Magnetic Ordering in Blocking Layer and Highly Anisotropic Electronic Structure of High-$T_c$ Iron-based Superconductor Sr$_2$VFeAsO$_3$: LDA+$U$ Studies

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We calculate electronic structures of a high-$T_c$ iron-based superconductor Sr$_2$VFeAsO$_3$ by LDA+$U$ method. We assume a checker-board antiferromagnetic order on blocking layers including vanadium and strong correlation in d-orbits of vanadium through the Hubbard $U$. While the standard LDA brings about metallic blocking layers and complicated Fermi surface as in the previous literatures, our calculation changes the blocking layer into insulating one and the Fermi surface becomes quite similar to those of other iron-based superconductors. Moreover, the appearance of the insulating blocking layers predicts high anisotropy on quasi-particle transports and new types of intrinsic Josephson effects.

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Since the discovery of high-$T_c$ superconductivity in LaFeAsO$_{1-x}$F$_x$ [1], its various family members have been piled up on the materials table of iron-based superconductors. The materials variety is characterized by their crystal structures and often classified by the numbering scheme, such as “111” (e.g., LaFeAsO$_{1-x}$F$_x$), “122” (e.g., Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [2]), “111” (e.g., LiFeAs [3]), and “11” (e.g., FeSe [4]). They have quasi-two-dimensional FeAs layers commonly, while a main difference among them comes from the non-superconducting blocking layers between the FeAs layers. The density functional theory with local density approximation (LDA) has predicted a common electronic structure, i.e., multiple cylindrical Fermi surfaces consisting of hole pockets around the Brillouin zone center and electron ones around the zone corners. Some experiments, e.g., ARPES’s have actually confirmed such an electronic structure [5]. In this case, a strong candidate of the glue of their superconducting pairs has been regarded to be a spin fluctuation due to the nesting between those Fermi pockets [6], though it still remains unsettled.

Recently, a new family which has a thick perovskite-type blocking layer has been discovered [7] and a controversial debate about the pairing mechanism has arisen [8–10]. These materials include non-iron transition-metal elements in their thick blocking layers, and the electronic structures can be relatively more complex than the other types, if 3d orbitals on the transition metals hybridize with Fe d-orbitals. Such hybridization can clearly break the typical stage composed of disconnected small hole and electron pockets. Sr$_2$VFeAsO$_3$ is one of such perovskite-type iron-based superconductors, who exhibits the highest $T_c \sim 37K$ in this family [11]. Initially, standard LDA calculations revealed much different and more complex structures due to the hybridization of the 3d orbitals of vanadium. Thus, the LDA result gave rise to the following two interpretations. Some reports suggested that the pairing is not originated from the nested Fermi surfaces [8], while the nesting feature is still alive even in such a complex structure [9]. Thus, Sr$_2$VFeAsO$_3$ can be regarded as a key material to check whether the typical Fermi-surface structure is essential for high-$T_c$ superconductivity. Therefore, we examine whether the electronic structure of Sr$_2$VFeAsO$_3$ is really different from the typical one in “conventional” iron-based superconductors.

Vanadium oxide is well known to be a strongly correlated system. For instance, V$_2$O$_3$ exhibits a phase transition into a Mott insulator at a certain temperature, though standard LDA calculations predict its metallic features [12]. On the other hand, the calculations considering the strong correlation such as LDA+$U$ [12] and LDA+DMFT [13] succeeded in reproducing the Mott insulating state. The nominal valence of V in V$_2$O$_3$ is trivalent, and V in Sr$_2$VFeAsO$_3$ is naively estimated to be also trivalent from the charge valence. This implies that the perovskite-layer including vanadium oxide becomes insulating and then the Fermi surfaces are not influenced by vanadium electrons. In this letter, we explore the electronic structures of Sr$_2$VFeAsO$_3$ by considering the correlation on 3d vanadium electrons. For this purpose, we use LDA+$U$ method for d-electrons of vanadium. As a result, we find that the calculated electronic structure becomes equivalent to those of other iron-based superconductors as expected above, by assuming a checker-board antiferromagnetic (AFM) order on vanadium layer. In this case, highly anisotropic electronic structures are also obtained in contrast to the standard calculation results.

The crystal structure of the present target material, Sr$_2$VFeAsO$_3$ is tetragonal, and the space group of the crystal structure is $P4/nmm$ as shown in Fig. [1]. Such a structure is characteristic to the perovskite-type iron-based superconductors but in contrast to most of other family materials whose mother compounds without dop-
there are methods to calculate them in first-principles as described in Fig. 1. The magnetic order is equivalent to the observed one in Sr$_2$CrFeAsO$_5$ [14], which does not exhibit superconductivity at all. The difference between these materials is an interesting issue, which will be discussed elsewhere. On the other hand, we do not set any magnetic order for the iron layers except for a case to compare the total energy. The calculation package employed throughout this paper is VASP [15, 16] that supports LDA+U method [17], in which we choose two parameters, the Hubbard $U$ and Hund’s coupling $J$. While there are methods to calculate them in first-principles manner, e.g., the constrained RPA [18], we treat them as input parameters conventionally. Instead, we examine how the electronic structure is affected by various parameter sets. We find that a combination of $U = 5.5$ eV and $J = 0.93$ eV is the most realistic among all sets used in this paper. The set is close to those employed in successful calculations on vanadium oxides using LDA + $U$ and LDA+DMFT [13, 19]. The lattice constants and internal coordinate of each atom are in accordance with the experimental data [11].

Figure 2 shows band dispersions and densities of states calculated by LDA+U method for the four parameter sets, (a) $U = 0, J = 0$, (b) $U = 3$ eV, $J = 0.93$ eV, (c) $U = 5$ eV, $J = 0$ (d) $U = 5.5$ eV, $J = 0.93$ eV. In all sets of $U$ and $J$, the checker-AFM order in vanadium layer is stable, and the calculated moments on vanadium become 1.36, 1.65, 1.86, and 1.79 $\mu_B$ for the parameter sets (a) to (d), respectively. In $U = 0$, that is, a standard LDA calculation, the bands of spin-down (majority-spin) d-electron of vanadium cross the Fermi level as shown in Fig. 2(a), though spin-up bands are away from the Fermi level. In this case, the perovskite layer is not insulating but half-metallic as pointed out in Ref. [10]. As $U$ increases, the occupied and unoccupied bands of vanadium split and both of those go away from the Fermi level. For reasonable values, i.e., $U = 5$ eV and $U = 5.5$ eV, they clearly split into upper and lower Hubbard bands, and the blocking layer becomes insulating.

The Fermi surfaces for the set of $U = 5.5$ eV and $J = 0.93$ eV are shown in Fig. 3. The surface is formed by only d-electrons of iron, since the perovskite layer including vanadium is not metallic any longer. In the figure, one finds that all Fermi surfaces are cylindrical around $\Gamma$-point and two of them are formed as hole pockets and other three as electron ones. We note that the present Brillouin zone is folded because of the checker-AFM ordering. As a consequence of the folding, the electron pockets seen in the zone center correspond to those around $M$-point calculated in other iron-based superconducting materials. Thus, we find that the calculated Fermi surfaces are quite equivalent to those of other typical iron-based superconductors. Moreover, our folded result clearly shows that the nesting between those hole and electron pockets is well and the spin fluctuation with the nesting vector is expected to be strongly enhanced. Very recently, Nakayama et al. actually reported typical Fermi surfaces as predicted above by using ARPES [20]. This is strong evidence that vanadium 3$d$ electrons do not contribute to band structure around the Fermi level, i.e., the vanadium layer is insulating.

In the case of $U = 5.5$ eV and $J = 0.93$ eV, we also calculate anisotropy of quasi-particle resistivity. Some experimental data qualitatively indicates that the anisotropy is quite large [21]. One of the clearest evidence is the broadening of the superconducting transition by the variation of the applied magnetic field, which is
well known on highly anisotropic high-$T_c$ cuprate materials such as Bi$_2$Sr$_2$CaCu$_2$O$_{8}$ (Bi-2212). The calculated anisotropy of the Fermi velocity, $\gamma_p = \langle v_{\alpha}^2 \rangle / \langle v_{\beta}^2 \rangle$ becomes 1351 which is much larger than those of LaFeAsO ($\gamma_p = 116.8$) and BaFe$_2$As$_2$ ($\gamma_p = 10.69$), but relatively smaller than perovskite-type Sr$_2$ScFePO$_3$ ($\gamma_p = 6.19 \times 10^3$). The anisotropy of the penetration depth $\lambda_{\alpha}$ at zero temperature is $\sim 37$, since $\gamma_{\alpha} = \sqrt{\rho_{\alpha}}$ at zero temperature. Although the calculated anisotropy is relatively smaller among the family of perovskite-type iron-based superconductors, it is still much larger than other families. Compared to those of high-$T_c$ cuprate superconductors, the anisotropy $\gamma_{\alpha} \sim 30$ is larger than YBa$_2$Cu$_3$O$_{7-x}$ and comparable to La$_{2-x}$Sr$_x$CuO$_4$ but smaller than Bi-2212. The value is fully over the lower bound anisotropy, in which intrinsic Josephson effects are observable. In fact, since intrinsic Josephson effects have been confirmed in 1111 systems whose $\gamma_{\alpha} \sim 10$ according to our first-principles calculations, the expectation is reasonable. Thus, intrinsic Josephson effects are promised. Moreover, we can predict some new effects originated from its multi-band superconducting gaps in the intrinsic Josephson junction systems. Some literatures report a new excitation called Josephson-Leggett mode in addition to the Josephson plasma due to multi-tunneling channels, and the others predict new type of Josephson effects originated from the multi-degree of freedom of the superconducting phases. At the present, Bi-2212 is intensively investigated to promote the functionality as THz wave radiation source. The single crystal of Sr$_2$VFeAsO$_3$ may work as multi-THz wave generators due to its multiple excitation modes.

Finally, let us discuss stability of the present checker-AFM state and mention the related issues. First, we compare the total energy of the checker-AFM magnetic state with that of non-magnetic one. The both are calculated by LDA+U with the parameter set, $U = 5.5$ eV and $J = 0.93$ eV. In our calculation, the total energy per formula of the non-magnetic state is 2 eV larger than
that of the checker-AFM state. This result clearly indicates that the checker-AFM state is more stable than non-magnetic one under the application of the Hubbard $U$ on the vanadium $d$-electrons. Very recently, Tatematsu et al., reported that a magnetic transition occurs around 150K at the vanadium layers by NMR measurement [20]. Although the transition is not yet proved to be the checker-AFM ordering, it can be ascribed to a magnetic ordering at vanadium layer at least. Otherwise, the transition is attributed to Fe stripe ordering but such ordering drastically changes the Fermi surfaces, which is not consistent with ARPES measurement [21]. On the other hand, we have another interesting calculation result, in which the total energy of Fe-stripe AFM together with the checker-AFM of vanadium is 0.2 eV smaller than that of non-magnetic Fe with the checker-AFM of vanadium. Then, the calculated Fe magnetic moment is 2.1 $\mu_B$, which is comparable to those calculated in most of other compounds of iron-based superconductors. It is well known that LDA calculations always predict that the stripe-AFM state with Fe moment $\sim 2\mu_B$ is stable even in the superconducting doping range. This result indicates that the stripe-AFM instability on the iron-layer strongly works even in Sr$_2$VFeAsO$_3$ similar to other compounds. Such an agreement is not an accident but a clear evidence for the magnetic instability on Fe layers common to all families of iron-based superconductors.

In conclusions, we calculate the electronic structure of Sr$_2$VFeAsO$_3$ using LDA+$U$ scheme under an assumption of the checker-AFM ordering on vanadium-layers. A reasonable choice of the parameter $U$ and $J$ leads to the insulating blocking layer and typical cylindrical Fermi surface structures. In addition, our results predict high anisotropy as observed in recent experiments. Consequently, we conclude that the electronic structures are quite equivalent to those of other iron-based superconductors and the similar magnetic instability may contribute to the pairing. Furthermore, the high-anisotropy in superconducting transport properties predicts new types of intrinsic Josephson effects originating from the multi-band superconductivity. The present result can settle down the controversial problem for the pairing mechanism and suggests a new application possibility.

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