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Computational search for itinerant n-type and p-type magnetic semiconductors: Arsenopyrites as a bipolar magnetic semiconductors

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We report a computational search for three dimensional bulk ferromagnetic semiconductors based on itinerant Stoner physics. Stoner based ferromagnetic semiconductors require an unusual combination of high band edge density of states and moderate transport effective mass. Nonetheless, several potential materials are found. We identify arsenopyrites, exemplified by FeAsS as materials that with suitable doping exhibit ferromagnetic semiconducting behavior for both *n*-type and *p*-type dopants. The existence of a material that becomes ferromagnetic for both *p*-type and *n*-type may enable new device concepts, for example ferromagnetic *p-n* junction devices.

Introduction: Magnetic semiconductors are an area where new materials are strongly needed for spintronic applications¹⁻⁴, and as platforms for investigating quantum criticality in low carrier density metals – a very interesting regime⁵⁻⁷. Magnetic semiconductors consisting of Mn-doped GaAs and related semiconductors doped with magnetic transition metal ions have been known for some time⁸⁻¹⁰. Nonetheless, and in spite of considerable effort, these materials suffer from generally low mobility at the doping levels where they are ferromagnetic as well as limits on the Curie temperature. This motivates searches, including computational searches, for alternate classes of materials and different approaches for obtaining favorable combinations of doping levels, mobility and ferromagnetic properties¹¹⁻¹⁴. Approaches that have been proposed for finding new magnetic semiconductors include the exploration of oxides, oxidized metallic glasses, 2D layered materials and doped magnetic insulators¹¹⁻¹⁵.

Computational searches and screens based on first principles results have emerged as a useful tool for identifying materials systems with sought after properties and in finding directions for obtaining difficult combinations of properties¹⁶. This includes magnetic materials and thermoelectrics^{17,18}. Recently, we investigated the possibility of an itinerant magnetic mechanism and identified *p*-type FeS₂ as a potential magnetic semiconductor based on this¹⁹. Importantly, FeS₂ is a diamagnetic semiconductor, meaning that there are no preformed Fe moments in pristine FeS₂. This allows one to obtain a low moment itinerant magnetic state when doped instead of a spin polarized electron system with random large embedded moments that may reduce mobility as may occur in semiconductors doped with magnetic ions. However, this itinerant mechanism relies on an unusual combination of properties, specifically a very high electronic density of states near the semiconductor band edge, while at the same time a sufficient band dispersion to obtain semiconducting rather than insulating behavior.

The implied seemingly contradictory requirement for both heavy and light band mass in a doped semiconductor is related to the challenge of finding high performance thermoelectrics, where a similar conundrum

arises. In thermoelectrics a high band mass is implied by the need for high thermopower, while a low band mass is implied for high conductivity, both of which are needed obtain a high power factor thermoelectric material^{18,20-22}. In that case, a band structure based fitness function, the so-called electronic fitness function (EFF), quantifies the decoupling of the conductivity and thermopower and has been used for screening materials as potential thermoelectrics^{23,24}. This function, which has been implemented in high throughput codes^{25,26}, provides an automatable screen for identifying materials. Interestingly, FeS₂ has also been suggested as a potentially good thermoelectric²⁷. However, it is presently unknown whether FeS₂ can be sufficiently heavily doped with mobile carriers to obtain the predicted *p*-type magnetic semiconductor. In general the question of whether a given material can be successfully doped and if so methods for doing so is a considerable challenge. As such, it is important to find multiple cases in order to make realization more probable.

Approach: Here we use computational screening of some binary and ternary transition element containing semiconductors seeking other materials that may become itinerant magnetic semiconductors when doped. We do this by screening 44 different non-magnetic but transition element containing semiconductors. First we screen the set of compounds using the calculated density of states to find materials that can become magnetic when doped. We also report effective masses, which are of interest for transport and the EFF, and correlations among these quantities. We then perform detailed calculations within the virtual crystal approximation for finite dopings. These are self-consistent calculations, which yield moments (non-zero moments correspond to magnetism), and constrained density functional calculations with the fixed spin moment approximation to assess magnetic energies.

In the Stoner model, a instability towards ferromagnetism occurs when the quantity $N_s(E_F)I \geq 1$, where $N_s(E_F)$ is the Fermi level electronic density of states on a per atom basis for one spin and I is an interaction parameter that is material dependent. Itinerant systems that

exceed the Stoner criterion and have low carrier density are generally ferromagnetic both within band structure theory and in many-body models²⁸. Typical values of I are ~ 1 eV for $3d$ transition metal elements and ~ 0.8 eV for $4d$ or $5d$ transition metal elements^{29,30}. We use those values in our screen, and then verify candidates using self-consistent virtual crystal approximation calculations as described below.

As mentioned, in order to achieve the Stoner criterion, which corresponds to a high density of states at the Fermi level, at a reasonable semiconducting doping level, one needs a very high density of states effective mass. On the other hand, for mobile carriers one requires a reasonably low transport effective mass. For a single isotropic parabolic band the density of states and transport effective mass are the same and are independent of doping level.

The density of states and transport masses are not, however, the same for a general non-parabolic band structure and in fact can have significant temperature and doping level dependence in that case. Here we seek materials where there is a decoupling of these two masses to identify candidate materials. We proceed using first principles electronic structure and transport calculations. The calculations were done using the all electron general potential linearized augmented plane-wave (LAPW)³¹ method as implemented in the WIEN2K code³². We used well converged basis sets including local orbitals and a planewave cutoff determined by $R_{min}K_{max} = 9$, where R_{min} is the smallest sphere radius and K_{max} is the planewave sector cutoff. We searched for materials with suitable electronic densities of states to reach the Stoner criterion at low carrier densities, and verified the results using self-consistent calculations in the virtual crystal approximation.

We used the BoltzTraP code³³ with transM³⁴ to determine the transport effective masses and the EFF. The calculations are based on the standard Perdew-Burke-Ernzerhof generalized gradient approximation (PBE GGA)³⁵ exchange-correlation functional. This is a conservative choice for studying itinerant magnetism as compared to functionals that produce greater degrees of localization.^{36–38}. Therefore, the choice of PBE is less likely to give a spurious magnetic solution. This is in the sense that approaches that better describe electron localization in correlated materials, such as DFT+ U , hybrid functionals and some meta-GGA functionals, particularly SCAN may predict strongly enhanced magnetism compared to experiment in itinerant metals^{38–43}. Thus, we use the PBE functional since it is less likely to give spurious magnetic solutions. As discussed below, we find arsenopyrite compounds, including FeAsS to become ferromagnetic semiconductors with doping. We tested for FeAsS that this is also the case in hybrid functional calculations using the HSE06 functional.

Screening and Verification: Table I lists the 44 considered materials. They are semiconductors and generally diamagnetic based on experiment. They have a variety

TABLE I. Compounds studied, doped Fermi levels, E_F in eV relative to conduction (E_{nS}) or valence band edge (E_{pS}) where Stoner criterion based on $N(E_F)$ is reached, and the transport effective masses for electrons and holes. Materials where the Stoner criterion is not reached within 0.3 eV of the band edge are listed as —. For this purpose the Stoner parameter, I is taken as 1 eV for $3d$ compounds, and 0.8 eV for $4d$ and $5d$ compounds.

	Space Group	E_{nS}	E_{pS}	m_n^*	m_p^*
FeAs ₂	$Pnnm$	—	-0.13	1.59	0.86
FeS ₂ -p	$Pa\bar{3}$	—	-0.08	0.48	3.12
FeS ₂ -m	$Pnnm$	—	-0.06	1.57	1.81
FeAsS	$P2_1/c$	0.20	-0.08	2.72	2.75
CrSi ₂ -h	$P6_222$	0.18	—	1.08	1.25
CrSi ₂ -o	$C222$	0.18	—	1.13	1.27
FeP ₂	$Pnnm$	—	-0.08	1.33	3.01
FeSi ₂	$Cmca$	—	—	—	—
FeGa ₃	$P4_2mnm$	0.14	-0.12	1.54	1.80
MoS ₂	$P\bar{6}m2$	—	—	—	—
Ru ₂ Ge ₃	$Pbcn$	—	—	—	—
Ru ₂ Si ₃	$Pbcn$	—	—	—	—
RuAs ₂	$Pnnm$	—	—	—	—
RuC	$F\bar{4}3m$	—	—	—	—
RuGe ₂	$Pa\bar{3}$	—	—	—	—
RuS ₂	$Pa\bar{3}$	—	-0.08	0.40	1.80
RuSi	$P2_13$	—	—	—	—
IrAs ₃	$Im\bar{3}$	—	—	—	—
IrS ₃	$Pbcn$	—	—	—	—
MoS ₂	$P6_3/mmc$	—	—	—	—
OsS ₂	$Pa\bar{3}$	—	-0.18	0.30	0.94
OsTe ₂	$Pa\bar{3}$	—	—	—	—
PtS ₂	$P\bar{3}m1$	—	—	—	—
RuTe ₂	$Pa\bar{3}$	—	-0.25	0.25	0.39
CoSbS	$P2_13$	—	—	—	—
CoSnTa	$F\bar{4}3m$	—	-0.22	1.32	1.37
IrGeTa	$F\bar{4}3m$	—	—	—	—
IrSbZr	$F\bar{4}3m$	—	—	—	—
IrSnTa	$F\bar{4}3m$	—	—	—	—
FeSbNb	$F\bar{4}3m$	—	—	—	—
Ir ₂ S ₃	$R\bar{3}c$	—	—	—	—
Ir ₂ S ₃	$Pbcn$	—	—	—	—
PdS ₂	$Pbca$	—	—	—	—
PtS	$P4_2/mmc$	—	—	—	—
FeP ₄	$P2_1/c$	—	-0.24	0.84	1.28
RuP ₄	$P2_1/c$	—	—	—	—
RuSe ₂	$Pa\bar{3}$	—	-0.10	0.37	1.71
FeAsTe	$P2_1/c$	0.19	-0.11	1.03	2.16
FeAsSe	$P2_1/c$	0.18	-0.19	3.16	2.58
Fe ₂ GeTi	$Fm\bar{3}m$	—	—	—	—
FePS	$P2_1/c$	—	-0.20	2.63	2.43
FeSbS	$P2_1/c$	0.18	-0.15	0.99	1.65
FeSbV	$F\bar{4}3m$	—	—	—	—
RuSbV	$F\bar{4}3m$	—	—	—	—

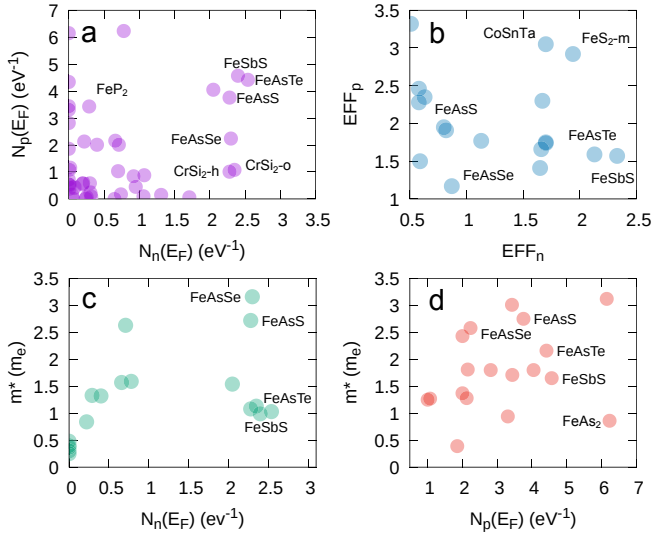


FIG. 1. Scatter plots showing correlation between different parameters for the set of compounds studied. (a) p -type vs. n -type $N(E_F)$ for E_F 0.2 eV below the valence band edge and 0.2 eV above the conduction band edge, shown on a per transition metal atom basis; (b) thermoelectric electronic fitness function (EFF) at 300 K and doping level of 10^{20} cm⁻³ in units of 10^{-20} W^{5/3} m s^{-1/3} K⁻²; (c) average transport effective mass vs. $N(E_F)$ for n -type and (d) average transport effective mass vs. $N(E_F)$ for p -type. The transport effective masses are calculated at doping levels of 10^{19} cm⁻³ and are obtained by averaging the direction dependent inverse transport effective mass.

of crystal structures, as indicated by the different space groups. The calculations were based on experimental crystal structures, with relaxation of free internal coordinates. Correlations between different properties are shown in Fig. 1. Fig. 1(a) shows the correlation of the p -type and n -type $N(E_F)$ for Fermi levels, E_F set 0.2 eV away from the band edges. The effective masses are the transport effective masses that are determined from the transport calculation using BoltzTraP and the transM code, as was also the case for the EFF.

As seen, there are several materials that would exceed the Stoner criterion of $N(E_F) \sim 2$ eV⁻¹ on a both spin basis for the corresponding doping level. This is the case for both p -type and n -type, and in a few cases for both p -type and n -type in the same material. Also there is only a weak correlation between the p -type and n -type values. This reflects the fact that more generally in semiconductors, even though band dispersions and bonding are closely related, the orbitals making up the band edges for p -type and n -type are different. This then often leads to very different band masses for p -type and n -type. Additionally, the common trend where p -type bands are usually heavier than n -type bands is seen in the usually higher values of $N(E_F)$ for p -type.

It is interesting to examine the relationship with the trends in the EFF. Fig. 1(b) shows the 300 K EFF val-

ues for some materials at a doping level of 10^{20} cm⁻³. This is a reasonable doping level in thermoelectric materials. The values shown are direction averages. As seen, there is a wide range of EFF values. This reflects the diverse band structures that differently decouple transport and density of states effective mass. Again there is little correlation between p -type and n -type. Thus these compounds do show a range of decoupling of different effective mass measures based on their non-trivial band structures as reflected in the EFF. Figs. 1(c) and 1(d) directly show the correlation between transport effective mass and $N(E_F)$ at 0.2 eV from the band edges. The transport masses shown are from the direction averaged inverse transport effective mass. These would be strictly proportional for a single isotropic parabolic band model. Materials that show both relatively low effective mass and high $N(E_F)$ include OsS₂, RuTe₂ and FeAs₂.

The essential ingredient for itinerant magnetism is that the value of $N(E_F)$ in the doped material should be at least 2 eV⁻¹ for 3d and 2.5 eV⁻¹ for 4d or 5d transition metal elements based compounds on a per transition element atom basis. The value of $N(E_F)$ generally increases with doping level away from the band edge, and so the question becomes how much doping is needed to reach the Stoner criterion if it can be reached at all. Table I lists the doping energy relative to conduction band edge or valence band edge for n and p -type to achieve this. The transport effective masses are given for those materials where the Stoner criterion can be reached within 0.3 eV of the band edge. Materials that would require a Fermi energy doped more than 0.3 eV from the band edge are not considered further.

This initial screen excludes most, but importantly not all compounds. Also, consistent with the tendency for p -type materials to have higher effective mass than n -type, we find more p -type cases than n -type cases where the Stoner criterion can be reached within 0.3 eV of the band edge. Some particularly interesting cases are FeAs₂, which was discussed previously⁷, RuS₂, which has a very interesting combination of moderate effective mass reaching the Stoner criterion only 0.08 eV away from the band edge, and cubic RuSe₂.

The n -type cases found include FeAsS, FeAsTe, FeAsSe and FeSbS. From the average EFF value, it may be that n -type FeAsTe is advantageous from the point of view of transport. The arsenopyrites, exemplified by FeAsS are particularly interesting cases. FeAsS, FeAsTe, FeAsSe and FeSbS all show the possibility of becoming magnetic semiconductors with both p -type and n -type doping. FeSbS has the lowest average transport mass among these. FeAsS is a diamagnetic semiconductor⁴⁴⁻⁴⁶, meaning that it does not contain Fe moments without doping. Similarly, FeAsSe and FeSbS are reported to have no Fe moments⁴⁷, while we are not aware of experimental studies of the magnetic properties of FeAsTe.

In the following, we focus on FeAsS, as exemplifying this group of materials since it has been studied more experimentally. Mineralogical samples are found in ar-

senopyrite, which is a common arsenic containing mineral. FeAsS has been discussed as a potential thermoelectric material based on first principles calculations⁴⁸, and on the fact that mineralogical samples can have both moderate resistivity and high thermopower. The reported thermopowers in tested mineralogical samples are negative and variable between samples. The effective masses are the transport effective masses that are determined from the transport calculation using BoltzTraP and the transM code, as was also the case for the EFF.⁴⁹, implying that at least for *n*-type high doping levels are possible. The phase diagram and stoichiometries of mineralogical samples imply that there is a range of S-As stoichiometries that can be synthesized, ranging from FeAs_{0.9}S_{1.1} to FeAs_{1.1}S_{0.9}⁵⁰. Considering the different valence states of S and As this additionally supports the possibility that the material may be heavily dopable perhaps for *p*-type as well as *n*-type. Uniquely among the compounds studied, the Stoner criterion can be reached for both *n*-type and *p*-type. This is an exciting possibility as if achieved this might enable functionalities such as magnetic bipolar devices including magnetic *p-n* homojunctions.

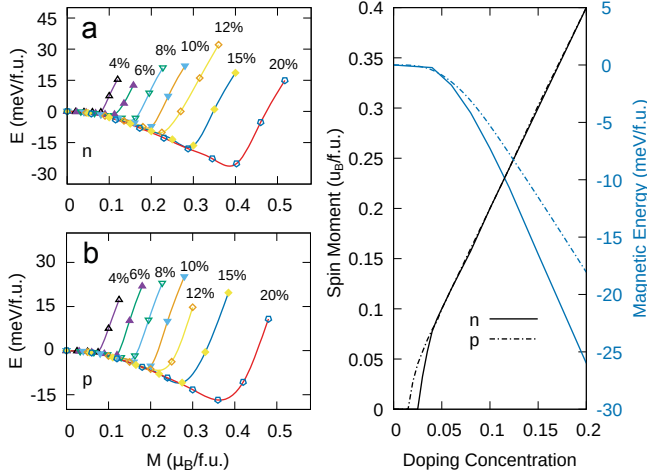


FIG. 2. Magnetic properties of doped FeAsS. (a) Fixed spin moment total energy for *p*-type (left up) and *n*-type (left down) FeAsS as a function of constrained spin magnetization on a per formula unit basis with virtual crystal doping on the anion sites. The energy for non-spin-polarized case was set to zero. (b) Calculated spin moment as a function of doping in *p* and *n*-type FeAsS. The percent values or concentration refer to the change in charge on the anion sites (electrons/hole per atom) on the As and S site. Since there is one As and one S per formula unit, the carrier concentration per Fe is twice the doping concentration.

We did self-consistent magnetic and transport calculations for FeAsS. FeAsS forms in a monoclinic structure space group $P2_1/c$. We used the experimental lattice parameters reported for stoichiometric mineralogical samples, $a=5.7612$ Å, $b=5.6841$ Å, $c=5.7674$ Å, $\beta=111.721^\circ$, with four formula units per cell⁵¹. The internal atomic

positions were relaxed by energy minimization.

We begin with magnetism. We used self-consistent and fixed spin moment constrained density functional theory calculations⁵² with doping on the anion sites using the virtual crystal approximation. The virtual crystal approximation (VCA) is a self-consistent average potential method. It does not rely on rigid bands and is appropriate for doping provided that the potential due to the dopant atoms is not too strong^{53,54}. Following experimental results mentioned above, we consider doping on the anion sites. In our all electron calculations, the VCA is implemented by changing the charge on the anion (S and As) sites by a small percentage, corresponding to the doping level. For example, a doping of +1% means *n*-type doping by increasing the charge of both As and S nuclei by 0.01, and correspondingly increasing the number of valence electrons. This would yield an *n*-type doping level 0.02 electrons per formula unit.

Results for *p*-type and *n*-type FeAsS are shown in Fig. 2. As seen, both for *p*-type and *n*-type doping, itinerant ferromagnetism starts at low doing, $\sim x = 4\%$, where as mentioned, x corresponds to substitution on the As and S site to provide one fewer or more valence electrons for *p*-type or *n*-type, respectively. In addition, over a wide range of doping level the predicted magnetization is equal to the doping level. These magnetizations shown are as directly obtaining from self-consistent calculations. This implies a high spin polarization, which is important for spintronic applications. We also tested this using hybrid functional calculations. For this purpose we selected the HSE06 functional⁵⁵ and did self-consistent virtual crystal calculations for 6% *p*-type and *n*-type doping, as described above for the PBE calculations. The calculations were done with the WIEN2k code, a screening parameter of 0.165 bohr^{-1} , and an $8 \times 8 \times 8$ mesh for sampling the Brillouin zone. For both *p*-type and *n*-type we find a moment of $0.12 \mu_B/\text{f.u.}$, as in the PBE calculation (Fig. 2). Finally, as a further test, we did supercell calculations where we replaced one S by either P or Cl and relaxed the atomic positions, to simulate *p*- or *n*-type doping, respectively. We note that these may not be ideal dopants for this system. Nonetheless, they confirm the conclusions of our VCA calculations. Specifically, we did self-consistent WIEN2k PBE calculations in supercells containing eight formula units with a Brillouin zone sampling by $8 \times 4 \times 8$ meshes. The substitutions correspond to a doping level of 6.25% in the notation used here. We find that in both the P and Cl doped cases, the magnetization is $0.125 \mu_B$ per formula unit. This is exactly the same as the VCA result.

We turn to the band structure and transport. Fig. 3 shows the band structure of FeAsS. Both symmetry and non-symmetry lines are shown in order to better illustrate the mixture of heavy and light features in the low symmetry crystal structure. We find an indirect band gap of 0.68 eV. An optical gap of 0.82 eV was estimated based on a fit assuming a direct gap⁵⁶, while an older optical experiment suggested a gap below 0.5 eV⁵⁷. Hul-

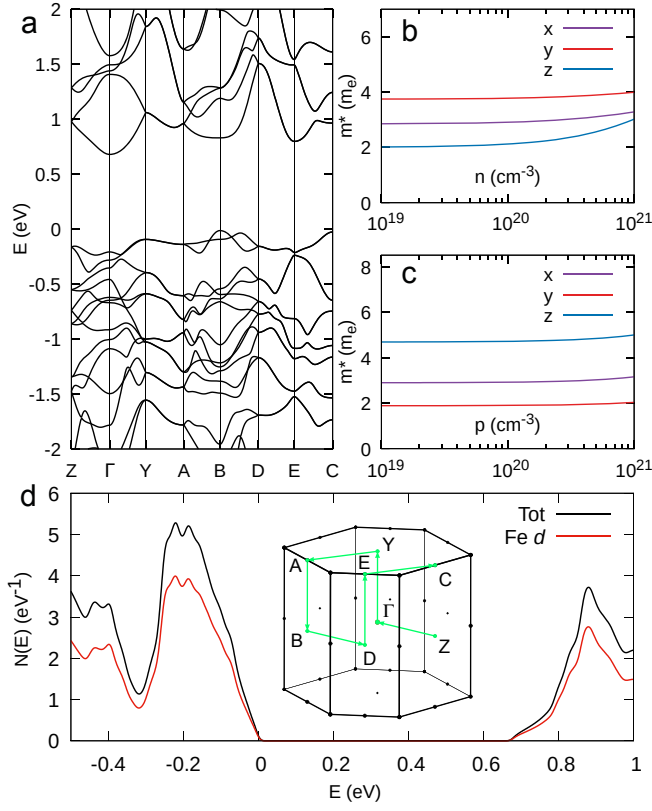


FIG. 3. Calculated band structure of FeAsS (top left). The valence band maximum is set to zero. Calculated direction dependent transport effective mass of *p*-type and *n*-type FeAsS function of carrier concentration at 300 K (top right). Calculated electronic density of states on a per formula unit basis and Fe *d* projection near the band edges (bottom). The inset shows the labeling of the Brillouin zone for the band structure plot.

liger reported transport measurements on different samples, finding transport gap values ranging from 0.3 eV to 0.5 eV⁵⁸. Our value is reasonably consistent with these experiments, although it could be noted that interpretation of experimental gaps requires care for example due to possible excitonic effects, possible dopant activation behavior in transport measurements, or missed weak absorption particularly in indirect gap materials. Underestimates are common for calculations done with the PBE-GGA, although there are arguments that for semiconductors with *d*-character of both the valence and conduction bands the underestimation may be small⁵⁹. In this regard, the calculated HSE06 band gap is 1.44 eV, which seems inconsistent with existing experiments. In any case, our value is in reasonable accord prior calculated values of 0.73 eV, 0.75 eV and 0.78 eV^{60–62}.

Importantly, besides the flat bands near the band edges, which provide the high DOS and the Stoner instability, there are also more dispersive bands features. For *n*-type one may note the anisotropy and the secondary carrier pockets at the points labeled E and B, while for

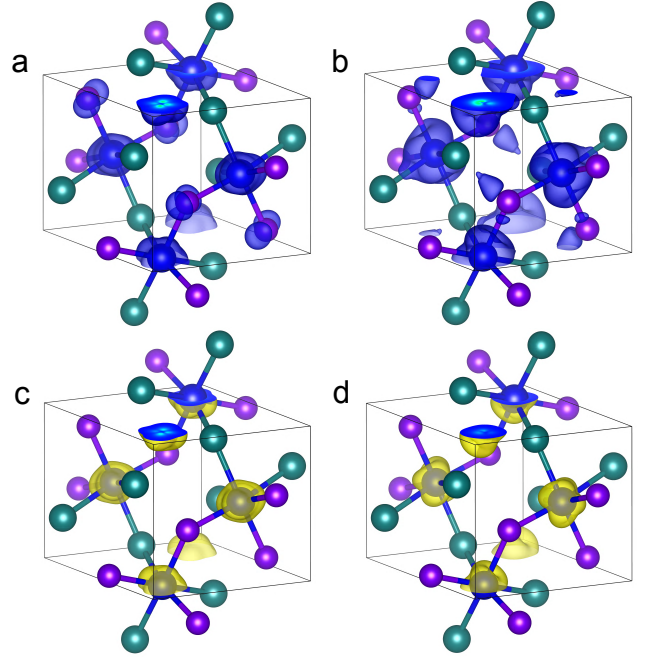


FIG. 4. Visualization of the charge density of the band edge states for *p*-type and *n*-type FeAsS (top) and visualization of the spin difference density (bottom). The spin difference was calculated for a very high doping level of 20%. The isosurface shown is at 0.005 per cubic bohr. Fe, As and S atoms are shown by blue, green and purple balls, respectively.

p-type, there is a band maximum near E formed from a dispersive band in close proximity to a flat band. The density of states and Fe *d* projections are shown in the lower panel of Fig. 3, showing the increase to reach the Stoner criterion near the band edges.

We used the BoltzTraP³³ and transM codes³⁴ to obtain the transport effective masses. The transport effective mass in general depends on both carrier concentration and temperature, but normally is weakly dependent on these. Fig. 3 shows the transport effective mass for *p*-type and *n*-type at 300 K. As seen, the transport effective masses for *p*-type and *n*-type are both anisotropic, and somewhat more so for *p*-type. In any case, for both carrier types effective masses of $\sim 2 m_e$ are found in the most favorable directions. It is noteworthy that even though there is a steep onset of the DOS near the band edges, the effective mass is not so high as to preclude reasonably good semiconducting transport. It is also interesting to note that the transport effective mass in valence band top and conduction bottom are both comparable, consistent with the possibility of bipolar devices.

Fig. 4 shows a visualization of the charge density from the electronic states near the valence and conduction band edges for undoped FeAsS, based on the calculated electronic structure in comparison with the self-consistent VCA spin difference density for *p*-type and *n*-type. A very high doping level of 20% is shown. Even for these artificially high doping levels there is a strong sim-

ilarity. The similarity shows the itinerant origin of the spin-polarization of doped FeAsS. Furthermore, as mentioned, the doped holes/electrons in FeAsS are highly polarized. It may be noted that there are different definitions of spin polarization depending on the particular probe, for example photoemission or transport. Spin polarization is expressed as $P_f = (f_{\uparrow} - f_{\downarrow})/(f_{\uparrow} + f_{\downarrow})$, for the quantity f , which can be the conductivity σ , for the transport spin polarization, P_{σ} , or the density of states, $D = N(E_F)$, for the density of states spin polarization, P_D or the doped carriers for the charge spin polarization P_c or other quantities. As seen, for n -type FeAsS at 10% doping level, the spin polarization is 1, i.e., fully spin polarized. For p -type FeAsS at the same doping level, the spin polarization depends on the property of interest. The charge spin polarization is 0.99. The DOS spin polarization, $P_D = -0.96$, is negative, which simply reflects the fact that it is doped holes that are polarized. Thus although not a half metal, p -type FeAsS does have very high spin polarization.

Summary and Conclusions: We performed a screening of non-magnetic generally diamagnetic semiconductors seeking materials that may exhibit itinerant Stoner ferro-

magnetism when doped. This is based on the possibility of having both reasonable effective mass and Stoner magnetism in materials that show complex band structures. We identified several possible cases, and found that some arsenopyrites, exemplified by FeAsS, can be ferromagnetic with both doping types, p -type and n -type. This material is found to have reasonable effective mass and high spin polarization both for p -type and n -type. It will be of interest to experimentally attempt doping of these materials, and if this is feasible to assess the Curie temperature as a function of doping level and to characterize the carrier mobilities. The possibility of having a ferromagnetic semiconductor for both p -type and n -type in the same material, if realized, may enable new device concepts, for example ferromagnetic p - n junction devices and new types of magnetic field effect devices.

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