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ABSTRACT

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High-throughput computational discovery of In$_2$Mn$_2$O$_7$ as a high Curie temperature ferromagnetic semiconductor for spintronics

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Materials combining strong ferromagnetism and good semiconducting properties are highly desirable for spintronic applications (e.g., in spin-filtering devices). In this work, we conduct a search for concentrated ferromagnetic semiconductors through high-throughput computational screening. Our screening reveals the limited availability of semiconductors combining ferromagnetism and a low effective mass. We identify the manganese pyrochlore oxide In$_2$Mn$_2$O$_7$ as especially promising for spin transport as it combines low electron effective mass (0.29$m_e$), a large exchange splitting of the conduction band (1.1 eV), stability in air, and a Curie temperature (about 130 K) among the highest of concentrated ferromagnetic semiconductors. We rationalise the high performance of In$_2$Mn$_2$O$_7$ by the unique combination of a pyrochlore lattice favouring ferromagnetism with an adequate alignment of O–2p, Mn–3d, and In–5s forming a dispersive conduction band while enhancing the Curie temperature.

Introduction

Materials combining semiconductivity and magnetism open up possibilities for novel electronic devices that utilise electron spin in addition to charge degrees of freedom. Ferromagnetic semiconductors (FMSs) are in particular valued for their potential in spintronics for spin-polarised transport. Compared to ferromagnetic metals, FMSs are more suited for injecting spin-polarised electrons into non-magnetic semiconductors. A closely related and technologically important phenomenon is spin filtering, which can be realised through the use of FMSs as the tunneling barrier for generating highly spin-polarised current.

FMSs used in spintronics are primarily based on magnetic impurities embedded into conventional non-magnetic semiconductors. The robustness of carrier-induced ferromagnetism is extremely sensitive to the growth conditions and processing methods, and the origin of room-temperature ferromagnetism of such diluted magnetic semiconductors remains a subject of debate.

In contrast, concentrated magnetic semiconductors exhibit long-range magnetism without resorting to extrinsic doping. A few concentrated FMSs have been reported, including Cr halides CrBr$_3$ and CrI$_3$, Cr spinel selenides, Mn pyrochlore oxides, and perovskites such as BiMnO$_3$, CuSeO$_3$, and YTiO$_3$. Among the most studied FMSs for spintronics are the Eu chalcogenides EuX (X = O,S,Se), while providing very good performances in spin-filter devices, the EuX exhibit very low Curie temperature (e.g., $T_C = 69$ K for EuO), which is characteristic for most FMSs known to date.

In addition, the electronic structure of FMSs needs to be tailored in the context of spin transport. For a barrierless electrical spin injection depicted in Fig. 1a, the efficiency is determined by the exchange splitting of the conduction band while a low effective electron mass is appreciated for achieving high carrier mobility.

Analogously, the exchange splitting is critical for spin filtering as it gives rise to spin-dependent potential barriers for the tunneling current (cf. Fig. 1b), resulting in spin-polarised current in favour of the spin with a lower potential barrier. As such, EuO is in particular attractive for spin injection and filtering because of its large exchange splitting of the conduction band (0.6 eV) and highly dispersive conduction band. Nevertheless, its poor air stability along with the low $T_C$ present major obstacles for practical applications.

Combining strong ferromagnetism and attractive semiconducting properties in one material is therefore desirable but remains an open problem. Here, we set out to identify systematically concentrated FMSs through a large-scale computational screening of known compounds. We report on the materials identified and especially their semiconducting properties, their Curie–Weiss temperatures, and their stabilities. In particular, we identify the Mn pyrochlore oxide In$_2$Mn$_2$O$_7$ as a very promising material. We discuss its potential use for spin transport and the inherent structural and chemical reasons for its high performances.

Results

We consider a material to be a good FMS candidate if it offers a high ferromagnetic transition temperature and good semiconducting properties. Because electrons have much longer spin lifetimes than holes, we focus on spin transport based on electrons as illustrated in Fig. 1, and hence look for FMSs with a large exchange splitting of the conduction band and a low electron effective mass. Starting from the materials project (MP) database comprising over 40,000 density-functional theory (DFT) calculations using the semilocal Perdew–Burke–Ernzerhof (PBE) functional and the Hubbard U correction (PBE + U) (for...
transition-metal oxides), we first screen the materials based on their thermodynamic stability (energy above convex hull at 0 K lower than 50 meV per atom) and electronic band gap (>100 meV). This step leads to about 15,300 semiconductors, out of which 3100 compounds show a finite magnetic moment (>0.5 μB) in the ground state (when the computation is initialised in a ferromagnetic state). Among these magnetic materials, only about 1000 compounds exhibit an electron effective mass (me) smaller than 1.5 m0. In comparison, typical semiconductors (e.g. GaAs, Si, and ZnO) present me ranging from 0.05 to 0.5 m0. Figure 2a shows the distribution of me for materials exhibiting a finite magnetisation compared to non-magnetic materials. It is clear that low me materials are mainly of s character. The poor effective mass and strong ferromagnetism are, for instance, present in CrBr3 and certain manganites such as LaMnO3, where a predominant 3d character in the lowest conduction band leads to a high me of over 10 m0. At variance, the low me of EuO (0.4 m0) is remarkable in that the ferromagnetism arises from an indirect exchange between the localised Eu–4f electrons in the valence and the delocalised 5d/6s electrons in the conduction band.33,42

The presence of a non-zero total magnetisation in the 0 K DFT computation with an initial ferromagnetic ordering does not imply that the ground state is necessarily ferromagnetic and that this ferromagnetic configuration is sustained at high temperature. We thereby estimate the magnetic ordering of the ~1000 compounds by comparing the total energies of the ferromagnetic ground state to the antiferromagnetic (AFM) or ferrimagnetic (FiM) one. The difference serves as an indicator of whether the compound in question is dominated by ferromagnetic exchange interactions. To determine the magnetic ground state, we use supercells that contain at least four atoms for each distinct magnetic species. An exhaustive search of the lowest-energy AFM (or FiM) configuration is carried out by enumerating all possible configurations in which half of the magnetic sites are initialised with a positive magnetic moment whereas the other half with a negative magnetic moment. The absolute value of the initial magnetic moment follows the calculated magnetic moment in the FM configuration. We consider only the collinear magnetic configurations as non-collinear calculations would be computationally prohibitive at this stage of screening. We find that less than 30 compounds favour an FM ground state by over 10 meV per formula unit compared to the AFM or FiM configurations (see Table S1 of Supplementary Information), manifesting already the difficulty of finding semiconductors with robust ferromagnetism.

Our computational screening thus far relies on the PBE(+U) calculations. While instrumental in determining the energetic stability among various magnetic orderings, PBE and PBE + U with U values calibrated for formation enthalpies do not warrant a faithful description of the underlying electronic structure. For a higher accuracy and a better treatment, particularly of localised d and f electrons, hybrid functionals such as the Heyd–Scuseria–Ernzerhof (HSE) functional43,44 should be used.45 We have thus performed HSE calculations on the candidates exhibiting the most favourable ferromagnetic ordering (The HSE calculations exclude the pyrochlore oxides containing the lanthanide elements with partially filled f electrons due to convergence issues. Nevertheless, these materials are expected to exhibit more exotic magnetic properties than the simple ferromagnetic ordering46). We report in Table 1 the electron effective mass as well as the Curie–Weiβ temperature θCW obtained from HSE calculations. The latter is defined from the paramagnetic response at high temperature, and is estimated with the random-phase approximation46 as described in Supplementary Information. When known, we also report on their experimental Curie temperature TC. The difference between θCW and TC indicates the degree of geometrical frustration in a magnetic system.44 Notably, the FMSs listed in Table 1 can be classified into five categories: Eu chalcogenides, Cr spinel...
chalcogenides, Bi manganites, Mn pyrochlore oxides, and Mn double perovskites. Figure 3 shows the HSE band structure for a representative compound in each category. Our screening recovers the well-known FMSs in the context of spintronics such as EuO, CdCr$_2$Se$_4$, and BiMnO$_3$. Less traditionally associated to spintronics are the Mn pyrochlores (e.g., In$_2$Mn$_2$O$_7$). The double perovskites, on the other hand, offer significant higher $T_C$ than the simple perovskite counterparts such as BiMnO$_3$ and LaMnO$_3$. The anomalously strong ferromagnetism of La$_2$NiMnO$_6$ stems from the fully occupied $e_g$ manifold of states. For Cr spinels, the strength of ferromagnetism reduces from selenides to sulfides, and eventually inverts to antiferromagnetism for oxides as the ferromagnetic $t_{2g}-e_g$ exchange interaction is outweighed by the AFM $t_{2g}-t_{2g}$ interaction. While the same competing mechanism is also at play for Mn spinels, the exchange interaction is outweighed by the AFM $t_{2g}-t_{2g}$ interaction. The remaining oxides are the pyrochlores and BiMnO$_3$. Among the pyrochlores, In$_2$Mn$_2$O$_7$ is especially noteworthy as it shows the highest $\theta_{CW}$ and the lowest $m^*_e$. While showing similar electronic and magnetic properties as BiMnO$_3$, In$_2$Mn$_2$O$_7$ exhibits a higher air stability thanks to their high stability of the oxidation states of its cations: In$^{3+}$ and Mn$^{4+}$. In comparison with EuO, it offers an even lower $m^*_e$ (0.29 m$_0$), better air stability, and a significantly higher $\theta_{CW}$ (155 K vs 76 K).

The calculated exchange splitting of the conduction band shown in Table 1 for the candidates confirms the good performance in spin filtering with EuO and BiMnO$_3$. Table 1 implies that In$_2$Mn$_2$O$_7$ should also present an excellent spin-filter effect. But as uncertainty remains in the exchange splitting with the HSE calculations and little is known from experiment, we resort to the self-consistent quasiparticle GW calculations (QSGW) with vertex corrections to calculate the electronic structure of In$_2$Mn$_2$O$_7$. The QSGW method does not depend on any adjustable parameter and starting point, and it has been shown to provide a reasonable description of the electronic structure for correlated transition-metal oxides. As shown in the QSGW band structure in Fig. 5a, the exchange splitting further opens up to 1.1 eV, in support of using In$_2$Mn$_2$O$_7$ for efficient spin filtering.

### DISCUSSION

Our large-scale computational screening shows that the viable routes toward ferromagnetism in semiconducting materials involve either the partially filled Eu–4f electrons or the partially filled 3d electrons of transition metals such as Cr, Mn, and to some extent, V. Indeed, the identified FMSs are mostly Cr spinels and Mn pyrochlores. They are commonly characterised by the high-spin $S = 3/2$ state in the 3$d^5$ configuration, which in the (pseudo)cubic crystal field results in an occupied $t_{2g}$ and an unoccupied $e_g$ manifold of states. For Cr spinels, the strength of ferromagnetism reduces from selenides to sulfides, and eventually inverts to antiferromagnetism for oxides as the ferromagnetic $t_{2g}-e_g$ exchange interaction is outweighed by the AFM $t_{2g}-t_{2g}$ interaction. While the same competing mechanism is also at play for the pyrochlores, the larger lattice constant stabilises the ferromagnetic configuration for a series of Mn and V pyrochlore oxides. The double perovskites, on the other hand, offer significantly higher $T_C$ than the simple perovskite counterparts such as BiMnO$_3$ and LaMnO$_3$. The anomalously strong ferromagnetism of La$_2$NiMnO$_6$ stems from the fully occupied $e_g$ state of Ni$^{2+}$, which is unique to this type of material. In comparison, the $e_g$ state is either partially occupied for the Mn$^{3+}$ in BiMnO$_3$ or simply empty for the Mn$^{4+}$ and Cr$^{3+}$ in the case of pyrochlores and spinels.

Our results confirm the challenge in combining adequate air stability, effective mass, Curie, and Curie–Weiss temperatures. In$_2$Mn$_2$O$_7$ offers an exceptional compromise between these three metrics. Among

### Table 1. Properties of identified ferromagnetic semiconductors evaluated with HSE hybrid functional, including the exchange splitting of the conduction band ($2\Delta_{ex}$), electron effective mass ($m^*_e$), and Curie–Weiss temperature ($\theta_{CW}$).

| Material | $2\Delta_{ex}$ (eV) | $m^*_e$ ($m_0$) | $\theta_{CW}$ (K) | $\theta_{CW}^{expt}$ (K) | $T_C^{expt}$ (K) |
|----------|---------------------|-----------------|-------------------|--------------------------|-----------------|
| EuO      | 1.04                | 0.38            | 101               | 76$^a$                   | 69$^a$          |
| EuS      | 0.60                | 0.44            | 30                | 19$^a$                   | 16.5$^a$        |
| EuSe     | 0.54                | 0.44            | 19                | 9$^a$                    | 7$^a$           |
| Cr spinels |                 |                 |                   |                          |                |
| CdCr$_2$S$_4$ | 0.11              | 0.29            | 202               | 152$^{b}$                | 84.5$^c$        |
| CdCr$_2$Se$_4$ | 0.21              | 0.51            | 237               | 204$^b$                  | 129.5$^c$       |
| MgCr$_2$S$_4$ | 0.46                | 0.70            | 170               |                          |                |
| MgCr$_2$Se$_4$ | 0.78                | 0.60            | 216               |                          |                |
| HgCr$_2$S$_4$ | 0.83                | 0.15            | 209               | 142$^d$                  | 36.0$^d$        |
| HgCr$_2$Se$_4$ | 0.54                | 0.12            | 241               | 200$^d$                  | 106$^d$         |
| ZnCr$_2$S$_4$ | 0.48                | 0.32            | 134               |                          | 7.9$^e$         |
| ZnCr$_2$Se$_4$ | 0.11                | 0.23            | 186               |                          | 90$^e$          |
| Mn(V)-pyrochlores |           |                 |                   |                          |                |
| In$_2$Mn$_2$O$_7$ | 0.62              | 0.29            | 133               | 155$^f$                  | 129$^f$         |
| Sc$_2$Mn$_2$O$_7$ | 1.05              | 0.80            | 68                | 77$^g$                   | 29$^g$          |
| Y$_2$Mn$_2$O$_7$ | 1.38              | 0.81            | 63                | 50$^g$                   | 16$^g$          |
| Lu$_2$Mn$_2$O$_7$ | 1.29              | 0.81            | 68                | 60$^g$                   | 15$^g$          |
| Y$_2$V$_2$O$_7$ | 0.87              | 0.62            | 40                | 97$^h$                   | 74$^h$          |
| Bi manganites |                 |                 |                   |                          |                |
| BiMnO$_3$ | 1.25                | 0.60            | 160               | 120$^i$                  | 105$^i$         |
| Double perovskites |             |                 |                   |                          |                |
| La$_2$NiMnO$_6$ | 1.33            | 1.12            | 268               | 302$^j$                  | 270–280$^j$     |
| La$_2$CoMnO$_6$ | 1.13              | 1.37            | 264               | 300$^j$                  | 225$^j$         |
| Bi$_2$NiMnO$_6$ | 1.51              | 0.70            | 174               | 140$^m$                  | 140$^m$         |
| Bi$_2$CoMnO$_6$ | 1.39              | 0.69            | 116               | 95$^m$                   |                |

The experimental Curie–Weiss and Curie temperature are given if available.

$^a$ref. 29
$^b$ref. 87
$^c$ref. 88
$^d$ref. 40
$^e$ref. 89
$^f$ref. 61
$^g$ref. 90
$^h$ref. 91
$^i$ref. 92
$^j$ref. 93
$^k$ref. 47,93
$^l$ref. 94
$^m$ref. 95
$^n$ref. 96
the AFM angles between 130° and 133°. Longer Mn compared to Y2Mn2O7 (not fully account for such strong ferromagnetism as all the highest electron mobility oxide being doped In2O3. Among Mn, the strong ferromagnetism present in In2Mn2O7, leading to the this does not explain the higher $\theta$ CW among Mn(5s)–O and Mn–O interactions at the CBM of the minority spin channel (see Table S2 and Fig. S2 of Supplementary Information). More intuitively, the enhanced ferromagnetism can be understood by the indirect-exchange mechanism involving virtual electron hopping from the O–p to the In–s states in the conduction band. This leaves the O–p state effectively spin polarised and enhances the ferromagnetic super-exchange through the O atom. For this mechanism to take effect, the atomic valence $s$ state needs to be in a reasonable proximity to the O–p state, which is exactly the case of the group 13 elements such as In and Ti, although $\theta$ In–O2 is a half-metal. While pyrochlore oxides comprising other group 13 elements (such as B, Al, and Ga) do not appear as a candidate because of their instability, they indeed exhibit a highly dispersive s-like CBM from the minority channel and a high $\theta$ CW comparable to In2Mn2O7 (see Table S3 of Supplementary Information for the properties of these hypothetical pyrochlore oxides).

Finally, the FMSs need to be $n$-type to facilitate the transport of spin-polarised electrons. To this end, we assess several dopants in In2Mn2O7, among which Sn and Mo are found to incorporate on the In site while acting as shallow donors, analogous to that in In2O3. The computational details of defect calculations are described in Supplementary Information, whereas the formation energies of the dopants in various charge states are given in Fig. S1. We additionally find no evidence of favourable self-trapping of electrons as small polarons in this material and a general unfavourability of native compensating centers like cation vacancies, which suggests that In2Mn2O7 can be effectively $n$-type doped.

In conclusion, we have carried out a large-scale computational screening in quest of concentrated FMSs. Among the very few identified materials, the pyrochlore oxide In2Mn2O7 emerges as a particularly interesting candidate that exhibits robust ferromagnetism, good air stability, and a low electron effective mass, an uncommon combination that is of great promise for high mobility spin transport. While In2Mn2O7 does not yet fulfill the requirement of room-temperature ferromagnetism, its Curie temperature could be potentially increased with epitaxial strain. Indeed, as shown in Supplementary Information, we find that tensile stress due to the lattice mismatch to some semiconductor substrates (such as Si and GaAs) can effectively increase the Curie temperature of In2Mn2O7, but it needs to be practiced with caution as it has adverse effects on the effective mass (see Fig. S3). Other routes, such as doping, can also be explored to enhance the Mn–t2g–O–p states, stabilising the ferromagnetic configuration by shifting the In–O states upward (downward) in the majority (minority) channel. This is supported by the band-resolved crystal orbital Hamilton population (COHP) analysis, showing the antibonding nature of In(5s)–O and Mn–O interactions at the CBM of the minority spin channel (see Table S2 and Fig. S2 of Supplementary Information).
METHODS

First-principles calculations

Collinear spin-polarised semilocal DFT-PBE and hybrid functional HSE calculations are performed with the Vienna ab initio simulation package (VASP). Electron-ion interactions are described by the projector-augmented-wave (PAW) method. We use the Pymatgen package to generate VASP input files based on the structures retrieved from the MP database. Throughout the calculations, the kinetic energy cut-off is set to 520 eV, and a regular \( \Gamma \)-centered \( k \)-point mesh is used with a grid density of 1600 \( k \) points per atom. For transition-metal oxides, the PBE calculation is carried out with the Hubbard \( U \) correction (PBE + \( U \)), for which the \( U \) parameters take the values adopted by the MP following the approach described by Wang et al.

Quasiparticle self-consistent GW calculations are performed with the ABINIT code using the PseudoDojo optimised norm-conserving pseudopotentials. Vertex corrections in the dielectric screening are accounted for through the use of the bootstrap exchange-correlation kernel. The dielectric function is evaluated through the contour deformation method including unoccupied states up to 150 eV above the Fermi level in the summations. The dielectric matrix is represented by a plane-wave basis set with an energy cut-off of 160 eV. The self-consistent iteration of the wavefunctions is restricted to the lowest 2\( N_v \) states where \( N_v \) is the number of the valence bands.

Band-resolved COHP calculations are carried out with a development version of the LOBSTER package. The pbeVaspFit2015 basis is used with the following basis functions: O: 2s, 2p; In: 5s, 5p, and 4d; Mn: 4s, 3p, and 3d. The wavefunctions are obtained using the PBE + \( U \) functional.

Effective mass calculation

The reported effective mass is defined as the conductivity effective mass

\[
(m^*)^{-1} = \frac{\sigma(T, \mu)}{n(T, \mu) e^2 \tau},
\]

where the electrical conductivity \( \sigma \) and the charge carrier concentration \( n \) are computed directly from the Boltztrap calculations with \( T = 300 \) K and a chemical potential \( \mu \) leading to \( n = 10^{18} \text{ cm}^{-3} \). The relaxation time \( \tau \) is assumed to be independent of \( T \) and \( \mu \) following previous high-throughput works.

DATA AVAILABILITY

All data generated or analysed during this study are included in this published article (and its Supplementary Information files).

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Fig. 5  Electron density distributions of the lowest conduction band at the \( \Gamma \) point and QSGW band structures for In\(_2\)Mn\(_3\)O\(_7\) \( a \) and Y\(_2\)Mn\(_3\)O\(_7\) \( b \) in the ferromagnetic configuration. The electron density is plotted on the \((111)\) plane centered at an In (Y) atom, whereas the characters associated with the states are resolved by the fat bands mapped onto the atoms. The significant \( s \) character in the lowest conduction band of In\(_2\)Mn\(_3\)O\(_7\) is absent in Y\(_2\)Mn\(_3\)O\(_7\).
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