Non-perturbative Super-exchange Interaction for High Curie Temperature in Intrinsic Magnetic Semiconductor

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Here a non-perturbative super-exchange interaction is unveiled in co-valency scheme which allows long-range ferromagnetic exchange interactions, thus naturally gives intrinsic room-temperature ferromagnetic semiconductors. To realize such a scheme in transition metal compounds, two comparable energy scales are indispensable: i) the electron-electron interactions are comparable to the onsite energy difference between ligand p and metal d orbitals and ii) the hopping strengths between p and d orbitals are comparable to their band widths. Guided by these principles, a paradigm based on first-principles calculation and Wannier downfolding is then built to search for realistic materials. Through thorough physical parameter mining on 36 FeSe-like trilayer structures, CrAs monolayer is mapped out to belong to co-valency scheme, which possesses a band gap $\sim 0.45$ eV, ferromagnetic nearest-/next-nearest-neighbor exchange coupling strength $\sim 57/40$ meV, and correspondingly a high Curie temperature about 1500 K.

**Introduction.** Room-temperature ferromagnetic semiconductors (FMSCs) are highly needed for next-generation spintronic devices, such as processing-in-memory, spin field-effect transistors, magnetic tunnelling junctions and so on [1–3]. However the incompatibility between semiconductivity and ferromagnetism makes their combination a highly non-trivial task. By doping magnetic ions into the nonmagnetic semiconductor [4–5], diluted FMSCs provide an encouraging way towards room-temperature FMSCs [6–8]. Nevertheless, the difficulty in manipulating magnetic impurities greatly hinders their developments [9]. Here we will focus on intrinsic FMSCs.

Traditional realization of intrinsic FMSCs relies on super-exchange interaction (SEI) [11–13] to mediate long-range FM order in Mott-Hubbard insulators [14–15]. In these insulators, ligand p shell is closed which makes a perturbative treatment of SEI possible. Two drawbacks are inherited from such a perturbative treatment: firstly, with an low-energy effective theory main described by narrow $d$ bands, the effective mass of charge carriers are generally heavy [14–15]. Secondly, antiferromagnetic (AFM) SEI always wins over the FM counterpart [16]. Consider the case where two metal ions are identical and share the same coordination environment, the AFM/FM SEI is then contributed by the 180° geometry respectively [11–13] as displayed in Fig. 1(a). Such geometrical difference makes FM only $J_H/2U$ of AFM SEI, where $J_H$ is the Hund’s (Hubbard) interaction of ligand $p$ (metal $d$) orbitals. Although AFM semiconductor can have Neel temperature around 1000 K, with $J_H$ one order smaller than $U$, it is hard for FMSCs to have Curie temperature ($T_c$) above room temperature. For example, two-dimensional (2D) CrI$_3$ and CrGeTe$_3$ only present a $T_c$ around 45 K [17–18].

In this work, we show a non-perturbative treatment of SEI can solve the above two inborn drawbacks simultaneously. Such a non-perturbative SEI can be achieved in co-valency scheme demonstrated below and thus offer a workable solution to intrinsic room-temperature FMSCs.

Figure 1: Diagrammatic illustration of co-valency scheme. (a) 90° and 180° geometry in SEI, ligand $p$ (blue filled circle) and metal $d$ orbital (red filled circle) are bonded by direct exchange interaction (black line). (b) The energy difference between ligand $p$ band and metal $d$ band (red dashed line) is $\varepsilon_{dp}$. With Hubbard $U$ on $d$ orbitals turning on, $d$ band is split into lower Hubbard and upper Hubbard band (LHB & UHB). Our starting point is $U/2 \sim \varepsilon_{dp}$. (c) With long-range FM order formed, each band is classified by spin degree of freedom (black arrows). The strong direct exchange in (a) leads to opposite energy shift between LHB and spin up $p$ band. (d) With $V_{dp} \sim W_p$ & $W_d$ switching on, a hybridization gap occurs which separates anti-bonding (yellow) and bonding (purple) bands. If bonding/anti-bonding band is filled/empty, long-range FM order is stabilized. (e) Schematic view of an effective orbital formed during $p$-d orbital hybridization. The dashed circle represents original atomic orbitals of (a). In (b)-(d), Fermi level is marked by the dashed line.
Co-valency scheme. In transition metal compounds, ligand p band (filled blue region in Fig. 1(b)) always has lower energy than metal d band (red dashed line in Fig. 1(b)) and the energy difference is labelled by \( \varepsilon_{dp} \). With Hubbard interaction of d orbitals (U) turning on, d band splits into lower Hubbard and upper Hubbard band (LHB & UHB, filled red line in Fig. 1(b)). With \( U/2 < \varepsilon_{dp} \), the system is Mott-Hubbard insulator. The region we are interested in is \( U/2 \sim \varepsilon_{dp} \) (Fig. 1(b)), akin to the charge-transfer insulator \( 14,15 \). Although charge-transfer insulators typically have AFM ground state like in cuprates \( 19,20 \), here we assume a FM ground state and the resulting energy diagram will be like Fig. 1(c). With up and down spins (black arrow) no longer degenerate, all the bands can be indexed by spin components, such as LHB is occupied by up spin electrons. Considering the fact that metal ions and nearby ligands are bonded by strong direct exchange (black line in Fig. 1(a)), ligands have opposite spin to nearby metal ions \( 21 \). Thus p band with up spin will shift upwards, in contrast to LHB (Fig. 1(c)). Such an opposite energy shift will reduces the Hubbard \( U \) needed in forming Fig. 1(b). Fig. 1(d) demonstrates the mechanism in stabilizing FM order. With hopping between ligand p and metal d orbitals (\( V_{dp} \)) switching on, LHB will hybridize with p band and a hybridization gap occurs when \( V_{dp} \) is comparable to their band width (\( W_p \) and \( W_d \)). By controlling the electron filling up to the hybridization gap, the FM state can be stabilized. Such stabilization can be clearly seen from orbital hybridization: the valence bands are no longer formed by atomic d and p orbitals but effective orbitals which are linear combination of these local orbitals as schematically depicted in Fig. 1(e). These effective orbitals are non-local with larger orbital spreading than the atomic ones (compare Fig. 1(a) and Fig. 1(e)) and the spreading can act as a characteristic length \( L \) for exchange coupling strength \( (J) \). Within \( L, J \) should have the same sign between any pairs of metal ions shown in Fig. 1(e) (thus ferromagnetic) and decay much slower than that beyond \( L \). Therefore, the competition between AFM and FM does not exist. In addition, thanks to the large spreading, these bands have large band width and small carrier effective mass. In this way, the inborn disadvantages of perturbative treatment no longer exists here. With comparative ferromagnetic nearest-neighbor (NN) exchange coupling strength \( (J_1) \) and next-nearest-neighbor (NNN) ones \( (J_2) \), the \( T_c \) will be greatly enhanced.

The coexistence of band gap and FM order in such a scheme offers a natural solution to intrinsic room-temperature FMSCs. Here it is called "co-valency scheme", for the reason that the formation of effective orbitals is in close analogy to the formation of covalent bonds. In Mott-Hubbard insulators, \( \varepsilon_{dp} \) is the leading energy scale which makes perturbation possible and p orbitals do not participate in low energy excitations. This is obviously not the case in co-valency scheme. There is no leading energy scale and both p and d orbitals are involved in excitations (see Fig. 1(d)) during the formation of effective orbitals, which makes the SEI non-perturbative. On this occasion, besides Hubbard U interaction of d orbitals, other electron-electron \( (e-e) \) terms like Hubbard interaction of p orbitals and even non-local interactions should also contribute to formation of FM order. For this reason e-e interactions will be used as the energy scale rather than \( U \) in subsequent.

Material searching paradigm. To search for a realistic material satisfying co-valency scheme, a paradigm based on basic material knowledges is built here. According to above discussion, there are three requirements: i) \( \varepsilon_{dp} \sim e-e \) interactions; ii) \( V_{dp} \sim W_p \) and \( W_d \) and iii) suitable electron filling. These requirements are almost decoupled in a given lattice structure: \( \varepsilon_{dp}, e-e \) interactions and electron filling are mainly element-related, while \( V_{dp} \) and \( W_{p/d} \) are mainly structure-determined \( 22 \). Accordingly, co-valency scheme can
be realized by placing various metal/ligand (labelled as M/X herein) on a lattice structure bearing strong $V_{dp}$. 2D FeSe-like trilayer structure \[23, 24\] is a fertile candidate for two related phenomenon: first of all, $J$ can be as large as 50 meV in monolayer FeSe \[25, 26\], which strongly indicates large $V_{dp}$. Secondly, by K$^+$ charge doping and Mn$^{3+}$ spin doping into the narrow gap semiconductor $\beta$ – BaZn$_2$As$_2$ (ZnAs shares FeSe-like structure), the obtained $T_c$ can reach 180 K [8]. A strong $V_{dp}$ is necessary for strong FM exchange interactions between Mn$^{3+}$ impurities \[27\].

For the M-X combinations, M=Cr, Mn, Fe, Co, Ni, Cu and X=P, As, Sb, S, Se, Te are chosen here. We focus on 3d transition metals for two reasons: firstly, they are lighter than their 4d and 5d cousins, the relativistic effect will be much weaker and won’t drive the FM phase to other phases like quantum spin liquid \[28\]. Secondly, 3d orbitals has large Hund’s coupling than 4d and 5d, therefore high spin state is preferred when multiple spin configurations are possible \[29\]. As for the ligand, the stable charge is 3-/2- for pnictogen/chalogen family, the common seen M$^{2+}$ and M$^{3+}$ will be covered which provides a way to modify the electron filling. It is noteworthy the widely distribution in ThCr$_2$Si$_2$- \[30, 31\] and ZrCuSiAs-family materials \[32, 33\] makes these monolayers easily accessible.

### Physical parameter mining.

Wannier downfolding allows us to obtain parameters $\varepsilon_{dp}$, $W_p$, $W_d$ through the investigation of paramagnetic (PM) phase \[40\]. Fig. 2 shows the fitted parameters for all the 36 monolayers. Seen from Fig. 2(a)-(b), there are three main types for $\varepsilon_{dp}$: Type-I where $\varepsilon_{dp} > 0$, most chalcogenides belong to this type except for M = Cu. In this type, large $e-e$ interactions are needed to push LHB close to $p$ band. Considering $U$ is around 3 eV in iron chalcogenides \[41\], such a small $U$ can only drive the systems into $d$ metal which prefers AFM configurations as in iron chalcogenides \[42, 43\] (Fig. S9). In contrary, Type-III has $\varepsilon_{dp} < 0$, this applies for copper pnictides. The left belong to Type-II where the energy levels of $p$ and $d$ orbitals are very close. This is the region we prefer since the first requirement of the co-valency scheme can be achieved with not-so-strong $e-e$ interactions.

As intra-$d/p$ orbital hoppings are small, $W_p$ and $W_d$ are approximated by their crystal field splitting (CFS). From Fig. 2(a)-(b), both $W_d$ and $W_p$ are small (< 1 eV) for most MX monolayers. Fig. 2(c)-(j) demonstrate the symmetry allowed $V_{dp}$. The point group of the trilayer structure is $S_4$, which can obtained from the planar D$_{3h}$ by introducing buckling (on X). In perturbative SEI, structural deviation from 90° and 180° is often deliberately avoided since it reduces the per-
turbation strength severely. This is not required in co-valency scheme illustrated here. In D_{4h} the five d orbitals split into four groups: \{d_{x^2}, d_{x^2-y^2}, d_{xy}, d_{xz}/yz\} and the symmetry allowed \(V_{dp}\) are shown in inset of Fig. 2(c)-(f). Without any buckling, the strongest interaction comes from the \(\sigma\)-type \(d_{x^2-y^2-p_{x/y}}\) (Fig. 1(f)), which can be as large as 1.3 eV in CuO_2 planes in cuprates [14]. When the structure is buckled, the splitting of d orbitals remain the same, but additional \(V_{dp}\) are now permitted as shown in inset of Fig. 2(g)-(j). Such buckling can not be regarded as perturbations since the strongest \(\sigma\)-type \(d_{x^2-y^2-p_{x/y}}\) interaction in D_{4h} is now even weaker than the \(\sigma\)-type \(d_{x^2-y^2-p_z}\) interaction (compare Fig. 2(d) and 2(h)). Next we focus on effective orbitals. Two of the corresponding anti-bonding orbitals \(\pi\)-type \(d_{xy-p_{x/y}}\) interaction (see Fig. 2(e)). These strong \(V_{dp}\) are compared or even larger than \(W_p\) and \(W_g\), meeting the second requirement of co-valency scheme.

Ferromagnetic CrAs monolayer. When e-e interactions are considered, local magnetic momenta (S) is formed and its effect on onsite energy can be investigated by studying the FM phase [33]. The obtained CFS for FM CrAs monolayer is shown on Fig. 3(a). Compared with PM, \(\varepsilon_{dp}\) undergoes a type change: Type-II (PM) \(\rightarrow\) Type-III (up) \(+\) Type-I (down), in accordance with Fig. 1(b). As demonstrated in Fig. 3(c), the \(\varepsilon_{dp}\) in the down spin is so large (more than 3 eV) that there is a large gap 2.82 eV regardless of the large \(V_{dp}\). For the up spin, the interaction is totally different: \(\varepsilon_{dp}\) between \(p_{xy}\) and \(\{d_{x^2}, d_{xy}, d_{xy}\}\) is even smaller than the corresponding \(V_{dp}\). Such strong \(V_{dp}\) pushes the anti-bonding orbitals so high that the corresponding band is separated from others with an indirect gap \(\sim 0.45\) eV as shown in Fig. 3(b). For the 18 electrons from Cr d and As p orbitals, 6 of them occupy the spin down bands and the left 12 electrons occupy the spin up bands. Seen from Fig. 3(b), these 12 electrons just fill bands up to the gap which makes CrAs monolayer special. Since P and As have same number of p electrons, CrP monolayer also belongs to co-valency scheme (Fig. S16). Next we focus on effective orbitals. Two of the corresponding anti-bonding orbitals are displayed in Fig. 3(d), the other two are connected to these two by C_2 rotation and ignored here. The effective orbital on the left is the linear combination of As1 \(p_y\), Cr2 \(d_{xy}\) and Cr1 \(d_{xz}\) while the right is constituted by As1 \(p_y\), Cr2 \(d_{xz}\) and Cr1 \(d_{xy}\), in accordance with the orbital composition of these bands depicted in Fig. 3(b). Such an orbital hybridization makes the effective orbitals highly non-local with L covering the NNN Cr dimers (see Fig. 3(d)). Two important results come along: on the one hand, the effective band width is wide, so the charge carriers have smaller effective mass. The calculated density of state effective mass for light hole (electron) at \(\Gamma\) (M) point is \(\sim 0.24\) (0.21) \(m_e\) (\(m_e\) is bare electron mass) (see Table S2). On the other hand, \(J_2\) should be comparable to \(J_1\) and the ground state is FM.

In order to map \(J_1\), \(J_2\) out, three symmetric magnetic orders are considered in a \(2 \times 2 \times 1\) supercell (see Fig. 4(a)-(c)): FM with magnetic ordering momentum \(q=(0, 0, 0)\), checkboard AFM (c-AFM) with \(q=(-\pi, \pi, \pi)\) and strip AFM (s-AFM) with \(q=(0, \pi, \pi)\). The spin model used here is the Heisenberg model:

\[
H = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \tag{1}
\]

where summation is over \(J_1\) and \(J_2\) as defined in Fig. 4(a). And the energy for these three magnetic orders are calculated as:

\[
E_{FM} = E_0 + 16J_1S^2 + 16J_2S^2
\]

\[
E_{c-AFM} = E_0 - 16J_1S^2 + 16J_2S^2
\]

\[
E_{s-AFM} = E_0 - 16J_2S^2
\]

where \(E_0\) is a reference energy. The calculated \(E_{FM}\), \(E_{c-AFM}\) and \(E_{s-AFM}\) with respect to an energy shift are \(0.0.511\) and \(0.632\) eV, respectively. Plugging \(S=\frac{3}{2}\) into above equations, the obtained \(J_1\) and \(J_2\) are \(-56.8\) and \(-39.7\) meV, both are ferromagnetic. \(J\) of further distance (\(J_3\) and \(J_4\)) are also considered and there is sharp jump from \(J_2\) to \(J_3\) with \(J_3\sim 0\) meV (Fig. S19), in agreement with the range of L. In perturbative SEI, one expects the \(J\) to be rather short-range, the real surprise here is the magnitude of \(J_2\) over \(J_1\). The ratio \(J_2/J_1 \sim 1/\sqrt{2}\) strongly implies linear-law scaling here, as opposed to the power-law decaying in perturbative SEI. As both \(J_1\) and \(J_2\) are ferromagnetic, the magnetic ground state in such square lattice is FM, in accordance with first-principles calculations. To determine \(T_c\), classical Monte Carlo (MC) simulations are performed for a \(32 \times 32 \times 1\) supercell (Fig. S20) based on Heisenberg Hamiltonian with \(J_1\) and \(J_2\) [40]. During FM-PM phase transition, magnetic sus-
ceptibility is calculated after the system reaches equilibrium at a given temperature, then $T_c$ corresponds to the position of peak in magnetic susceptibility plot as shown in Fig. 4(d). As anticipated, an ultra-high $T_c \sim 1500$ K is obtained. For 2D magnets, strong magnetic anisotropy energy (MAE) is needed to break the Hohenberg-Mermin-Wagner theorem \cite{45, 46}. Since the highest occupied and lowest unoccupied orbital are mainly contributed by Cr $d_{xz/yz}$ and $d_{xy}$ in the up spin (see Fig. 3(b)), the orbital angular momentum difference ($|\langle L_z \rangle|$) between these orbitals is 1, the prefer spin orientations of magnetic ions should be perpendicular to out-of-plane direction \cite{49, 50}. To verify this point, spin-orbit coupling (SOC) is taken into account in calculating the relative energies along (001) and (100) direction. It is (100) that is the easy axis, in accordance with orbital composition analysis. The calculated MAE is $\sim 0.37$ meV/Cr, comparable to that in Cr$_3$ \cite{51}.

Discussion and Conclusion. To explore more properties about the non-perturbative SEI, here charge doping is used as a pump. Generally, extra charge doping will introduce itinerant ferromagnetism into the system which will enhance the ferromagnetism. From Fig. 1(c), the doping of holes (electrons) will decrease (increase) the occupation of bonding (anti-bonding) states, hence doping will destabilize the FM ground state. To see the competence of these two factors, here moderate $(7 \times 10^{13}/\text{cm}^2)$ and heavy $(14 \times 10^{14}/\text{cm}^2)$ electron/hole doping are considered in CrAs monolayer. Fig. 4(e) displays $J_1$ and $J_2$ of different doping. With moderate charge doping, $J_1$ and $J_2$ are smaller than that without doping, suggesting the destabilization even overcomes the itinerant enhancement. If we further magnify the doping concentrations to heavy regime, the destabilization becomes larger and both $J_1$ and $J_2$ further decline. Fortunately original $J_1$ and $J_2$ are quite large, the small decrements still afford high $T_c$ over 1300 K (see Fig. S21).

Finally, the experimental preparation of CrAs monolayer is proposed. The existence of bulk CrAs in nature \cite{52, 53} suggests the 1:1 stoichiometric ratio in CrAs monolayer is charge feasible. The stability of CrAs monolayer is confirmed by both phonon spectrum and ab-initio molecular dynamics (AIMD) (Fig. S22). With layered material BaCr$_2$As$_2$ \cite{52} and LaCrAsO \cite{39} been synthesized in experiments, CrAs monolayer can be obtained by either etching \cite{54} or electrochemical reactions \cite{55} from these layered materials. Another synthetic way is molecular-beam epitaxy and BaZrO$_3$ (001) (or MgO (001)) is a perfect substrate with 1:1 lattice match. Such a strategy has shown success in CoSb monolayer preparation \cite{55, 57}.

In conclusion, a non-perturbative SEI is found in covalency scheme. With protections from hybridization gap, such non-perturbative SEI gives long-range exchange interaction according to $L$ and provides a natural way towards intrinsic room-temperature FMSCs. In addition to FM order alone, covalency scheme is also a good platform for the combination of FM and other orders (like topology, ferroelectricity) as a high $T_c$ is ensured. In this regard, it is expected that covalency scheme will arouse broad interest in condensed matter physics.

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\begin{thebibliography}{99}

\bibitem{1} A. Fert, Rev. Mod. Phys. \textbf{80}, 1517 (2008).
\bibitem{2} A. Aysar, H. Ochoa, F. Guinea, B. Özyilmaz, B. J. van Wees and I. J. Vera-Marin, Rev. Mod. Phys. \textbf{92}, 021003 (2020).
\bibitem{3} X. Li and J. Yang, \textit{Natl. Sci. Rev.} \textbf{3}, 365-381 (2016).
\bibitem{4} J. K. Furdyna, \textit{J. Appl. Phys.} \textbf{64}, R29 (1988).
\bibitem{5} H. Ohno, A. Shen, F. Matsukura, A. Iwai,A. Endo, S. Katsunoto and Y. Iye, \textit{Appl. Phys. Lett.} \textbf{69}, 363-365 (1996).
\bibitem{6} T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, \textit{Science} \textbf{287}, 1019-1022 (2000).
\bibitem{7} J. M. D. Coey, M. Venkatesan and C. B. Fitzgerald, \textit{Nat. Mater.} \textbf{4}, 173-179 (2005).
\bibitem{8} K. Zhao et al. \textit{Nat. Commun.} \textbf{4}, 1412 (2013).
\bibitem{9} R. Chen et al. \textit{Nat. Commun.} \textbf{12}, 3952 (2021).
\bibitem{10} T. Dietl and H. Ohno, Rev. Mod. Phys. \textbf{86}, 187-251 (2014).
\bibitem{11} J. B. Goodenough, \textit{Phys. Rev.} \textbf{100}, 564 (1955).
\bibitem{12} P. W. Anderson, \textit{Phys. Rev.} \textbf{115}, 2 (1959).
\bibitem{13} J. Kanamori, \textit{J. Phys. Chem. Solids} \textbf{10}, 87-89 (1959).
\bibitem{14} J. Zaanen, G. A. Sawatzky and J. W. Allen, \textit{Phys. Rev. Lett.} \textbf{55}, 418-421 (1985).
\bibitem{15} J. Zaanen and G. A. Sawatzky, \textit{J. Solid State Chem.} \textbf{88}, 8-27 (1990).
\bibitem{16} H. Huang, J. Feng, J. Zhou, H. Xiang, K. Deng and E. Kan, \textit{J. Am. Chem. Soc.} \textbf{141}, 12413-12418 (2019).
\bibitem{17} B. Huang et al. \textit{Nature} \textbf{546}, 265-270 (2017).
\bibitem{18} C. Gong et al. \textit{Nature} \textbf{546}, 265-270 (2017).
\bibitem{19} J. G. Bednorz and K. A. Müller, Z. Phys. B \textbf{64}, 189-193 (1986).
\bibitem{20} P. A. Lee, N. Nagaosa and X.-G. Wen, Rev. Mod. Phys. \textbf{78}, 17-85 (2006).
\bibitem{21} X. Li and J. Yang, \textit{J. Am. Chem. Soc.} \textbf{141}, 109-112 (2019).
\bibitem{22} J. C. Slater and G. F. Koster, \textit{Phys. Rev.} \textbf{94}, 1498-1534 (1954).
\bibitem{23} F.-C. Hsu et al. \textit{Proc. Natl. Acad. Sci.} \textbf{105}, 14262-14264 (2008).
\bibitem{24} Q.-Y. Wang et al. \textit{Chinese Phys. Lett.} \textbf{29}, 037402 (2012).
\bibitem{25} F. Ma, W. Ji, J. Hu, Z.-Y. Lu and T. Xiang, \textit{Phys. Rev. Lett.} \textbf{102}, 177003 (2009).
\bibitem{26} J. K. Glasbrenner, I. I. Mazin, H. O. Jeschke, P. J. Hirschfeld, R. M. Fernandes and R. Valenti, \textit{Nat. Phys.} \textbf{11}, 953-958 (2015).
\bibitem{27} J. K. Glasbrenner, I. Zutic and I. I. Mazin, \textit{Phys. Rev. B} \textbf{90}, 140403(R) (2014).
\bibitem{28} W. Witzczak-Krempa, G. Chen, Y. B. Kim and L. Balents, \textit{Annu. Rev. Condens. Matter Phys} \textbf{5}, 57-82.
\end{thebibliography}
(2014).

[29] G. Cao and P. Schlottmann, *Rep. Prog. Phys.* **81**, 042502 (2018).

[30] Z. Ban and M. Sikirica, *Acta Cryst.* **18**, 594-599 (1965).

[31] M. Shatruk, *J. Solid State Chem.* **272**, 198-209 (2019).

[32] K. A. Filsinger, W. Schnelle, P. Adler, G. H. Fecher, M. Reehuis, A. Hoser, J.-U. Hoffmann, P. Werner, M. Greenblatt and C. Felser, *Phys. Rev. B* **95**, 184414 (2017).

[33] A.-N. Ma, P.-J. Wang and C.-W. Zhang, *Nanoscale* **12**, 5464 (2020).

[34] J. Gu, Z. Zhao, J. Huang, B. G. Sumpter and Z. Chen, *ACS Nano* **15**, 6233-6242 (2021).

[35] V. Johnson and W. Jeischko, *J. Solid State Chem.* **11**, 161-166 (1974).

[36] R. Pöttgen and D. Johrendt, *Z. Naturforsch.* **63b**, 1135-1148 (2008).

[37] X. Li, X. Wu and J. Yang, *J. Am. Chem. Soc.* **136**, 5664-5669 (2014).

[38] Y. Kamohara, T. Watanabe, M. Hirano and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296-3297 (2008).

[39] S.-W. Park, H. Mizoguchi, K. Kodama, S. Shamoto, T. Otomo, S. Matsushita, T. Kamiya and H. Hosono, *Inorg. Chem.* **52**, 13363-13368 (2013).

[40] See Supplementary Material at [http://link.aps.org/supplemental](http://link.aps.org/supplemental) for calculation details and additional results.

[41] A. van Roekeghem, L. Vaugier, H. Jiang and S. Biermann, *Phys. Rev. B* **94**, 125147 (2016).

[42] S. Manna, A. Kamlapure, L. Cornils, T. Hänke, E. M. J. Hedegaard, M. Bremholm, B. B. Iversen, Ph. Hoffmann, J. Wiebe and R. Wiesendanger, *Nat. Commun.* **8**, 14074 (2017).

[43] Y. Zhou et al., *Phys. Rev. Lett.* **120**, 097001 (2018).

[44] M. Ogata and H. Fukuyama, *Rep. Prog. Phys.* **71**, 036501 (2008).

[45] H. J. Xiang, S.-H. Wei and M.-H. Whangbo, *Phys. Rev. Lett.* **100**, 167207 (2008).

[46] F. Lou, X. Y. Li, J. Y. Ji, H. Y. Yu, J. S. Feng, X. G. Gong and H. J. Xiang, *J. Chem. Phys.* **154**, 114103 (2021).

[47] P. C. Hohenberg, *Phys. Rev.* **158**, 383-386 (1967).

[48] N. D. Mermin and H. Wagner, *Phys. Rev. Lett.* **17**, 1133-1136 (1966).

[49] M.-H. Whangbo, E. E. Gordon, H. Xiang, H.-J. Koo and C. Lee, *Acc. Chem. Res.* **48**, 3080-3087 (2015).

[50] Z. Liu, G. Zhao, B. Liu, Z. F. Wang, J. Yang and F. Liu, *Phys. Rev. Lett.* **121**, 246401 (2018).

[51] J. L. Lado and J. Fernández-Rossier, *2D Mater.* **4**, 035002 (2017).

[52] K. Selte, A. Kjekshus, W. E. Jamison, A. F. Andresen and J. E. Engbretsen, *Acta Chem. Scand.* **25**, 1703 (1971).

[53] W. Wu, J. Cheng, K. Matsubayashi, P. Kong, F. Lin, C. Jin, N. Wang, Y. Uwatako and J. Luo, *Nat. Commun.* **5**, 5508 (2014).

[54] B. Anasori, M. R. Lukatskaya and Y. Gogotsi, *Nat. Rev. Mater.* **2**, 16098 (2017).

[55] S. Yang, P. Zhang, A. S. Nia and X. Feng, *Adv. Mater.* **32**, 1907857 (2020).

[56] W. Ding, J. Zeng, W. Qin, P. Cui and Z. Zhang, *Phys. Rev. Lett.* **124**, 027002 (2020).

[57] C. Ding et al., *ACS Nano* **13**, 10434-10439 (2019).