# Multiple magnetic transitions and complex magnetic structures in $Fe_2SiSe_4$ with the sawtooth lattice

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The sawtooth lattice shares some structural similarities with the kagome lattice and may attract renewed research interest. Here we report a comprehensive study on the physical properties of $Fe_2SiSe_4$, an unexplored member in the olivine chalcogenides with the sawtooth lattice of Fe. Our results show that $Fe_2SiSe_4$ is a magnetic semiconductor with band gap of 0.66 eV. It first undergoes an antiferromagnetic transition at $T_{m1} = 110$ K, then an ferrimagneticlike one at $T_{m2} = 50$ K, and finally a magnetic transition at $T_{m3} = 25$ K, which is likely driven by the thermal populations of spin-orbit manifold on the Fe sites. Neutron diffraction analysis reveals a noncollinear antiferromagnetic structure with propagation vector $\mathbf{q_1} = (0, 0, 0)$ at $T_{m2} < T < T_{m1}$. Interestingly, below $T_{m2}$, an additional antiferromagnetic structure with $\mathbf{q_2} = (0, 0.5, 0)$ appears, and $Fe_2SiSe_4$ exhibits a complex double-$\mathbf{q}$ magnetic structure which has never been observed in sawtooth olivines. Density functional theory calculations suggest this complex noncollinear magnetic structure may originate from the competing antiferromagnetic interactions for both intra- and interchain in the sawtooth lattice. Furthermore, band-structural calculations show that $Fe_2SiSe_4$ has quasi-flat-band features near the valence and conduction band structure. Our results have shown that $Fe_2SiSe_4$ could serve as a new material playground for further research on magnetic devices and the flat-band effect through chemical doping.

## I. INTRODUCTION

Materials with the sawtooth lattice have attracted attention from the condensed-matter physics community for several reasons. First, the sawtooth antiferromagnetic (AFM) chain with corner-sharing triangles of spins represents one of the fundamental models of geometrically frustrated quantum magnetism as that in triangular and kagome lattices [1,2]. Secondly, the sawtooth lattice also exhibits flat-band feature [3], which may give rise to high thermoelectric performance [4], quantum topological phase [5–7], flat-band spin dynamics and phonon anomalies [8]. Besides, a two-dimensional kagome lattice can be viewed as the combination of one-dimensional sawtooth chains. Therefore the recent discoveries of novel physical properties in kagome material [9–13] may generate renewed interest in sawtooth material, since these two kinds share structural similarities and connections.

The $A_2BX_4$ ($A$ = Mn, Fe, Ni; $B$ = Si, Ge; $X$ = O, S, Se, Te) olivines represent a large material family where the transitional-metal atoms form a sawtooth lattice. Most members in this series are ferrimagnets or antiferromagnets whose spin structure could be described by magnetic propagation vector $\mathbf{q}$ = (0,0,0) [14,15]. Among them, magnetic frustration is observed for $Mn_2SiSe_4$ [16]. $Mn_2SiS_4$ and $Mn_2GeS_4$ are reported to exhibit anomalous magnetic properties resulting from the quantum fluctuations near a spin-flop bicritical point [17]. $Mn_2GeO_4$ is identified as a functional material that exhibits coupled ferromagnetism and ferroelectricity [18]. $Fe_2GeS_4$ and $Fe_2GeSe_4$ are theoretically proposed as promising candidates with good thermoelectric performance due to their quasi-flat-band feature [4]. These findings highlight the exotic physical properties which are closely related to the peculiar sawtooth lattice.

In the $A_2BX_4$ series, we noticed that although the magnetic properties of $Fe_2SiO_4$ and $Fe_2SiS_4$ have been reported [15,19], $Fe_2SiSe_4$ remains an unexplored member whose chemical phase is even missing in the current inorganic crystal structure database (ICSD). So it would be interesting to check whether the $Fe_2SiSe_4$ phase with sawtooth lattice really exists. In this paper we report the synthesis of $Fe_2SiSe_4$ single crystals, which is characterized by the sawtooth lattice of Fe. Using magnetization, heat capacity, neutron-scattering techniques, and band-structure calculations, $Fe_2SiSe_4$ is identified as a magnetic semiconductor with multiple magnetic transitions, noncollinear double-$\mathbf{q}$ magnetic structures, and as quasi-flat-band. The underlying physical mechanism for the magnetic properties and potential applications of $Fe_2SiSe_4$

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are discussed combined with the results of density-functional theory (DFT) calculations.

## II. EXPERIMENTAL METHODS

Single crystals of $Fe_2SiSe_4$ were grown by the chemical vapor transport method. The pure powders of Fe, Si, and Se were mixed in molar ratio 1:2:4 (total mass 1 g) and placed into a quartz tube (inner diameter of 12 mm, length 10 cm) with 100 mg iodine. Then the quartz tube was evacuated to $3.0 \times 10^{-3}$ Pa and sealed before being put into a two-zone tube furnace. The quartz tube was heated to $590\,°C$ in the raw material end and $660\,°C$ in the other end in 750 min, then maintained at those temperatures for 5760 min. The next step is a so-called "temperature reversing process" in which the two ends switch temperatures in 70 min and are held in the new temperatures for 12.5 days before being cooled with the furnace. The shining black single crystals of $Fe_2SiSe_4$ appeared in the final cold end with typical dimensions of $1\,mm \times 2\,mm \times 0.5\,mm$.

X-ray diffraction (XRD) patterns of powder samples were collected from a Bruker D8 Advance x-ray diffractometer using Cu K$\alpha$ radiation. Magnetization measurements were carried out in Quantum Design MPMS3. Resistivity and heat capacity of the samples were measured on Quantum Design PPMS-14T. The powder neutron diffraction experiments were carried out on Xingzhi cold neutron triple-axis spectrometer at the China Advanced Research Reactor (CARR). For neutron experiments on Xingzhi, the incident neutron energy was fixed at 16 meV with a neutron velocity selector used upstream to remove higher-order neutrons [20]. About 3 g $Fe_2SiSe_4$ powders (crushed from single crystals) were used in neutron experiments. The FULLPROFSUITE program package was used in the Rietveld refinement of neutron powder diffraction data [21,22], and the software SARAH was used for the representational analysis [23].

The electronic structure and magnetic properties calculations were performed using the DFT as implemented in the Vienna *ab initio* simulation package (VASP) code [24,25]. The generalized gradient approximation (GGA) in the form of a Perdew-Burke-Ernzerhof (PBE) [26] functional was used for exchange correlation. The projector-augmented-wave (PAW) method [27] with a 300-eV plane-wave cutoff energy was employed. The valence electron configurations for each atom were $3d^74s^1$ for Fe, $3s^23p^2$ for Si, and $3d^{10}4s^24p^4$ for Se. A $\Gamma$-centered $3 \times 2 \times 5$ $k$-point mesh within the Monkhorst-Pack scheme was used for Brillouin-zone sampling. The Hubbard $U$ [28] for the $3d$ electrons of Fe was chosen as 2 eV to reproduce the experimental magnetic moments and band gap of $Fe_2SiSe_4$. A $1 \times 2 \times 1$ supercell was adopted due to the noncollinear AFM structure. The direction of the magnetic moment was constrained, that is, the superimposed double-**q** magnetic structure was adopted. All calculations were performed using the experimental structural parameters. Convergence criteria employed for both the electronic self-consistent iteration and the ionic relaxation were set to $10^{-6}$ eV and 0.01 eV/Å, respectively. Heisenberg exchange interactions were calculated by the four-states method [29]. A $1 \times 2 \times 2$ supercell was adopted to avoid spurious interaction by the periodic boundary conditions.
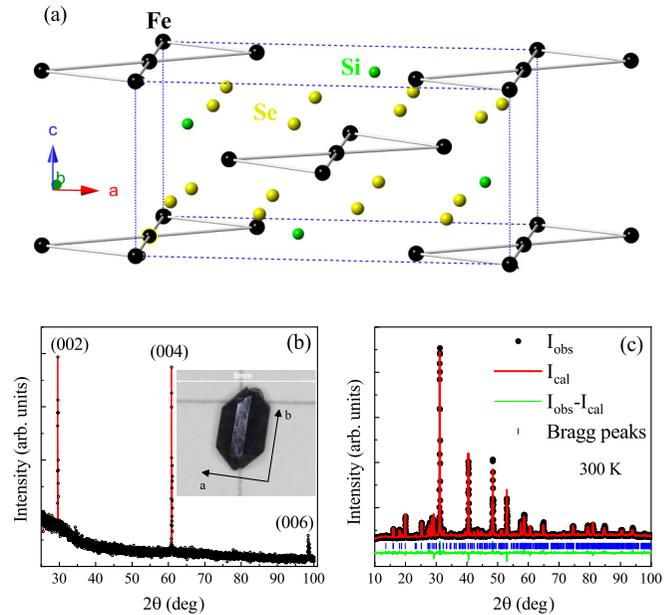


FIG. 1. (a) Crystal structure of $Fe_2SiSe_4$. The Fe-Fe bond is plotted to demonstrate five Fe sawtooth chains. (b) The x-ray reflections from the $ab$ plane of $Fe_2SiSe_4$ single crystal. The inset shows the photo of one crystal. (c) Room-temperature XRD patterns of powders (crushed from single crystals) and the Rietveld refinement results.

## III. RESULTS AND DISCUSSION

### A. Crystal structure and magnetization

In Fig. 1(c), the XRD patterns on powder samples (crushed from single crystals) and Rietveld refinement confirm $Fe_2SiSe_4$ adopts the orthorhombic symmetry with space group *Pnma* (No. 62), which belongs to the olivine-type structure, same as $Fe_2SiS_4$ and $Fe_2SiO_4$ [14,15]. The obtained lattice parameters are $a = 13.020$ Å, $b = 7.544$ Å and $c = 6.119$ Å. The x-ray reflection pattern from the $ab$ plane of $Fe_2SiSe_4$ single crystal in Fig. 1(b) also confirms the above results. As shown in Fig. 1(a), the Fe atoms form infinite sawtooth chains along the $b$ axis.

The Laue diffraction patterns allow us to distinguish the major crystal axes with respect to the three-dimensional shape of $Fe_2SiSe_4$ single crystal. So the temperature-dependent magnetization along the $a$, $b$, and $c$ axis were performed, respectively; the results are shown in Fig. 2. Three successive magnetic transitions could be identified. At $T_{m1} = 110$ K, a cusp appears which is most prominent under $H \parallel b$, indicating an AFM transition. At lower temperatures, a second magnetic transition occurs at $T_{m2} = 50$ K. Its temperature-dependent magnetization behavior seems to be AFM-like under $H \parallel b$ while being ferromagneticlike along other field directions. Then at $T_{m3} = 25$ K, the magnetization anomalies along all three directions suggest the existence of a third magnetic transition.

The temperature-dependent magnetization shows strong anisotropic behavior along three different directions. Even in the paramagnetic region, the magnetization under $H \parallel a$ or $H \parallel c$ exhibits typical Curie-Weiss (CW) behavior while that under $H \parallel b$ shows an anomalous linear temperature
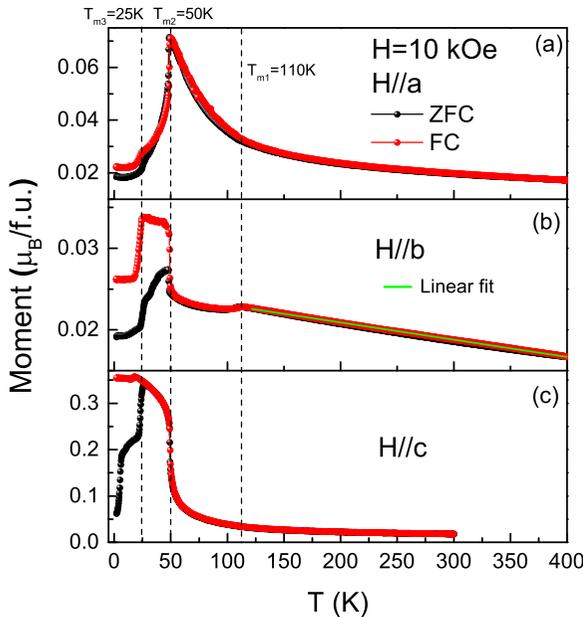
FIG. 2. Temperature-dependent magnetizations with applied field along the $a$, $b$, and $c$ axis are shown respectively in (a), (b), and (c).

dependence up to 400 K. The CW fit of the high-temperature magnetization data yields $\mu_{\text{eff}}/\text{Fe} = 4.02\,\mu_B$ and $\theta_{CW} = -66$ K for $H \parallel a$, $\mu_{\text{eff}}/\text{Fe} = 4.08\,\mu_B$, and $\theta_{CW} = -51$ K for $H \parallel c$. This result indicates dominant antiferromagnetic correlations in $Fe_2SiSe_4$. Meanwhile the derived effective moment is obviously smaller than the theoretical value $4.90\,\mu_B/\text{Fe}^{2+}$ without orbital contribution. This discrepancy gives rise to a question of whether CW fitting could be applied to $Fe_2SiSe_4$ or the fitting results could be interpreted in the conventional way. Specifically, the abnormal high-temperature T-linear magnetization exists for $H \parallel b$. Similar behavior was observed in Fe-based superconductors and parent compounds [30–32], which is explained as a result of AFM spin fluctuations in the normal state [33]. Further theoretical works are needed to check whether this explanation applies to $Fe_2SiSe_4$.

### B. Magnetic structure

Since the T-dependent magnetization indicates the existence of three possible magnetic transitions, powder neutron diffraction on $Fe_2SiSe_4$ was performed at 150, 80, 35, and 3.5 K to determine the magnetic structure. As shown in Fig. 3, the Bragg peaks at 150 K could be well indexed by the nuclear scattering with high-quality refining parameters. At 80 K, magnetic contributions and peaks can be easily identified near $2\theta = 22°$ and $35°$. Detailed analysis using FULLPROF software [21,22] shows that all magnetic reflections overlap with the nuclear reflections (except for some nuclear peaks with diffraction extinction) and could be well defined by the propagation vector $\mathbf{q_1} = (0, 0, 0)$. Figure 4(b) shows that the intensities of Bragg peak $(0,0,1)$ could be served as the magnetic order parameter for the first AFM transition at $T_{m1} = 110$ K.

Below $T_{m2} = 50$ K, new magnetic peaks with half integer are identified (Fig. 3). As shown in Fig. 4(b), the
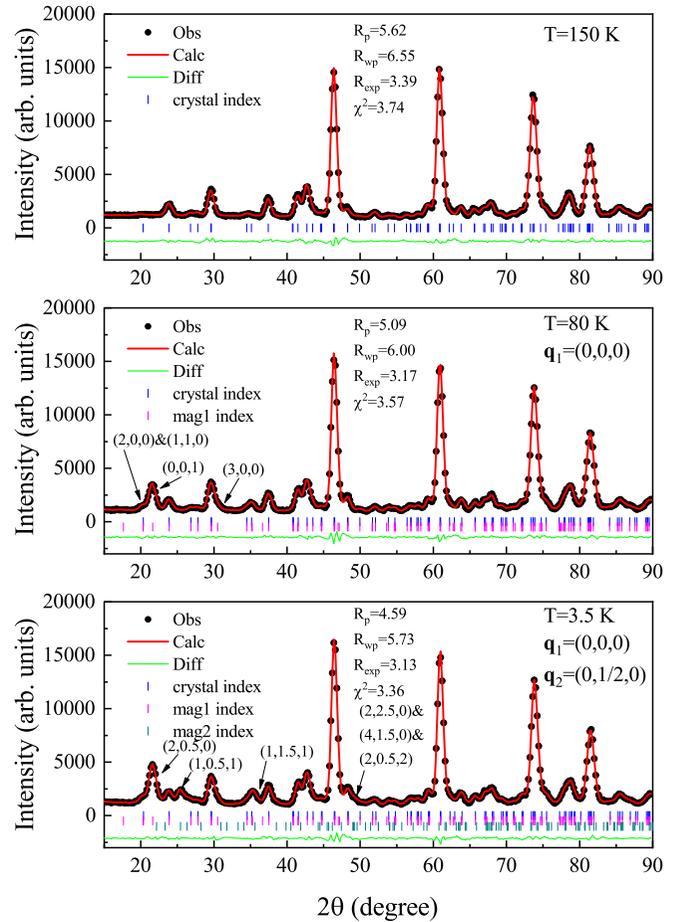


FIG. 3. The powder neutron diffraction spectra and Rietveld refinement results for $Fe_2SiSe_4$ at 150, 80, and 3.5 K. Some of the magnetic peaks are labeled with arrows.

temperature-dependent intensity of $(1,0.5,1)$ signifies new magnetic order develops below $T_{m2}$. It should be noted there is almost no difference for the diffraction patterns at 35 and 3.5 K within our instrumental resolution. Therefore the magnetic transition $T_{m3}$ may not change the zero-field magnetic structure.

The identification of considerable magnetic peaks allows us to determine the magnetic structures at different temperatures through Rietveld refinement. The detailed representational analysis and refinement process are presented in the Supplemental Material [34]. The magnetic structures resolved from the best fit are plotted in Fig. 4 and are discussed in detail.

First of all, at 80 K the noncollinear AFM structure with magnetic wave vector $\mathbf{q_1} = (0, 0, 0)$ is identified and illustrated in Fig. 4(a). The Fe ions occupy two inequivalent Wyckoff positions. We label those at the $4a$ site as Fe1 (black spheres) and those at $4c$ sites as Fe2 (gray spheres). The magnetic moments all lie in the $ab$ plane, and the data refinement yields a total moment of $1.45\,\mu_B/\text{Fe}$ for Fe1 and $4.04\,\mu_B/\text{Fe}$ for Fe2. The latter points parallel to the $b$ axis while the former is canted to the $a$ axis to a certain degree. This magnetic structure is quite similar as that in olivine-type $Fe_2SiO_4$ and $Fe_2SiS_4$ [14,15]. Therefore, similar physical interpretations

FIG. 4. (a) Schematics of refined magnetic structure of $Fe_2SiSe_4$ at 80 K. (b) The temperature-dependent intensities of magnetic peaks (0,0,1) and (1,0.5,1). (c) The refined magnetic structures of $Fe_2SiSe_4$ at 3.5 K with different propagation vectors are illustrated.

TABLE I. Calculated magnetic exchange coupling constants between different Fe sites, positive value means AFM coupling.

| Constant | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ | $J_6$ | $J_7$ | $J_8$ |
|---|---|---|---|---|---|---|---|---|
| Value (meV) | 8 | 9 | 15 | 12 | 15 | 9 | 8 | 0.3 |

are shown in Fig. 4(b). The new magnetic peaks developed below $T_{m2}$ can be well defined by a new propagation vector $\mathbf{q_2} = (0, 0.5, 0)$. We found that only a combined model which includes both the magnetic structure with $\mathbf{q_1}$ and that with $\mathbf{q_2}$ could achieve a good fit to the data collected at 3.5 K. The refined two magnetic structures with different wave vectors are illustrated in Fig. 4(c). One can see that the one with $\mathbf{q_1}$ is quite similar as that at 80 K, except for a slightly increased ordered moment and different canting angle for the Fe1 moment. The magnetic structure with $\mathbf{q_2}$ is also noncollinear and more complex; the magnetic unit cell is doubled along the *b* axis. The moments of Fe2 have two different values, and one of them is almost negligible (0.03 $\mu_B$).

The magnetic order at 3.5 K has two different propagation wave vectors. These two modulations may either reside in different domains independently, known as the multidomain state, or coexist in a single domain in the form of a superimposed double-$\mathbf{q}$ state. These two states may be indistinguishable in diffraction experiments performed on powder samples. The multi-$\mathbf{q}$ magnetic order is not a common case in magnetic material. Some famous examples include a double-$\mathbf{q}$ spin-density wave in the Fe-based superconductor $Sr_{1-x}Na_xFe_2As_2$ with tetragonal crystal symmetry [35] and triple-$\mathbf{q}$ magnetic state in $Na_2Co_2TeO_6$ with hexagonal crystal symmetry [36]. For $Fe_2SiSe_4$, whether there is a double-domain state or a double-$\mathbf{q}$ state, this state in a orthorhombic crystal symmetry is particularly rarely observed.

To explore the underlying mechanism for the complex magnetic structure of $Fe_2SiSe_4$ at 3.5 K, we investigate its exchange couplings based on a simple Heisenberg model:

$$H = \sum_{i<j} J_{ij} S_i S_j. \qquad (1)$$

Our DFT calculations reveal the values of exchange coupling constant $J_i$ between Fe ions at different sites [illustrated in Fig. 4(c)], and the results are listed in Table I. We can see that all of the $J_i$ values are positive, which means each side of the sawtooth chains are AFM coupling. The intrachain exchange coupling $J_1$, $J_2$, $J_6$, and $J_7$ are connected by an exchange path Fe-Si-Se-Fe with distance $d(J_1) = 3.78$ Å. The interchain exchange couplings $J_3$, $J_4$, $J_5$ are instead realized through the exchange path Fe-Se-Se-Fe with the distance $d(J_4) = 4.89$ Å. Furthermore, the exchange coupling values of interchain are almost twice as large as those of intrachain. This is probably due to the strong hybridization of Se 4*p* and Fe 3*d* orbits near the Fermi level. A very large Fe-Fe distance $d(J_8) = 7.17$ Å results in a much weaker magnetic interaction. Therefore the competition of AFM interactions on different sides of the sawtooth chain combined with the interchain exchange interaction may be responsible for a complex noncollinear double-$\mathbf{q}$ magnetic order in $Fe_2SiSe_4$. Based on this model, we employ a superimposed double-$\mathbf{q}$ magnetic structure to

of this magnetic structure considering the indirect superexchange interactions between Fe cations via Se atoms could be given. As marked in Fig. 4(a), the Fe2-Se-Fe2 angle is closer to 180° and gives rise to a strong AFM interaction, while the angle of Fe1-Se-Fe1 is much smaller, which may largely reduce the AFM interaction [15]. A competition between crystal-field anisotropy and AFM exchange via spin-orbit coupling results in the canting of Fe1 moments [14].

Secondly, at 3.5 K the above magnetic model with $\mathbf{q_1} = (0, 0, 0)$ can only partially fit the neutron diffraction patterns and could not explain new magnetic peaks with half integers appearing below $T_{m2}$ (Fig. 3). The most prominent one is indexed as (1,0.5,1), whose temperature-dependent intensities

FIG. 5. Isothermal magnetizations under magnetic field applied along the $a$, $b$, and $c$ axes at selected temperatures are shown.

constrain the direction of the magnetic moment. The calculated spin configuration at low temperature of $Fe_2SiSe_4$ is shown in Table S9 and is qualitatively consistent with the superimposed double-$q$ magnetic structure determined experimentally (Table S8).

## C. Isothermal magnetization, AC susceptibility, and heat capacity

Further measurements on $Fe_2SiSe_4$ single crystal were performed to get insights on its magnetic state. As shown in Fig. 5, the isothermal magnetizations under $H \parallel a$ and $H \parallel b$ are linear with increasing field for most temperatures, which is consistent with an AFM state. Nevertheless, for $H \parallel c$, a nonlinear M(H) curve appears below $T_{m2} = 50$ K. Especially for 30- and 40-K data, they first show a ferromagneticlike fast magnetization to about 0.13 $\mu_B$/Fe at low field then increase linearly with field. This fast magnetization seems to gradually disappear below $T_{m3} = 25$ K. The above observations suggest the magnetic transition at $T_{m2}$ is a ferrimagnetic one. The magnetic hysteresis behavior at 35 K in Fig. 6(a) and the peak in the imaginary part of AC susceptibility $\chi''$ at $T_{m2}$ [Fig. 6(b)] further support this conclusion.

In the previous section, the double-$q$ magnetic structure below $T_{m2}$ identified from neutron diffraction is actually antiferromagnetlike without a net moment component in any direction. This seems to contradict the ferrimagnetic behavior observed in magnetization measurements. The explanation might be that the net magnetization 0.13 $\mu_B$/Fe observed in Fig. 5(c) is quite small. This small ferrimagnetic component is not easily detected due to the neutron instrumental resolution. We also need to point out that the moment of Fe has no component along the $c$ axis at 80 K, but Fe2 actually has a $c$-axis component of 1.14 $\mu_B$ at 3.5 K, which can be seen from Tables S7 and S8. This indicates the magnetic anisotropy has notable change below $T_{m2}$.

Another question that needs to be answered is the nature of magnetic transition at $T_{m3} = 25$ K. The experimentally measured specific heat of $Fe_2SiSe_4$ is shown in Fig. 7. From the raw data $C_p(T)$, the magnetic transitions at $T_{m1}$ and $T_{m2}$ can be identified by the jumps, while there is no detectable feature at $T_{m3}$. Then, if using an Einstein-model–based curve to account for the phonon part of the specific heat, we can obtain the magnetic specific heat $C_{mag}$ shown by the blue

curve in Fig. 7. The $C_{mag}(T)$ shows a shoulder at $T_{m3} = 25$ K. The inset of Fig. 7 shows the calculated magnetic entropy of $Fe_2SiSe_4$ as compared with the limiting value $2R \ln 5$ by assuming the spin-orbit manifold is fully occupied and there are $2S + 1 = 5$ equally occupied states for each $Fe^{2+}$. It should be noted that we have failed to synthesize samples with possible $Zn_2SiSe_4$ phase for a more accurate phonon estimation. We also have tried to use the Debye model or an amalgamation
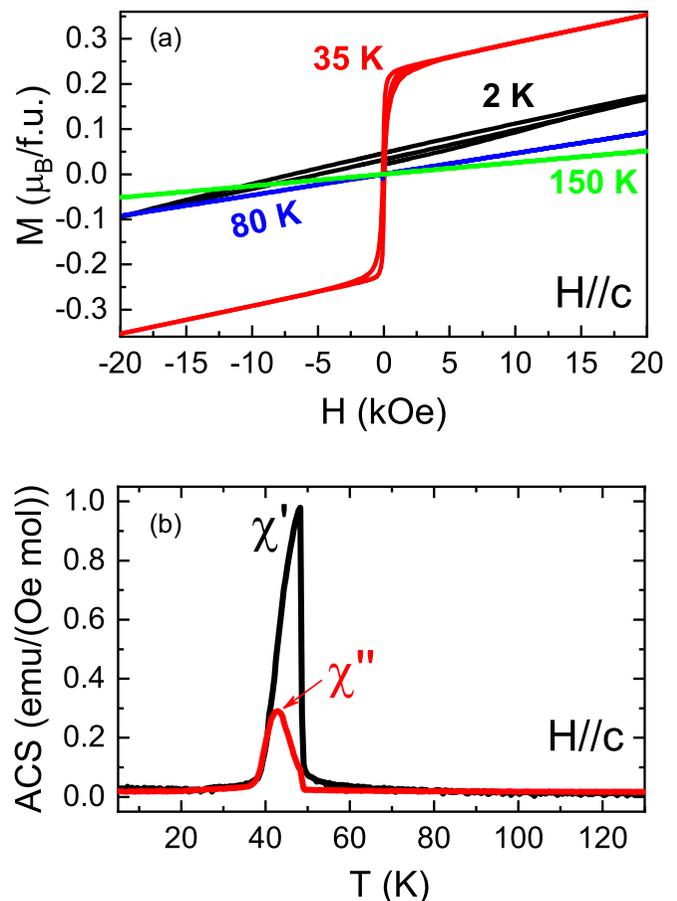


FIG. 6. (a) Magnetic hysteresis under $H \parallel c$ for $Fe_2SiSe_4$ at selected temperatures. (b) The temperature-dependent AC susceptibilities measured under an oscillated AC field of 5.0 Oe applied along the $c$ axis.
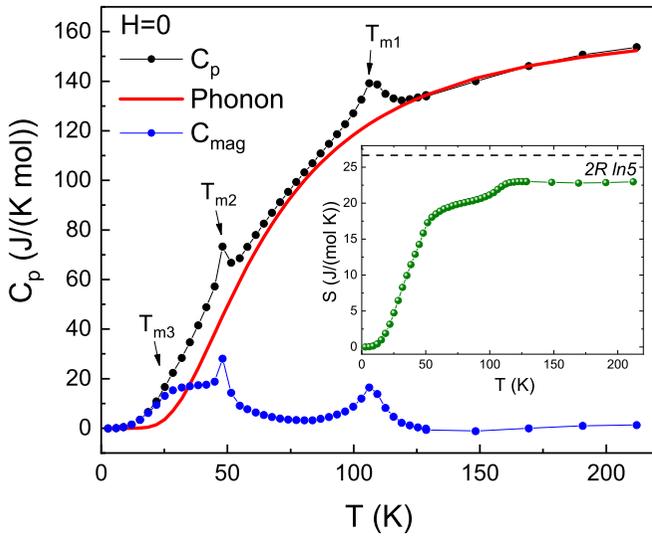
FIG. 7. Temperature-dependent specific heat of $Fe_2SiSe_4$. The magnetic specific heat $C_{mag}$ is derived by subtracting phonon contributions through an Einstein-model-based curve fit on the data above 110 K. Then the calculated magnetic entropy is shown in the inset.

of both Einstein and Debye models to estimate the phonon contribution. All results have shown a similar shoulderlike feature at $T_{m3}$ in $C_{mag}(T)$, and the Debye model gives lower magnetic entropy value (17.3 J mol$^{-1}$ K$^{-1}$ at 120 K).

We found this shoulderlike transition also exists in isostructural $Fe_2SiO_4$ at similar temperature (20 K), and its origin has been uncovered as a Schottky anomaly arising from the spin-orbit manifold of the $Fe^{2+}$ ion [19]. To be specific, for $Fe_2SiO_4$, Aronson *et al.* found that the lowest cystal-field splitting $t_{2g}$ level is further split into five states due to spin-orbit coupling. These spin-orbit energy levels are determined through inelastic neutron experiments and have a dominant influence on the low-temperature physical properties. Then the shoulder in specific heat can be quantitatively
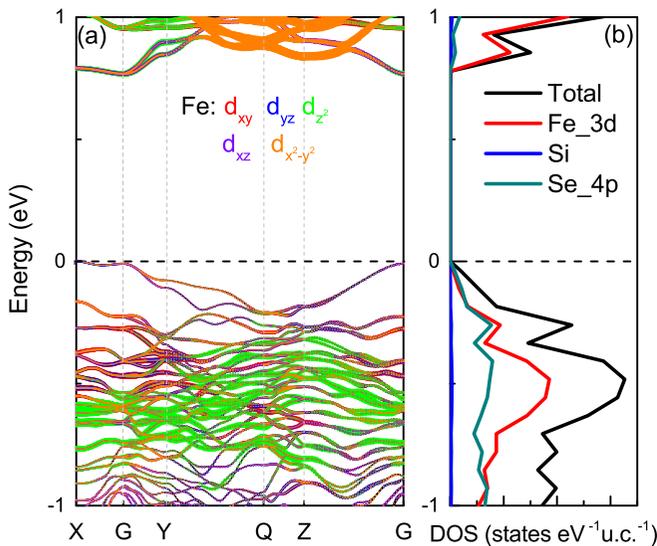


FIG. 8. Calculated band structure (a), total and projected density of states (b) of $Fe_2SiSe_4$.
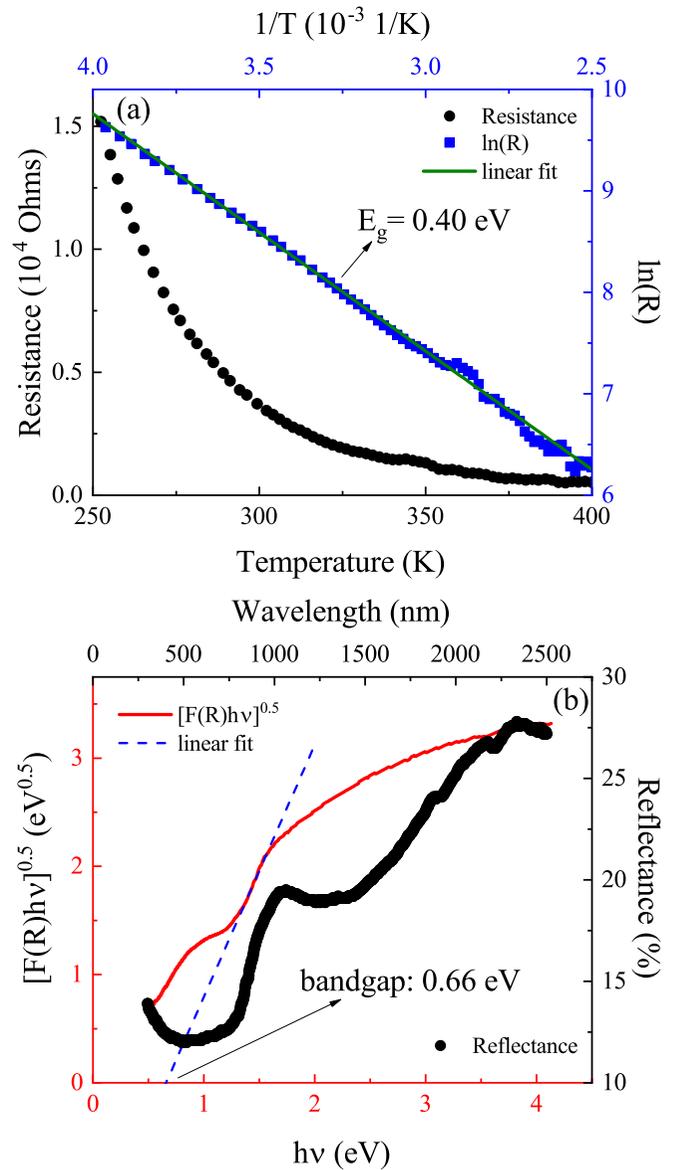


FIG. 9. (a) The temperature-dependent resistance of $Fe_2SiSe_4$. (b) The diffusion reflectance spectroscopy of the $Fe_2SiSe_4$ powder sample (top and right coordinates) and the plot of $[F(R)h\nu]^{0.5}$ vs photoenergy $h\nu$ (bottom and left coordinates).

calculated and simulated by a Schottky anomaly arising from the spin-orbit excitations [19]. This explanation may also apply to the anomalous magnetic transition at $T_{m3}$ for $Fe_2SiSe_4$. On the other hand, Considering the absence of a visible $C_p(T)$ anomaly at $T_{m3}$ and the discrepancy between zero-field-cooled and field-cooled magnetic susceptibility below $T_{m3}$, it is also plausible that the $T_{m3}$ anomaly arises from spin glass phenomena.

The thermal population in different spin-orbital states may drastically change across $T_{m3}$, which leads to rich magnetic behaviors in $Fe_2SiSe_4$. As demonstrated in Figs. 5 and 6, the magnetization switches from AFM to ferromagnetic behavior then back to AFM behavior as deceasing temperature. In addition, magnetic-field-induced spin-flop transitions are also observed for the M(H) curve at 15 and 2 K under

$H \parallel c$. Combined with the semiconductor nature of this compound, which will be discussed in the next section, $Fe_2SiSe_4$ may find applications in optoelectronics and magnetic devices.

### D. Band structure

The sawtooth lattice is known to have flat bands similar to the kagome lattice. The band structure of $Fe_2SiSe_4$ obtained by DFT calculations is shown in Fig. 8. The result reveals that $Fe_2SiSe_4$ is a semiconductor with an indirect band gap of 0.7 eV. The gap value is close to that determined from experiment. As demonstrated in Fig. 9(a), the temperature-dependent resistance of $Fe_2SiSe_4$ shows a typical semiconducting behavior, and the value is beyond the instrument limit below 250 K. Through fitting the resistance data using the thermal activation model as described by $R(T) = R_0 e^{(E_g/2k_B T)}$, a band gap $E_g = 0.40$ eV could be obtained. The diffusion reflectance spectroscopy of $Fe_2SiSe_4$ was also measured to check the band gap. The data are presented in Fig. 9(b), and an absorption band at around 800 nm is detected. The plot of $[F(R)h\nu]^{0.5}$ versus photo energy $h\nu$ is also shown in the figure. F(R) is the Kubella-Munk function, defined as $[F(R)h\nu]^{0.5}$ [37]. R is the experimentally observed reflectance. Using the methods proposed in [37,38], the band gap of $Fe_2SiSe_4$ is calculated to be 0.66 eV, which agrees well with the DFT calculated value.

From Fig. 8(a), $Fe_2SiSe_4$ is found to have flat bands from the G-X crystallographic direction, similar to other sawtooth materials such as $Mn_2SiSe_4$ and $Fe_2GeSe_4$ [4,16]. The corresponding total and projected density of states (DOS) for $Fe_2SiSe_4$ are shown in Fig. 8(b). The states near the Fermi level mainly come from the contributions from Fe $3d$ states and Se $4p$ states. Strong hybridization of Se $4p$ and Fe $3d$ orbits could be observed below the Fermi level.

For kagome metals where the flat band is quite close to the Fermi level, novel properties including emergent ferromagnetism, anomalous Hall effect, superconductivity, and topological phases have been extensively reported in recent years [9–11,39–42]. We find the band gap of $Fe_2SiSe_4$ is not large; there are possibilities that one could use pressure or chemical doping to tune it into a metal. Then it would be worthwhile to check whether a quasi-flat-band near Fermi level would enable realization of other versatile quantum phenomena.

### IV. CONCLUSIONS

In summary, we present a comprehensive study on the sawtooth lattice chalcogenide olivines $Fe_2SiSe_4$. This material has shown intriguing magnetic properties. Three magnetic transitions are identified: an AFM one at 110 K, a ferrimagnetic one at 50 K, and the last one at 25 K, possibly due to the spin-orbit excitation. We determined the magnetic structures at different temperatures through neutron diffraction and discovered a noncollinear double-**q** magnetic order below 50 K. DFT calculations suggest this complex magnetic structure may be due to the competition of AFM interactions on different sides of the sawtooth chain combined with the interchain exchange interaction. Through band-structure calculation and spectral experiments, $Fe_2SiSe_4$ was identified as a magnetic semiconductor with an indirect band gap of 0.66 eV and quasi-flat-band. We propose that $Fe_2SiSe_4$ may provide a new material playground for further research on magnetic devices and the flat-band effect through chemical doping.

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