Layered transition-metal pnictide SrMnBi₂ with metallic blocking layer

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The physical properties and the band structure of the layered pnictide SrMnBi₂ were investigated. This compound has a crystal structure similar to that of the superconducting Fe pnictides, and is a bad metal with large residual resistivity. Magnetic order sets in at very high temperatures, around 290 K, as shown by magnetization, resistivity, and specific heat data. Band structure calculations using density functional theory (DFT) are consistent with the thermodynamic and transport measurements, suggesting a checkerboard antiferromagnetic (cAFM) ground state and a localized picture for the magnetism. Moreover, DFT results indicate that the Mn 3d electrons are strongly correlated, and that, unlike in the known superconductors, the Sr-Bi₁₁ compound is metallic. One more notable feature of the DFT calculation is the multiple Dirac-cone-like dispersion close to the Fermi level.

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I. INTRODUCTION

With the ongoing interest in layered iron pnictide (Fe-Pn) and iron chalcogenide (Fe-X) superconductors, one generally accepted thesis is that superconductivity appears close to a magnetic instability, at the crossover between itinerant and local moment magnetism. This strategy was successfully employed in tuning the layered Fe-Pn and Fe-X compounds from a spin density wave (SDW) ground state to superconductivity by either chemical doping or pressure. The ability for such tuning lies within the altering of the Fermi surface by either changes in the crystal structure, directly observed as a structural phase transition preceding or simultaneous with the SDW transition, or by changing the charge count, or both.

From the structural point of view, the Fe-Pns are even more versatile than, for example, their older cousins, the cuprates, because the superconducting layer has finite thickness in the former case. In turn, the thickness, or the Pn-Fe-Pn angle, respectively, is empirically correlated with the superconducting temperature Tc, such that Tc is maximized close to the ideal tetrahedral angle. A natural direction to look for new superconductors is in materials where transition metals are tetrahedrally coordinated by pnictogen atoms, with the Pn₄ tetrahedra close to ideal. There are also various choices for the blocking (B) layer separating the Fe-Pn layers; in the known pnictide superconductors, B is insulating, and plays the role of charge reservoir. Shim et al. have predicted that the 112-type compounds BaFeAs₂ and BaFeSb₂, if they existed, would have metallic B layers. The presence of the additional metal layer in between the T-Pn layers (T = transition metal) may shed some light on the controversial mechanism for superconductivity in the pnictides, if such 112 compounds could be synthesized, and if they showed the predicted physics.

Two years after the Shim prediction, the BaFePt₂ compounds remain elusive, as several groups have failed to synthesize them in either polycrystalline or single-crystal form. Our efforts to synthesize other T-Pn 112 compounds have been successful in the Sr-Mn-Bi ternary space. Single crystals of SrMnBi₂ with plate-like geometry were grown using a liquid flux technique. This compound has previously been reported in polycrystalline form, and only structural information was known. Very recently, Park et al. have characterized this compound, emphasizing the presence of anisotropic Dirac fermions. In this paper, we report the physical property measurements on SrMnBi₂, together with results of band structure calculations. Our results are in good agreement with those in the recent paper by Park et al. Furthermore, we show that there are structural and physical similarities between SrMnBi₂ and the theoretical BaFePn₂ compounds. In addition, similarities also exist between ours and the theoretical 112 compounds, on one hand, and the known Fe-Pn superconductors, on the other hand. Most importantly, SrMnBi₂ has a metallic B layer, as predicted for the theoretical 112 compounds, and in contrast with the insulating B layer in the layered iron pnictides. These similarities and differences between the three classes of compounds will be discussed in light of the current understanding of the mechanism for superconductivity in the layered T-Pn compounds.

II. EXPERIMENTAL METHODS

Single crystals of SrMnBi₂ were grown using Bi self-flux, with an initial composition Sr : Mn : Bi = 1 : 1 : 8. An alumina crucible containing the initial materials was sealed under partial Ar atmosphere in a silica tube, heated up to 600°C, followed by slow cooling at a rate of ~2.4 ºC/h and decanting at 400 ºC. Well-formed square crystals with tapered edge facets were obtained, with in-plane dimensions 2–4 mm and thicknesses 0.5–2 mm. Anisotropic magnetization measurements up to 400 K were performed in a Quantum Design (QD) Magnetic Property Measurement System (MPMS), and above 310 K in a vibrating sample magnetometer in a QD Physical Property Measurement System (PPMS). The specific heat and resistivity were measured in a QD PPMS. Room-temperature powder X-ray diffraction data were recorded on a Rigaku D/max diffractometer, using Cu Ka radiation and a graphite diffracted beam monochromator. The measured data is shown in Fig. 1 (black symbols) together with the
FIG. 1. (Color online) The measured powder X-ray diffraction pattern of SrMnBi₂ (black symbols) together with the calculated positions (blue lines) for space group $I\bar 4_1/mmm$ and lattice parameters $a = 4.56 \, \text{Å}, c = 23.09 \, \text{Å}$. Minute impurity peaks belonging to Bi are marked by asterisks [most of the marked peaks coincide with peaks for SrMnBi₂ (blue vertical lines)].

Calculated peak positions (indicated by blue lines) for space group $I\bar 4_1/mmm$ and lattice parameters $a = 4.56 \, \text{Å}, c = 23.09 \, \text{Å}$. The unit cell parameters are very close to those previously reported. A small amount of remnant Bi flux was also present in the powder pattern. Of the numerous calculated Bi peaks, very few might be detected in our measurement (marked by asterisks in Fig. 1), and most of them coincide with SrMnBi₂ peaks. This indeed implies that only a minute amount of flux is present in the pattern.

Similarities and differences between the crystal structure of SrMnBi₂ and the well-known superconducting parent compounds LaOFeAs and BaFe₂As₂ are readily apparent, as illustrated in Fig. 2. The $T_X4$ tetrahedral layer (where $T$ = transition metal and $X$ = P, As, or Se) is a feature common to all known Fe-X superconductors. What differentiates these types of compounds structurally is the blocking layer $B$. For example, the 122 unit cell is comprised of two staggered Fe-As layers [Fig. 2(c)], and similarly, SrMnBi₂ consists of two staggered Mn-Bi(2) layers [Fig. 2(a)], separated by Sr-Bi(1) layers. By comparison, the hypothetical BaFePn₂ compounds were predicted to form in a structure with Fe-Pn layers stacked on top of each other, and separated by Ba-Pn layers [Fig. 2(b)]. As a consequence, the SrMnBi₂ unit cell is nearly twice as large in the $c$ direction as that of BaFePn₂.

In the MnBi(2) layer of SrMnBi₂, the Bi-Mn-Bi angles for Bi atoms with the same and different $z$ coordinates [as illustrated in Fig. 2(d)] are $\alpha_1 = 104.62^\circ$ and $\alpha_2 = 111.95^\circ$, respectively. These values are closer to the perfect tetrahedron angle $\alpha = 109.47^\circ$ than in BaFe₂As₂, where the respective values are $\alpha_1 = 103.39^\circ$ and $\alpha_2 = 112.60^\circ$. If the empirical relation between superconducting transition temperature $T_c$ and angle $\alpha$ also holds for SrMnBi₂, then SrMnBi₂ is a promising parent compound for superconductivity when doped or under pressure. Such experiments are currently underway.

To further the comparison between SrMnBi₂ and the parent compounds of the known Fe-X superconductors, we performed anisotropic magnetization measurements in an applied magnetic field $H = 1 \, \text{T}$, as shown in Fig. 3. Two transitions can be identified around 250 and 290 K for $H \parallel ab$ (black symbols, top inset, Fig. 3). The upper transition likely corresponds to antiferromagnetic ordering, as antiferromagnetism is shown to be the ground state through DFT calculations (see below). In this case the lower temperature transition at $T_2$ may be magnetic (due to spin reorientation), associated with a structural distortion, or both. Except for temperatures close to these two transitions, the susceptibility for both $H \parallel ab$ and $H \perp ab$ decreases with

FIG. 2. (Color online) The crystal structures of (a) SrMnBi₂ (space group $I\bar 4_1/mmm$, from Ref. 14), (b) hypothetical compound BaFeAs₂ (space group $P4_2/nmm$, predicted in Ref. 13), and (c) BaFe₂As₂ (space group $I\bar 4_1/mmm$). The red atoms are alkaline earth atoms, the green atoms are transition metal atoms, and the blue atoms are pnictogen atoms. $\Delta_T$, $\Delta_{\perp T}$, and $\Delta_{\parallel T}$ represent the distance between adjacent $T$ layers, and the distance between Pn planes above and below the same $T$ plane, respectively.

FIG. 3. (Color online) Anisotropic $M(T)$ data for $H = 1 \, \text{T}$. The two transitions at $T_1$ and $T_2$ are marked by vertical arrows (top inset). Bottom inset: high-temperature $M(T)$ data for $H \parallel ab$, showing the melting temperature for SrMnBi₂ (vertical arrow).
temperatures up to 350 K. Around the two transitions, the $H \perp ab$ susceptibility (black symbols, Fig. 3) increases, reminiscent of a charge density wave transition (CDW). This behavior is similar to what was recently observed on single crystals grown from a stoichiometric melt. However, the two transitions were indistinguishable in the latter case. In the CDW scenario, a magnetic moment of $1.3\mu_B$/Mn can be estimated from the Curie-Weiss-like susceptibility below 100 K. This value is significantly smaller than that for Mn$_2$As. Additional measurements up to 800 K and $H = 2$ T (bottom inset, Fig. 3) revealed that the susceptibility decreases with $T$ above $\sim 320$ K and up to the 550 K melting temperature. The absence of Curie-Weiss behavior at high temperatures may be due to a large anisotropy of the magnetic coupling. This would be consistent with the two-dimensional character of the electronic structure, revealed by band structure calculations. Similar non-Curie-Weiss behavior was reported for BaFe$_2$As$_2$. Temperatures may be due to a large anisotropy of the magnetic coupling.

The $H = 0$ resistivity data confirm the high-temperature transitions observed in the susceptibility: $\rho(T)$ shows a small drop around 290 K on cooling, while the lower transition is marked by a local maximum (full symbols, Fig. 4). Above 250 K, a clear difference between warming and cooling measurements is observed (open and full symbols, respectively, Fig. 4), indicating that one or both of the two transitions is first order. The residual resistivity value $\rho_0 \approx 160 \mu\Omega$cm suggests that SrMnBi$_2$ is a bad metal, albeit slightly more metallic than the 122 or 1111 iron pnictides. Fermi-liquid-like behavior is observed in SrMnBi$_2$ below $\sim 25$ K, as shown in the inset of Fig. 4: a linear fit of $\rho$ vs $T^2$ yields a coefficient $A = 0.125 \mu\Omega$cm/K$^2$ in $\rho(T) = \rho_0 + AT^2$, with small deviations from linearity at the lowest temperatures possibly due to the small amount of Bi seen in powder diffraction. Notable differences exist between our data and that recently reported on stoichiometrically grown crystals: the two transitions observed in the current $M(T)$ and $\rho(T)$ data are obscured in the resistivity measurements by Park et al. Although Fermi-liquid behavior is observed in both cases, the coefficient $A$ for the quadratic term is different, presumably due to the different crystal-growth procedure.

The two transitions seen in $M(T)$ data for $H \perp ab$ in Fig. 3 are marked by peaks in the derivative plot $d(MT)/dT$ [Fig. 5(a)] at $T_1 = 292$ K and $T_2 = 252$ K. Moreover, for an antiferromagnetically ordered metal, it is expected that $d(MT)/dT$ will be qualitatively similar to $d\rho/dT$. Indeed, the $d(MT)/dT$ plot for $H \perp ab$ in Fig. 5(a) (black symbols) reveals the two peaks at the same temperatures as those from $d\rho/dT$ [Fig. 5(b)]. Because of the high temperatures at which these transitions occur, only a broad peak can be seen in the $H = 0$ specific heat measurement [Fig. 5(c)] around $T_1$, with a barely visible signature at $T_2$. The lower-temperature transition may correspond to a spin-reorientation or a structural transition, or both, and neutron diffraction experiments are necessary to better characterize the magnetically ordered state in SrMnBi$_2$. The low-$T$ specific heat data plotted as $C_p/T \sim T^2$ is shown in the inset in Fig. 5(c). A linear fit (red line) below $T \sim 10$ K gives an enhanced value for the electronic specific heat coefficient $\gamma = 36.5$ mJ/mol K$^2$. According to the linear fit of resistivity and specific heat at low temperatures, the Kadowaki-Woods (KW) ratio is about $A/\gamma^2 = 9.38 \times 10^{-5}$ $\mu\Omega$cm K$^2$ mol$^{-2}$/mJ$^2$. This is one order of magnitude larger than for heavy fermion materials, suggesting the presence of enhanced electronic correlations in SrMnBi$_2$. 

![FIG. 4. (Color online) $\rho(T)$ data for $H = 0$ and current $i \parallel ab$, measured on warming (open symbols) and on cooling (full symbols). Inset is the linear fit of $\rho \sim T^2$ for cooling data, with the resistivity coefficient $A = 0.125 \mu\Omega$cm/K$^2$.](064428-3)

![FIG. 5. (Color online) The transition temperatures could be obtained from maxima in (a) $d(MT)/dT$ (open symbols for $H \perp ab$ and full symbols for $H \parallel ab$) and (b) $d\rho/dT$ (measured on warming). (c) Specific heat $C_p(T)$ shows a broad peak at $T_1$. Inset: $C_p/T$ vs $T^2$ (blue symbols), with a linear fit below $T \approx 10$ K (red line), from which the electronic specific heat coefficient $\gamma$ is determined to be $\gamma = 36.5$ mJ/mol K$^2$.](064428-3)
III. BAND-STRUCTURE CALCULATIONS

To explore the electronic properties of SrMnBi$_2$, we performed band structure calculations using the full-potential linearized augmented plane-wave method implemented in the WIEN2K package.\textsuperscript{24} We used the generalized gradient approximation (GGA) for the exchange correlation potential. The radius of muffin-tin (RMT) values are set to 2.8, 2.2, 2.5, and 2.5 a.u.\textsuperscript{25} for Sr, Mn, Bi(1)$_1$, and Bi(2)$_2$ [as defined in Fig. 2(a)], respectively. We use the fitted lattice parameters and internal positions taken from Ref. 14, and it is assumed that no structural transitions occur down to 0 K. The calculations were performed in the paramagnetic (PM), ferromagnetic (FM), checkerboard antiferromagnetic (cAFM), or striped antiferromagnetic (sAFM) states, with the Mn ion magnetic moments ordered in the $ab$ plane. The total energies (relative to the PM state) of the FM, cAFM, and sAFM phases are $-2.804$ eV, $-3.394$ eV, and $-3.232$ eV per unit cell (4 formula units), respectively. This corresponds to a cAFM ground state. However, the total energy difference between the cAFM and sAFM states is small, which may lead to phase competition upon doping or pressure. Due to the large distance between adjacent Mn-Bi(2)$_2$ layers, only magnetic configurations with moments within the plane were considered.

Compared with the superconducting Fe-Pns, SrMnBi$_2$ and the hypothetical BaFePn$_2$ share much more localized 3$d$ electrons. In the SrMnBi$_2$ case, all the magnetic moments are localized within the muffin-tin spheres (2.2 a.u.), and the magnitude of moment for the Mn ion is 3.858 $\mu_B$ in the cAFM state. To verify the calculated value, we measured the anisotropic magnetization $M(H)$ at $T = 2$ K up to 7 T (not shown) but no saturation was observed. Considering also the deviation of the susceptibility from the Curie-Weiss law, the experimental values of Mn moments could not be determined. Since DFT within GGA can severely overestimate the moments in Mn, experimental moment could be smaller than the calculated value.

The density of states (DOS) in the PM state (Fig. 6) shows a pronounced Mn peak at the Fermi level, indicative of a magnetic instability and consistent with half filled Mn 3$d$

As emphasized in the inset in Fig. 6, both Mn-Bi(2)$_2$ and Sr-Bi(1)$_1$ layers contribute to the total DOS at the Fermi level. This implies that SrMnBi$_2$ is drastically different from LaOFeAs and BaFe$_2$As$_2$: the blocking layer $B$ is metallic in the former compound, and insulating in the latter two.\textsuperscript{26,27} However, the metallic $B$ layer is consistent with the theoretical prediction\textsuperscript{13} on the related hypothetical compounds BaFePn$_2$. There is also an important difference between ours and the hypothetical 112 compounds with regard to the number of 3$d$ electrons: Fe$^{2+}$ has an even number of electrons per formula unit in the discussed Fe compounds. In the PM DOS plots of these systems, the peaks for the 3$d$ bands are generally pushed below the Fermi level. In contrast, Mn$^{2+}$ has a 3$d^5$ electron configuration, and consequently, a peak in the PM DOS close to the Fermi level. The implication is that stronger correlations can be expected in the Mn-based compound compared with their Fe analogs. Indeed, $T_N$ in SrMnBi$_2$ is close to 290 K, nearly twice as large as that of BaFe$_2$As$_2$,\textsuperscript{4} and the $\gamma$ and $A$ coefficients are larger in SrMnBi$_2$ than that of typical metals.

The band structure of the PM state is shown in Fig. 7. Highly dispersive bands that cross the Fermi level come from the Sr-Bi(1)$_1$ layer (green), and they are well decoupled from the flat Mn 3$d$ bands (red). Interestingly, Dirac cones\textsuperscript{28} are observed along the $M$-$\Gamma$ and $A$-$Z$ paths. They are even more pronounced in the cAFM state, as seen in Fig. 8. Such features near the Fermi level were predicted to be important in understanding the exotic electronic properties of BaFe$_2$As$_2$.\textsuperscript{29} An additional observation from the band structure in the cAFM state is that the Mn 3$d$ bands are largely removed from the Fermi level via exchange splitting. But the bands with 6$p$ character (Bi$_{11}$, green) are hardly changed by the magnetic ordering. This is indicative of very weak inter-layer coupling, which implies more two-dimensional electronic character of SrMnBi$_2$, similar to the prediction for the hypothetical BaFePn$_2$.\textsuperscript{13}

![FIG. 6. (Color online) The total and partial DOS of SrMnBi$_2$ in PM state, with Bi(1)$_1$ and Bi(2)$_2$ defined in Fig. 2. Inset is the enlarged plot near the Fermi level.](image_url)

![FIG. 7. (Color online) Band structure of SrMnBi$_2$ in PM state. The bands with red color are the Mn 3$d$ electrons, and the bands with green color are the 6$p$ bands from the Sr-Bi(1)$_1$ layer (Ref. 30).](image_url)
The calculated DOS in the cAFM state is shown in Fig. 9. Like in the PM state, the Sr-Bi(1) layer has a large contribution to the total DOS at the Fermi level (inset). The exchange splitting between the spin-up and -down 3$d$ bands is about 4 eV, larger than the 3$d$ band width, which is \( \sim 1.5 \) eV. The Fermi level sits in a valley of DOS sandwiched between the upper minority and lower majority spin bands. Such a local minimum in the DOS at the Fermi level implies poor metal behavior, and this is indeed confirmed experimentally by the resistivity values of several \( 10^2 \) \( \mu \)Ωcm (Fig. 4). The strong magnetic polarization is in accordance with the high Néel temperature (290 K) observed experimentally. For this study the on-site Hubbard interactions have not been taken into account. For the half filled 3$d$ bands in the PM state, the Hubbard interactions may also contribute to electron correlations within the Mn-Bi(2) layer. A full understanding of electron correlations in SrMnBi$_2$ requires a thorough comparison between LDA+\( U \) results and experimental measurements.

The Fermi surface of the PM phase is plotted in Fig. 10. The V-shaped sheets centered at the X points come from the Sr-Bi(1) layer. The other cylindrical or spherical pockets belong to the Mn-Bi(2) layer. Pockets with very weak dispersion along the \( c \) direction were observed, and this two-dimensional character mainly belongs to the Mn 3$d$ electron. Such two-dimensional features were also reported in the Fe-Pn\(^{26}\) and the hypothetical BaFePn\(_2\).\(^{13}\) However, in SrMnBi$_2$, no apparent Fermi-surface nesting exists between electron/hole pockets near the \( \Gamma \) point and hole/electron pockets near the \( M \) point. This may explain why the sAFM state is not favored in our compound, in sharp contrast with Fe-Pn. Due to the different Fermi-surface topologies, the spin fluctuations in SrMnBi$_2$ should affect the in-plane and interplane conductivities in different ways from the Fe pnictides, and the physical consequences deserve further investigation.

**IV. CONCLUSIONS**

SrMnBi$_2$ is a layered transition-metal pnictide with structural similarities to the known iron-based superconductors\(^3,4,12\) and the hypothetical BaFePn$_2$ compounds.\(^{13}\) The relative thickness of the T-Pn layer \( \Delta z_{\text{Pn}}/\Delta z_{\Gamma} \) [\( \Delta z_{\text{Pn}} \) and \( \Delta z_{\Gamma} \) defined in Fig. 2(a)] is smaller in SrMnBi$_2$ (0.308) than in BaFe$_2$As$_2$ (0.48)\(^2\) and comparable with that of LaOFeAs (0.302),\(^3\) larger only than the respective value in the hypothetical 112 compounds (0.23).\(^{13}\) However, of all these layered T-Pn compounds, SrMnBi$_2$ has Pn-T-Pn angles \( \alpha_1 = 104.62^\circ \) and \( \alpha_2 = 111.95^\circ \), closest to the perfect tetrahedron angle (109.47$^\circ$). The \( \Delta z_{\text{Pn}}/\Delta z_{\Gamma} \) and \( \alpha_{1,2} \) values render SrMnBi$_2$ most two-dimensional of the known T-Pn materials. Additionally, DFT calculations indicate that the blocking layer \( B = \text{SrBi}(1) \) is metallic in SrMnBi$_2$. All these observations suggest that this compound is a promising candidate for superconductivity upon doping or under pressure. If the superconducting temperature \( T_c \) is commensurate with the magnetic ordering temperature, the large \( T_N \) value \( T_N = 290 \) K suggests the possibility of high \( T_c \) in this system.
In conclusion, we conducted both an experimental and theoretical investigation of the layered transition-metal pnictide compound SrMnBi$_2$. Consistent with experimental observations, the half filled bands lead to a strongly correlated nature for the Mn $3d$ electrons. Fermi-liquid behavior is found in SrMnBi$_2$ at low temperatures, with a large coefficient $A$ of the quadratic temperature term in $\rho(T)$ (inset, Fig. 4). Specific heat measurements suggest that the electronic specific heat coefficient $\gamma$ is also enhanced (inset, Fig. 5), leading to a KW ratio one order of magnitude larger than that of heavy fermions. Thus this material appears to be a strongly correlated system. Moreover, the absence of Curie-Weiss behavior of the magnetic susceptibility in the paramagnetic state suggests complex spin dynamics, to be further investigated with neutron scattering. Lastly, doping the 3$d$ bands away from the half-filling condition will likely suppress the magnetism. It is very possible for superconductivity to occur on the verge of such a transition, and measurements on doped polycrystalline samples are currently being carried out.

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