Abstract The highly two-dimensional superconducting system Sr$_2$(Mg$_y$Ti$_{1-y}$)O$_3$FeAs, recently synthesized in the range of 0.2 ≤ y ≤ 0.5, shows an Mg concentration-dependent $T_c$. Reducing the Mg concentration from y=0.5 leads to a sudden increase in $T_c$, with a maximum $T_c$ $\approx$ 40 K at y=0.2. Using first principles calculations, the unsynthesized stoichiometric y=0 and the substoichiometric y=0.5 compounds have been investigated. For the 50% Mg-doped phase (y=0.5), Sr$_2$(Mg$_y$Ti$_{1-y}$)O$_3$ layers are completely insulating spacers between FeAs layers, leading to the fermiology such as that found for other Fe pnictides. At y=0, representing a phase with metallic Sr$_2$TiO$_3$ layers, the $\Gamma$-centered Fe-derived Fermi surfaces (FSs) considerably shrink or disappear. Instead, three $\Gamma$-centered Ti FSs appear, and in particular two of them have similar size, like in MgB$_2$. Interestingly, FSs have very low Fermi velocity in large fractions: the lowest being 0.6×10$^6$ cm/s. Furthermore, our fixed spin moment calculations suggest the possibility of magnetic ordering, with magnetic Ti and nearly nonmagnetic Fe ions. These results indicate a crucial role of Sr$_2$(Mg$_y$Ti$_{1-y}$) layers in this superconductivity.

Keywords Superconductivity · Fe-pnictides · Electronic Structure · Fermiology

1 Introduction

Since Hosono and coworkers discovered superconductivity in hole-doped LaFeAsO at $T_c$ = 26 K,[1] Fe-pnictides have been the cause of much excitement.[2] The mechanism of the superconductivity has yet to be uncovered, but many have discussed the nesting of two Fermi surfaces at the $\Gamma$ and $M$ points.[3][4][5][6] However, some experimental and theoretical investigations of a few superconducting Fe-pnictides have shown the absence of a nested fermiology, though these compounds are expected to share a common mechanism of the superconductivity.[7][8][9][10]

In the pnictide family, the recently synthesized 21322 systems Sr$_2$MO$_3$FePn ($M$=transition metal, and $Pn$=P or As), with a thick perovskite-like spacer between FePn layers, have stimulate a great enthusiasm due to its possible bimetallic character as well as its high two-dimensionality.[11][12][13][14][15][16] Sato et al. synthesized a member of the 21311 system Sr$_2$(Mg$_y$Ti$_{1-y}$)O$_3$FeAs in the range of 0.2 ≤ y ≤ 0.5.[17] With 50% Mg doping of the Ti sites (i.e., y=0.5), the superconductivity appears at $T_c$ = 10 K, but with a small superconducting volume fraction, which thus implies that there is no intrinsic superconductivity. On reducing the Mg concentration, $T_c$ increases sharply to $\sim$ 34 K at y = 0.45, and reaches a maximum $\sim$ 40 K at y=0.2, slightly higher than that in a stoichiometric Sr$_2$VO$_3$FeAs. Throughout all of the doping range considered, no significant changes in the lattice constants were observed. Although synthesis of a sample below y=0.2 has not been successful yet, the Ti rich phase may be expected to have a higher $T_c$. This implies that the Ti ions play a crucial role in the superconductivity of this system.

From the viewpoint of formal charge, the y=0.5 phase (i.e., 50% Mg doping) consists of tetravalent Ti ions of $d^0$, leading to a wholly insulating block between FeAs layers. Replacing a fraction of the sites containing Mg ions with Ti ions, Ti$^{4+}$ ion becomes metallic $d^{1-2v}$ Ti$_{(3+2v)}^{(3+2v)+}$ on the average. Thus, this system is a

Effects of metallic spacer in layered superconducting Sr$_2$(Mg$_y$Ti$_{1-y}$)O$_3$FeAs

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In our calculations, based on the tetragonal unit cell with \( P4/nmm \) space group, the experimentally measured lattice constants \( a=3.935 \) Å and \( c=15.952 \) Å were used, resulting in a slightly larger volume by 2\% than in \( \text{Sr}_2\text{VO}_3\text{FeAs}. \) In the cell, Fe atoms lie at \( 2a \) sites \((\frac{1}{4},\frac{1}{4},0)\), Ti/Mg, Sr, As, and O atoms lie at \( 2c \) sites \((\frac{1}{4},\frac{1}{4},z)\), and another O atoms sit at the \( 4f \) sites \((\frac{1}{4},\frac{1}{4},z)\). Using the local density approximation (LDA), the internal parameters were optimized to \( 0.3072 \) for Ti, \( 0.8210 \) and \( 0.5898 \) for two Sr sites, \( 0.0772 \) for As, \( 0.4270 \) for O at \( 2c \) sites, and \( 0.2939 \) for O at \( 4f \) sites. These values lead to the As-Fe-As bond angle of \( \alpha=116^\circ \), which is measured in one side of the Fe layer, corresponding to \( T_c \approx 25 \) in the literature. This significant difference from \( T_c \approx 40 \) K suggests a crucial role of the \( \text{Sr}_2\text{MO}_3 \) layer. The Mg-rich phase \( \text{Sr}_2\text{Ti}_2\text{Mg}_4\text{O}_7\text{FeAs} \) was understood with a \( 2 \times 1 \) supercell using our optimized internal parameters. In these optimization processes, the residual Hellman-Feynman forces on the atoms were lower than \( 1 \) meV/Å.

In all calculations, the local spin density approximation (LSDA) implemented in the accurate all-electron full-potential local orbital code, FPLO, was used. A regular mesh containing 196 \( k \) points in the irreducible wedge was used to sample the Brillouin zone. The magnetic tendencies in the \( y=0 \) phase were studied using the fixed spin moment (FSM) method, with a much denser mesh of up to 726 irreducible \( k \) points.

### 2 Structure and Calculation Method

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### 3 Results

#### 3.1 50\% Mg doped phase: \( \text{Sr}_2\text{Ti}_4\text{Mg}_4\text{O}_7\text{FeAs} \)

First, we will address the electronic structure of the \( y=0.5 \) phase having the insulating spacer. Figure 2 displays the enlarged band structure with the fatband of the Ti \( t_{2g} \) manifold (top panel) and the fatband of the Fe \( d \) manifold (bottom panel). Note that the \( X \) and \( M \) points in the unit cell are folded into the \( \Gamma \) and \( X \) points in the \( 2 \times 1 \) supercell, respectively. The corresponding DOS near the Fermi energy \( E_F \) is given in Fig. 3. As expected, in the \( y=0.5 \) phase, the \( 3d \) orbitals of the Ti ions are completely unoccupied. The Ti \( t_{2g} \) manifold expands from \( 0.5 \) eV to \( 2 \) eV. In this phase, the details near \( E_F \) are very similar to those observed for other superconducting Fe-pnictides. At the \( \Gamma \) point, three hole pockets derived from the Fe \( d_{x^2−y^2}, d_{xz}, \) and \( d_{xy} \) bands appear, while two-fold \( M \)-centered electron pockets with the character of these three bands also appear. Considering that there is no intrinsic superconductivity at this phase and the similar fermiology with other superconducting Fe-pnictides, the nesting effects may not be a necessary ingredient for Fe-pnictides to be superconductors.

#### 3.2 Electronic structure of nonmagnetic \( y=0 \) phase

Now, we will focus on the \( y=0 \) phase, which contains only the metallic \( d^3 \) \( \text{Ti}^{3+} \) ions. Thus, this represents the phase of the range of \( 0 \leq y < 0.5 \), consisting of metallic spacers. In this subsection, we will address the electronic structure of the NM state. The enlarged band
Effects of metallic spacer in layered superconducting Sr$_2$(Mg$_y$Ti$_{1-y}$)O$_3$FeAs

![Fig. 2](image-url) **Fig. 2** Top: Band structure, with the fatband of Ti $t_{2g}$ manifold, of nonmagnetic 2(Sr$_2$Ti$_y$Mg$_{1-y}$O$_3$FeAs) in the 2 $\times$ 1 supercell. The Ti $d_{xz}$ band lying around 1.8 eV is nearly dispersionless and separated from the Ti $d_{yz}$ band. Bottom: Enlarged fatband representation of Fe $d$ bands near the Fermi energy $E_F$, which is set to zero. The character of Fe $d_{xy}$ band appears in the range of –2.2 to -1.1 eV and 0.6 to 1.6 eV (not shown here). In the fatband representation, the size of the symbols is proportional to the fractional character of each orbital.

structure near $E_F$ and the fatband of the Ti $t_{2g}$ manifold are displayed in the top panel of Fig. 4. The incomplete TiO$_5$As octahedron results in a breaking of the symmetry of the $t_{2g}$ manifold. The partially filled Ti $d_{xy}$ band spreads over the range of –0.7 to 1.6 eV (here, $E_F$ is set to zero), which is a width that is 15% larger than that of the V $d_{xy}$ band in Sr$_2$VO$_3$FeAs. This band can be described by a single-band tight-binding model with nearest neighbor hopping of $t=0.28$ eV and next neighbor hopping of $t'=0.08$ eV, i.e., values that are about 15% larger than in Sr$_2$VO$_3$FeAs. The other bands of Ti are mostly unoccupied, but there is some $E_F$ crossing in the $d_{yz}$ and $d_{zx}$ bands near the $\Gamma$ point, as shown in the bottom panel of Fig. 4. Although the hybridization of FeAs layers and the intervening Ti layers is negligible in almost the whole regime due to high two-dimensionality, small mixing with Fe $d_{yz}$ and $d_{zx}$ leads to this $E_F$ crossing (see below).

Compared with other superconducting Fe-pnictides, the bands having Fe character, as displayed in the middle panel of Fig. 4 show both similarities and remarkable distinctions. Similar to other superconducting Fe-pnictides, the $d_{yz}$ and $d_{zx}$ bands lead to electron pockets at the $M$ point. However, instead of three Fe-derived hole pockets at the $\Gamma$ point, only one Fe $d_{zx}$-derived hole pocket appears, but this is considerably shrunk in this system compared to other Fe-pnictides (see below). This may imply that the role of Fe for the superconductivity is substantially reduced in this phase.

Most of the Fe bands are separated from the Ti-derived bands, reflecting strong two-dimensionality. Exceptions occur around the $M$-point and near the $\Gamma$ point, near $E_F$. Near the $\Gamma$ point, the Fe and Ti $d_{zx}$ bands are hybridized with each other, leading to a 0.1 eV gap at $E_F$. On the other hand, around the $M$ point, the Ti $d_{zx}$ are more strongly hybridized with the Fe $d_{zx}$ and $d_{yz}$, with the gap of 0.6 eV that occurs above $E_F$, resulting in surviving $M$-centered electron pockets. This difference to Sr$_2$VO$_3$FeAs results from the different $d$-orbital filling between V and Ti ions in these systems: namely $d^2$ for V$^{3+}$ and $d^1$ for Ti$^{3+}$.

![Fig. 3](image-url) **Fig. 3** Total and atom-projected densities of states (DOSs) on nonmagnetic Sr$_2$Ti$_y$Mg$_{1-y}$O$_3$FeAs in the 2 $\times$ 1 supercell. DOS at $E_F$ $N(E_F)$ is 1.82 states per eV per formula unit, 30% smaller than the value in LaFeAsO. [21]
Fig. 4 Top: Band structure, overlapped with the fatband of Ti $t_{2g}$ manifold, on nonmagnetic Sr$_2$TiO$_3$FeAs. Middle: Fatband representation of Fe $d$ bands. Bottom: Enlarged band structure near $E_F$ with the fatband of Ti $t_{2g}$ manifold, which shows interesting features (see text).

Fig. 5 Total and atom-projected densities of states (DOSs), near $E_F$, on nonmagnetic Sr$_2$TiO$_3$FeAs. $E_F$, denoted by the vertical dashed line, lies on a sharp peak. DOS $N(E_F)$ at $E_F$ is 8.0 states/eV per formula unit: 55% Ti, 25% Fe, and 5% for each O.

As shown in the bottom panel of Fig. 4, noticeable features appear close to $E_F$. At the $\Gamma$ point, two-fold bands at -40 meV and 58 meV, and a single band at -30 meV appear. One of the two-fold valence bands is dispersionless near the $\Gamma$ point along the $\Gamma$–$X$ line, leading to a van Hove singularity at -40 meV. On the other hand, one of the doublet conduction bands almost touches with $E_F$ along the $\Gamma$–$X$ line, leading to a van Hove singularity almost exactly at $E_F$. Additionally, one band lying on $E_F$ appears along the $M$–$\Gamma$ line (actually a few meV above $E_F$).

These features are reflected in the total and atom-projected densities of states (emphasized near $E_F$), given in Fig. 5. A valley appears at -20 meV between the two van Hove singularities at -40 meV and $E_F$, indicating sensitivity to hole (or electron) doping. This may imply that the stoichiometric sample is near to the optimal doping. $N(E_F)$ is twice as large than for most other Fe pnictides due to the greater contribution of Ti, but is only two thirds of that found in Sr$_2$VO$_3$FeAs. Remarkably, except for the Ti contribution, the magnitude of $N(E_F)$ is similar with that of LaFeAsO. It is interesting that the $T_c$ of hole-doped LaFeAsO is comparable with the $y = 0.5$ system described herein, in which Ti ions are insulating. This fact suggests that metallic Ti ions can play an important role in the superconductivity of this system.
3.3 Fermi surface of nonmagnetic $y=0$ phase

The Fermi surfaces (FSs) consist of five $\Gamma$- and two $M$-centered pockets, as illustrated in Fig. 6. Three large $\Gamma$-centered electron pockets have Ti character and the others have Fe character, derived from the $d_{zx}$ band. The character of the $M$-centered FSs is mostly derived from the $d_{zx}$ and $d_{yz}$ bands and partially from the $d_{x^2-y^2}$ bands. The $M$-centered electron pockets possess the shape of an elliptical cylinder (in Fig. 6(a)) and a rhombus (in Fig. 6(b)). In the regime between the two Fe-derived $\Gamma$-centered FSs, electrons reside in a coaxial distorted rectangular box-like shape (see Fig. 6(d)). A Fe-derived $\Gamma$-centered hole pocket is considered to be a crucial ingredient for the formation of pairings in Fe pnictides, but in this system the pocket is shrunk considerably, implying the opposing view that the metallic Ti ions have a more important role. The three $\Gamma$-centered electron pockets are derived from Ti $d_{xy}$, $d_{yz}$, and $d_{zx}$, see Figs. 6(a) to (c). The first two FSs, which are of similar size, are much like MgB$_2$.

A large portion of the FSs has remarkably low Fermi velocity $v_F$, with the lowest being $0.6 \times 10^6$ cm/s. In particular, throughout the $M$-centered elliptical cylinder and the $\Gamma$-centered concentric Fe-derived FSs, $v_F$ is close to its lowest value. For the Ti-derived $\Gamma$-centered FSs, $v_F$ is quite low along the $\Gamma$–$M$ line for the two similar sized FSs and along the $\Gamma$–$X$ line in the remaining FS given in Fig. 6(c).

3.4 Magnetic tendencies of the $y=0$ phase

In this subsection, we will address briefly the possible magnetic tendencies in the Mg-free phase. The competition between superconductivity and magnetic ordering widely observed in Fe pnictides is unclear for this compound, since no magnetic ordering has been observed. Allowing for a ferromagnetic (FM) state, FM has an energy that is a little lower by 5 meV/Fe than for NM. The total magnetic moment is $0.46 \mu_B$/Fe, mostly comprised of contributions from the Ti ions (0.37 $\mu_B$). The Fe ions are nearly nonmagnetic, less than 0.1 $\mu_B$.[25] suggesting that the magnetic fluctuation due to Ti ions is of more importance than that due to the Fe ions in this phase.

The fixed spin moment (FSM) method was employed to investigate this magnetic behavior, using a cell that allows only FM and NM states. As obtained from LSDA calculations, FSM shows the minimum energy at a total fixed moment of $M=0.45 \mu_B$/Fe, with an energy 6 meV/Fe lower than in the NM state. From $M=0$ to around the minimum energy state, the Fe moment is quite small and most of the contribution to $M$ results from the Ti moment. After the minimum energy is reached, the moment of Fe increases monotonically, coinciding with a sharp increment in energy with a slope of $\sim 220$ meV/M ($M$: total moment per formula unit), while that of Ti stays at around 0.6($\pm0.05$) $\mu_B$. The Stoner $I$ is 0.47 eV, so $IN(E_F)=2.2$ with $N(E_F)=4.6$. 

Fig. 6 Fermi surfaces (FSs) of nonmagnetic Sr$_2$TiO$_3$FeAs. (a)–(c) Fermi velocities $v_F$ colored dark (blue) for the lowest $0.06 \times 10^7$ and lighter (red) for the highest $2 \times 10^7$, in units of cm/s. Throughout FS of (d), $v_F$ is remarkably low, $0.6 - 7 \times 10^6$ cm/s. Only (d) and the $M$-centered FSs have Fe character.
states per eV per formula unit obtained from the FM calculations, indicating strong magnetic instability.

4 Discussion and Summary

For the $g=0$ phase, the on-site Coulomb repulsion $U$ to Ti ions was applied using both popular double-counting schemes in the LDA+U approach,[20,27] to investigate whether or not a Mott transition in the $d^1$ Ti$^{3+}$ ions occurs. Up to $U=7$ eV $\sim$ $3W$, which is a much larger value than what has been used in perovskite $R$TiO$_3$ ($R$=rare earth elements),[28] the Sr$_2$TiO$_3$ layers are still metallic. This failure of LDA+U has previously been observed in some 4$d$ or 5$d$ systems, in which no integer occupation can occur due to strong $p$-$d$ hybridization, since an integer occupation is required to lead to a Mott transition by the LDA+U method.[29]

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In this system, the calculated occupation number is significantly larger than the formal number $d^1$, resulting from the absence of rigorous definition of oxidation state in solids, as recently discussed.[30,31] This may prevent the LDA+U approach from driving a Mott transition.[32]

In summary, we addressed the electronic structure of Sr$_2$(Mg$_y$Ti$_{1-y}$)O$_3$Fe$_3$As for the $g=0.5$ and $g=0$ phases, which represent insulating and metallic Ti layers, re- spectively. At $g=0.5$, which shows no intrinsic superconductivity, the fermiology is just like that for other Fe-pnictides. Introducing metallic Ti ions, the $\Gamma$-centered Fe-derived FSs are reduced considerably or disappeared. Instead, three $\Gamma$-centered Ti FSs appear, and two of them have similar sizes like in MgB$_2$. Our FSM calculations further suggest possible magnetic ordering in the Ti ions. Although no magnetic ordering has been observed in this compound, the high temperature resistivity measurement shows a kink for samples below $g=0.5$ at $T \sim 200$ K,[13] thus implying magnetic transition. Consequently, a detailed magnetic measurement is required for this compound. Our results indicate that the metallic Ti ions play a crucial role in the superconductivity, suggesting that the mechanism of supercon- ductivity in Fe-pnictides should be reconsidered.

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