic channel, Fe 3d orbitals are only occupied by three electrons, hence the corresponding band crosses the Fermi energy.

This model could theoretically explain the integer magnetic moments for MnN4, CoN4 and NiN4. Since Mn and Co have one less and one more 3d electron compared with Fe, their moments are, therefore, 3\(\mu_B\) and 1\(\mu_B\), respectively. In both cases, their VBs are fully occupied by five 3d electrons in their non-metallic channels. For Ni, its 3d orbitals will be occupied by eight 3d and two 4s electrons, leading to full occupations in both channels. Hence, it is a semiconductor.

Considering spin interactions in a linear Fe-N2-Fe way, a double-exchange like mechanism may be applicable here to establish the long-range magnetic ordering, see Fig. 5(f). If an electron hops from Fe 3d orbitals to the neighboring N2 dimer \(\pi^*\) orbitals by thermal excitations in the metallic channel, the vacancy will be filled by another spin-down electron from another neighboring N2 dimer. This is rather probable because these orbitals are overlapped to some extent, see Fig. 5(b). This way will help retain the spin direction and hence maintain the FM state.

The self-doping phenomena of Fe can be understood from the electronegative point of view. A N2 dimer, as a chemical spice, is quite inert and low electronegative as it meets the octet electron rule. It, however, can act as a non-metallic element and form a variety of compounds with active metals. The reason is that a N2 dimer has empty \(\pi^*\) orbital, which can accommodate electrons from active metals. Such metals are usually alkali and alkaline-earth metals with high-enough energy \(s\) electrons. Typical examples are SrN and SnN2 [50], both containing N2 dimers in their structures and electrons in the \(\pi^*\) orbitals. Similarly, electron transfer to O2 dimer occurs in magnetically frustrated Rb2O6 [51-53]. Here less active Fe has a little stronger electronegativity than Sr, whose 4s\(^2\) electrons are expected not to transfer to the N2 dimers’ \(\pi^*\) orbitals. Instead, they go to Fe’s 3d orbitals, that is, the self-doping of Fe. Our above calculations support that in the ground state, the \(\pi^*\) orbitals are unoccupied.

The robustness of half metallicity is examined for FeN4. Fig. 5(f) shows that the magnetic moment and energy difference \((E_{FM}-E_{AFM})\) under strains, where the strain was simulated by \(\varepsilon=(a-a_0)/a_0\times100\%\). The half metallicity keeps against AFM until a tensile strain \(\sim10\%\), but collapses at a \(\sim4\%\) compressive strain. The large spin gap depends much on the splitting of \(\pi\) and \(\pi^*\) energy level. To check the effects of N-N bondlength on the spin gap of FeN4, we enlarged the N-N distance while keeping the Fe-N distance intact. As N-N being far away, \(\pi\) and \(\pi^*\) get close to each other, resulting in decreased spin gap but a constant magnetic moment, see Fig. 6. Hence, the large spin gap originates from the appropriate bondlength of N-N. These calculated results agree well with our proposition that N2 dimers act as an electron receiver accommodating by their \(\pi^*\) orbitals with a reduced electronegativity. The reduced electronegativity is consistent with the self-doping phenomenon in FeN4.

| Compounds | MnN4 | FeN4 | CoN4 | CrO2 | Sr2FeMoO6 | NiMnSb | Fe3O4 | Co2FeSi |
|-----------|------|------|------|------|-----------|--------|-------|--------|
| \(T_c\) (K) | 1.90×10\(^4\) | 2.70×10\(^4\) | 8.18×10\(^4\) | 386 | 419 | 947 | 730 | 835 | 851 | 1100 |
| Gap (eV) | 2.36 | 2.65 | 2.56 | >1.5 | 0.8 | 12 | 0.4 | 13 | 0.5 | 14 | 0.86 | 14 |

TABLE II. Half-metallic gaps (PBE) and \(T_c\)s for MnN4, FeN4, CoN4 and known compounds.
Recently, Chen et al. \cite{54} predicts that FeN4 has space groups of P1 and Cmmm under different pressures using CALYPSO methodology \cite{55}. Bykov et al. \cite{56} synthesized another FeN4 with space group P1 by high-pressure and laser-heating method. To compare the relative stability among them, we computed the enthalpies of them at different pressures, see Fig. 7. The results show that our diamond-like FeN4 will transform to P1 symmetry under 2.78 GPa. Hence, high pressures may not work for synthesizing FeN4 we predict here. But it is similar to T-carbon \cite{57} in both structure and low density. The latter compound has been successfully synthesized by picosecond laser irradiation under a nitrogen atmosphere \cite{58}. It might be a choice to apply similar conditions to synthesize MN4.

**IV. CONCLUSIONS**

By first principles calculations, we predicted three half metals MnN4, FeN4 and CoN4. They crystallize in a diamond-like structure with space group Fd̅3m. They are not only favored in energy, lattice-dynamically and mechanically stable, but also possess robust FM coupling with the highest Curie temperature \( T_C \sim 10^3 \) K. Band structures indicate the largest spin gap is around 5 eV (HSE06). The proposition of self-doping of these 3d transition metals caused by the reduction in electronegativity of N2 dimers, well explains the calculated integer...
magnetic moments of $MN_4$. The $N_2$ dimer plays an important role in enlarging the spin gap for half metal $MN_4$ ($M$=Mn, Fe, Co). Other emergent magnetic properties are expected in compounds consisting of $d$ metals and $N_2$ dimers with modified structures.

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