Quasi-2D magnetism and origin of the Dirac semimetallic behavior in nonstoichiometric Sr$_{1-y}$Mn$_{1-z}$Sb$_2$ ($y, z < 0.1$)

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Nonstoichiometric Sr$_{1-y}$Mn$_{1-z}$Sb$_2$ ($y, z < 0.1$) is known to exhibit a coexistence of magnetic order and the nontrivial semimetallic behavior related to Dirac or Weyl fermions. Here, we report inelastic neutron scattering analyses of the spin dynamics and density functional theory studies on the electronic properties of Sr$_{1-y}$Mn$_{1-z}$Sb$_2$. We observe a relatively large spin excitation gap $\approx 8.5$ meV at 5 K, and the interlayer magnetic exchange constant only 2.8% of the dominant intralayer magnetic interaction, providing evidence that Sr$_{1-y}$Mn$_{1-z}$Sb$_2$ exhibits a quasi-2D magnetism. Using density functional theory, we find a strong influence of magnetic orders on the electronic band structure and the Dirac dispersions near the Fermi level along the Y-S direction in the presence of a ferromagnetic ordering. Our study unveils novel interplay between the magnetic order, magnetic transition, and electronic property in Sr$_{1-y}$Mn$_{1-z}$Sb$_2$, and opens new pathways to control the relativistic band structure through magnetism in ternary compounds.

Topological semimetals are newly emerged frontier in condensed matter physics and have stimulated tremendous research interest because they give access to new quantum phenomena and are very attractive for both fundamental research and technological application. Particular attention has focused on Weyl or Dirac semimetals that exhibit a coexistence with magnetism as a promising route to modify and control Weyl/Dirac fermions, electronic transport properties and band topology, among which SrMnSb$_2$ has attracted much interest recently. Liu et al.$^{[4]}$ reported a nontrivial semimetallic behavior related to Dirac or Weyl fermions including nearly massless quasiparticles with a $\pi$ Berry phase coupled to ferromagnetism in nonstoichiometric Sr$_{1-y}$Mn$_{1-z}$Sb$_2$. For the magnetic behavior, it displays ferromagnetic (FM) order below $T_C \sim 565$ K, followed by a transition to canted antiferromagnetic (AFM) order with a net FM component below $T_{FM-AFM} \approx 304$ K.$^{[3]}$ The nontrivial topological semimetal behavior was further supported by optical conductivity and ultrafast optical pump-probe measurements.$^4$ Nevertheless, Ramakuttty et al.$^{[5]}$ reported zero Berry phase indicative of trivial topology in nearly stoichiometric SrMnSb$_2$. Previous density functional theory (DFT) calculations$^{[6,7]}$ showed that the lattice distortion in the orthorhombic structure prevents the formation of the Dirac points near the Fermi level by opening a gap. Both results cannot account for the observed topological semimetallic behavior reported in Ref.$^3$. It is therefore challenging to explore whether there are indeed Dirac/Weyl points in proximity to the Fermi level and what drives their formation in Sr$_{1-y}$Mn$_{1-z}$Sb$_2$. Furthermore, SrMnSb$_2$ offers a wonderful opportunity to address an important question whether there is a close correlation between magnetic order and band topology in 3D Dirac compounds.

In addition to SrMnSb$_2$, other Alkaline earth ternary AMnC$_2$ “112” compounds (A = Sr, Ca, Ba, C = Bi or Sb)$^{[8,12]}$ were reported to be Dirac semimetal candidates with the coexistence of AFM order. An interplay between magnetic order and electronic transport properties was found in CaMnBi$_2$ due to coupling of the interlayer ferromagnetic component to the planar Bi electrons. The Dirac carriers in Bi layers were reported to enhance the interlayer exchange coupling $J_{\perp}$ significantly between magnetic layers in AMnBi$_2$ ($A$ = Ca, Sr) by the Raman spectroscopy.$^{[13]}$ However, Rahmet et al.$^{[8]}$ argued that the neglect of single-ion anisotropy $D$ in the Raman analysis may significantly exaggerate the obtained interlayer magnetic coupling since $D$ and $J_{\perp}$ are correlated. All of these facts emphasize the importance of an accurate determination of the interlayer magnetic coupling and the magnetic dimensionality in “112” compounds.

Here, by a combination of inelastic neutron scattering and linear spin wave theory, we report the magnetic excitation spectra and determination of the accurate magnetic exchange couplings and the single-ion anisotropy, which evidences a quasi-2D magnetism in Sr$_{1-y}$Mn$_{1-z}$Sb$_2$. More interestingly, we found a strong coupling between various magnetic orders and the relativistic band structures near the Fermi level by density functional theory (DFT), which reveals that FM order with the moment along $b$ axis induces the Dirac
points near the Fermi level in the band structure whereas various AFM orders have a disfavoring effect on it in Sr\textsubscript{1−y}Mn\textsubscript{1−z}Sb\textsubscript{2}.

Sr\textsubscript{1−y}Mn\textsubscript{1−z}Sb\textsubscript{2} crystals were grown using a flux technique [4]. Several single crystals with a total mass of approximately 600 mg were co-aligned at the (0 K L) horizontal scattering plane within ~ 3 degrees mosaicity. Inelastic neutron measurements were performed using the Spallation Neutron Source’s SEQUOIA spectrometer with its high-flux mode at Oak Ridge National Laboratory. The data were collected at 5 K and 350 K using a few different incident energies of 35, 70, 100, 160, 200 meV. The wave vectors \( \mathbf{Q} \) reported here are defined in reciprocal lattice unit (rlu). The constant-energy (\( E \)) cuts were fitted using a Lorentz function to obtain both the spin wave dispersion and intensity. The fits to spin wave dispersion and intensity using the SpinW package [15] yield the magnetic exchange constants and single-ion anisotropy. DFT was performed using the generalized gradient approximation and projector augmented wave approach [16] as implemented in the Vienna simulation package (VASP) [17, 18].

Figure 1 (a) shows the crystal and magnetic structures in Sr\textsubscript{1−y}Mn\textsubscript{1−z}Sb\textsubscript{2}. It crystallizes in the orthorhombic structure with space group \( \text{Pnma} \) (No. 62), consisting of a MnSb layer with edge-sharing MnSb(2)\(_4\) tetrahedral and flat Sb(1) layer sandwiched between two staggered Sr planes. Note that all the Sb(1) square net, Sr and MnSb(2)\(_4\) are distorted, different from the tetragonal structure in Bi-based “112” compounds. The two magnetic structures previously determined [3] for \( T < T_{\text{FM-AFM}} \) and \( T_{\text{AFM}} < T < T_{\text{C}} \) are illustrated in Fig. 1 (a). Fits to the order parameter of the magnetic Bragg peak (001) in Fig. 1 (b) to a power law of the form \( I \propto (T_{\text{C}} - T)^{2\beta} \) yields a critical exponent \( \beta \approx 0.25 \). Such a value falls in the region 0.1 < \( \beta < 0.25 \) expected for quasi-2D systems [19] (compared to the 0.36 in the 3D Heisenberg model) and is similar to that in typical quasi-2D pnictide LuMnSbO (Lu=La or Ce) [20]. This implies that Sr\textsubscript{1−y}Mn\textsubscript{1−z}Sb\textsubscript{2} may be magnetically quasi-two-dimensional. The field dependence of the magnetization in the inset of Fig. 1 (b) confirms a clear ferromagnetism below \( T < T_{\text{C}} \) down to 5 K.

To investigate the spin dynamics of Sr\textsubscript{1−y}Mn\textsubscript{1−z}Sb\textsubscript{2}, we performed inelastic neutron scattering measurements. Figure 1 (c,e) and (d,f) compares the magnetic excitations near the AFM zone center (0 0 1) at 5 K (\( T < T_{\text{FM-AFM}} \)) and 350 K (\( T_{\text{FM-AFM}} < T < T_{\text{C}} \)). At 5 K within the AFM ordered state, a clear spin gap \( E_g \approx 8.5 \text{ meV} \) is observed indicative of the existence of a single-ion anisotropy. The spin gap closes at 350 K when the long-range AFM order disappears. Another difference between these two temperatures is that, whereas the spin wave dispersion exists at 5 K, the dispersion disappears, and evolves into a spin fluctuation spectra near the AFM zone centers at 350 K. The magnetic excitations along out-of-plane \( H \), in-plane \( K, L \) and diagonal \([0 K L]\) directions at 5 K are displayed in Fig. 2 (a-d) (the high-symmetric brillouin symbols are illustrated in the inset of Fig. 2 (a)). There is a steep dispersion along in-plane directions extending to \( \approx 70 \text{ meV} \) at the AFM zone boundary \( Z \) and \( T \) points, but the dispersion along out-of-plane \( H \) direction is much weaker, with \( E \approx 18 \text{ meV} \) at the zone-boundary \( X \) point. This indicates that the out-of-plane magnetic interaction is much weaker than the in-plane one suggesting a quasi-2D magnetism.

Figure 3 compares constant-energy slices in the (0 K L) scattering plane at energy transfers around 5, 17 and 30 meV at 5 and 350 K. At 5 K, no magnetic excitations are apparent around 5 meV in Fig. 3 (a) owing to the existence of higher spin gap of \( E_g \approx 8.5 \text{ meV} \). As the transferred \( E \) increases, a ring of scattering emerges at AFM zone center positions such as (0 0 ±1) and (0 ±1 0). The diameter of the rings increases with increas-
indicating there is no signature of strong spin frustration.

Moreover, the AFM NN\(^{-}-\)NN\(^{+}\) anisotropy parameter \(A\) is found to be negligible, i.e., \(A_{\perp}=0\). Thus, the leading E transfer (see Fig. 3(b) and (c)), indicative of dispersive spin waves. In sharp contrast, the magnetic excitations exhibit different features at 350 K. A diffuse magnetic excitations can be seen in Fig. 3(d) at around 5 meV due to the closure of the spin-gap. As E transfer increases, the magnetic excitations become more diffuse and spread out without the ring-like feature, as shown in Fig. 3(e) and eventually evolve to be hardly visible at high E transfer region in Fig. 3(f). This indicates the existence of the low-E AFM spin fluctuations at 350 K. It is worthwhile pointing out that we do not observe clear dispersion between spins and \(A\)\(\perp\) is suppressed when the ordered Mn moment \(M_{s}\) is less than 2.8 % of the in-plane \(J_{1}\), signaling the quasi-2D magnetism. The \(J_{\perp}\) is considerably weaker than that proposed in Ref. 1 on AMnBi\(_2\) (A=Ca,Sr) (with similar interlayer Mn-Mn distances), which was claimed as enhancement due to the Dirac carrier Bi layers. 3). The emergence of the spin gap is ascribed to the uniaxial single-ion anisotropy matrices \(A_{\alpha,\beta}\)\(\perp\).

To gain insight into the experimental observations, we performed DFT calculations for stoichiometric SrMnSb\(_2\) using the high-temperature structure at 315 K and the low-temperature one at 5 K 3. For Sr, a potential, in which semi-core \(s\) and \(p\) states are treated as valence states, is used (Sr\(sv\)), and for Mn and Sb, standard potentials were used (Mn and Sb, respectively, in the VASP distribution). In most cases, we use a 2 \(\times\) 8 \(\times\) 8 \(k\)-point grid and an E cutoff of 500 eV with spin-orbit coupling included. The +U correction is not included because SrMnSb\(_2\) is an itinerant magnetic system.

We first investigate the magnetic properties at high temperature. Using the 315 K structure, we compute the total E of several symmetry-allowed magnetic configurations 3, including C-type AFM (CAF), G-type AFM, A-type AFM, and FM with spin orientation taken along the \(a\), \(b\) or \(c\) axis (the spin orientation will be indicated as a subscript as for example CAFM\(_a\)). It turned out that CAFM\(_a\) is most stable, while the FM\(_b\) state is more stable than FM\(_a\) and FM\(_c\). This discrepancy is resolved by constrained magnetization calculations. As shown in Fig. 4(a), the relative E between FM\(_b\) and CAFM\(_a\) is reversed when the ordered Mn moment \(M_{s}\) is suppressed at around \(M_{s}=1.6\mu_{B}\). In the PM state (\(M_{s}=0\)), the density of states (DOS) has a sharp peak near the Fermi level (\(E=0\)) as shown in Fig. 4(b). Thus, the leading
instability in the high-temperature PM phase is toward FM ordering due to the Stoner instability, followed by the first-order transition from FM$_b$ to CAFM$_a$ at lower temperature with much larger $M_s$ ($\approx 3.6\mu_B$ at 5 K [3]). This provides a natural explanation for the sequence of magnetic transitions reported from experiments [3].

Now we turn to the low-temperature electronic property using the structural information at 5 K. We computed the total energy of several magnetic configurations using the low-temperature structure at 5 K. We found it is robust that the in-plane (out-of-plane) exchange is uniaxial [22], which indicates that the CAFM$_a$ state is most stable, and the FM$_b$ is metastable at 5 K. It is insightful to examine the electronic band structures of the PM, the CAFM$_a$, and the FM$_b$ states, as shown in Figure 4 (c), (d), and (e), respectively. Because of the non-symmorphic symmetry, Dirac cones are expected at the Y and the T points [5, 23] (X and M points in the notation of Ref. [5]). In the PM state, the Dirac cones are observed at $E \sim -0.5$ eV at the Y point, but those at the T point are not clearly resolved in this E window. The band structure is influenced by magnetic order. In the CAFM$_a$ state, the Dirac cone at the T point is clearly seen at $E \sim -1.3$ eV. This dispersion relation is consistent with the one reported in Refs. [5, 23] except for the current semimetallic behavior due to the difference in the exchange correlation potential or local $U$. As discussed in Ref. [5], the location of the Dirac cone is too far from the Fermi level to account for the $\pi$ Berry phase reported in Ref. [3]. Interestingly, when the metastable FM$_b$ state is considered, the Dirac cone appearing in the PM state at the Y point splits due to the spin polarization, and one of them becomes closer to the Fermi level ($E \sim -0.3$ eV) [Fig. 4 (e)]. As shown in Fig. 4 (f)-(h), these Dirac cones form a line node along the Y-S direction, and two Dirac cones merge at the S point. This is a consequence of two units of MnSb(2)$_4$ and Sb(1) layers, each of which supports two-dimensional Dirac cones, and the mixing between the two units is suppressed at $k_z = \pi$.

Once the Fermi level is tuned near the Dirac cones, the $\pi$ Berry phase should be manifested in the quantum oscillations of magnetoresistance or magnetization. A natural question is how one can realize this condition in SrMnSb$_2$. In reality, the $\pi$ Berry phase is observed only in non-stoichiometric Sr$_{1-y}$Mn$_{1-z}$Sb$_2$ samples in Ref. [3]. Thus, the current study suggests the following scenario. The relative energy between the CAFM$_a$ and FM$_b$ in non-stoichiometric samples could be much smaller than that in stoichiometric samples. As a result, the FM$_b$ state could remain in place more easily at low temperatures, resulting in either canted AFM order [5] or possi-
bile phase separation between collinear AFM$_a$ and FM$_b$ phases. The FM state induces the splitting of Dirac cone at Y point with one of them being closer to the Fermi level. Moreover, the Fermi level is expected to be lowered by Sr and/or Mn off-stoichiometrically to locate near Dirac cones. In order to verify this scenario, it is necessary to control the defect density and magnetism, and isolate FM regimes from others.

In summary, we have examined the magnetic excitations, and investigated the origin of the Dirac semimetallic behavior in nonstoichiometric Sr$_{1−y}$Mn$_{1−z}$Sb$_2$. The magnetic exchange constants are determined, indicative of a quasi-2D magnetism, with no significant enhancement of $J_\perp$ by the Dirac carrier Sb layers. The constrained magnetization calculations by our DFT interpreted the occurrence of the successive PM-FM-AFM transition. We further demonstrated that while the AFM order does not favor the formation of the Dirac cones near the Fermi level, the FM order/component plays a key role in inducing the Dirac points in proximity to the Fermi level to drive the system to be Dirac semimetal in Sr$_{1−y}$Mn$_{1−z}$Sb$_2$. Our study provides a new clue to the understanding of the origin of Dirac semimetals and to seek for novel Dirac semimetals by adjusting the magnetic order.

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[22] By mapping the total energy of different magnetic ordering to that of a Heisenberg-type model consisting of in-plane (out-of-plane) exchange $J_1$ between Mn moments $S = 1.8\mu_B$ with the single ion anisotropy $K$, we found $J_1 = 25.0$ (AFM), $J_2 = -0.23$ (FM), and $K = -0.16$ (uniaxial along the a) in unit of meV. The precise values of these parameters depend on the value of local U on a Mn site and the exchange correlation potential, which could reconcile why these values are larger than those obtained from the fits to experimental spin waves.
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