Magnetic states of iron-based superconducting compounds calculated by using GGA+$U$ method with negative $U$

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Abstract

The magnetic moments per Fe atom in high-$T_c$ iron-based superconducting compounds, BaFe$_2$As$_2$ and LaFeAsO obtained from the first-principles calculation with local-spin-density approximation are much larger than those obtained from experiments. To resolve the contradictory results between theory and experiment we employed the so-called LDA+$U$ (or more exactly GGA+$U$) technique with negative $U$ in the first-principles calculation. The calculated values with negative $U$, $-$0.09 Ry and $-$0.10 Ry for BaFe$_2$As$_2$ and LaFeAsO, respectively, are in excellent agreement with the experimental ones. By comparing the differences in $d$-orbital occupation numbers and spin densities calculated by using a simple GGA and GGA+$U$ with negative $U$, the magnetic moments of the two compounds are found to be similar to the case of low-spin state of metamagnetic Fe$_3$Al alloy.
I. INTRODUCTION

The discovery of iron-based superconductors\(^1\) attracted many researchers to devote themselves into searching for possible room-temperature superconductors. Another important aspect of this system is the possibility of coexistence of seemingly mutually exclusive properties; magnetism and superconductivity. Some important issues were resolved, but there are many other aspects whose underlying physical mechanisms are still unsolved. In cases of BaFe\(_2\)As\(_2\) (referred to it as the 122-compound hereafter) and LaFeAsO (referred to it as the 1111-compound hereafter) compounds, the former undergoes the simultaneous structural, from tetragonal to orthorhombic structures, and magnetic phase transitions, from paramagnetic to antiferromagnetic (AFM) phases, at \(\sim 140\) K,\(^2\) while the latter undergoes the structural phase transition from tetragonal to monoclinic (or orthorhombic\(^3\)) structures at \(\sim 155\) K, and develops long-range spin-density-wave type AFM order at \(\sim 137\) K.\(^4\) The magnetic moment per Fe atom of the 122-compound determined experimentally is about 0.87 \(\mu_B\),\(^2\) but the theoretical value is about 2.6 \(\mu_B\),\(^5\) and that of the 1111-compound is about 0.36 \(\mu_B\) in experiment,\(^4\) but is about 1.6 \(\mu_B\) in theory.\(^6\) For both cases, the calculated values are about 3 – 4 times overestimated over the experimental results.

At the first glance, it is usually tempted to apply the so-called ‘LDA (local-density approximation) +\(U\)’ method. This method was developed to properly describe the strongly-correlated-electron (SCE) systems which usually have very localized electrons with high angular momentum. Due to the strong on-site Coulomb repulsion among well-localized electrons, a Hubbard-type onsite repulsion is ‘manually’ included in the exchange-correlation functional during the self-consistent-field (SCF) calculation. This method was very successful for many SCE systems, however, it is well known that the onsite repulsion (i.e, \(U > 0\)) enhances the magnetism, which is not desirable for our system. Therefore, we performed the first-principle calculations with generalized-gradient approximation (GGA)+\(U\) method, especially by using the negative \(U\). The negative \(U\), more exactly \(U_{\text{eff}} = U - J\), implies that there is an effectively attractive force among \(d\)-electrons of Fe, which is very odd, however, there have been some theoretical suggestions already.\(^7\)–\(^9\) Moreover, the material systems, especially superconductors, with a negative effective \(U\) are not rare.

We found that, in high-\(T_c\) iron-based superconducting compounds, the use of GGA+\(U\) with negative \(U\) of similar magnitudes (–0.09 Ry and –0.10 Ry) leads to the well-matched
values with experimental magnetic moment per Fe. We demonstrate the validity of the negative $U$ by calculating band structures, density of states (DOS), $d$-electron occupation numbers and spin densities of the two compounds. Through these results, we can carefully deduce that the use of negative $U$ in the first-principle study can give more accurate results of magnetic moments of iron-pnictide systems. More specifically, the magnetic states of the two compounds are found to be similar to the case of low-spin state of metamagnetic Fe$_3$Al alloy.

II. THEORETICAL CALCULATIONS

We used the WIEN2k package\textsuperscript{10} implemented with full-potential linearized-augmented-plane-wave method. The exchange-correlation functional was chosen to be GGA version of Perdew, Burke and Ernzerhof.\textsuperscript{11} The spin-orbit coupling was not included. We used $RK_{\text{max}} = 7$ and $\sim 270$ (for the 122-compound) and $\sim 220$ (for the 1111-compound) augmented plane waves for the basis functions. For SCF cycles we generated 1000 k-points in the whole Brillouin zone (BZ) corresponding to 423 (for the 122-compound) and 424 (for the 1111-compound) k-points in the irreducible wedge of the BZ. After self consistency was achieved, we further increase the number of k-points to 5000 in the whole BZ to obtain DOS and charge densities.

The AFM and the so-called fixed-spin-moment (FSM) calculations featured in the WIEN2k package were used. It is possible to constrain the total spin magnetic moment per unit cell to a fixed value and thus force a particular ferromagnetic solution (which may not correspond to the equilibrium). This is particularly useful for systems with several metastable magnetic solutions, where conventional spin-polarized calculation would not converge or the solution may depend on the starting density.\textsuperscript{10} Since the two compounds are in the AFM state, the total magnetic moment are fixed to be zero in FSM calculations.

We included the orbital-dependent potentials, the so-called LDA+$U$ (or GGA+$U$) method.\textsuperscript{12} When we calculate the effective potential $U_{\text{eff}} = U - J$, we set the exchange parameter $J = 0$, and the onsite Coulomb interaction $U = -0.09$ Ry and $-0.10$ Ry for the 122- and 1111-compounds, respectively. These negative $U$’s give very well-matched results with experimental ones. We used experimental lattice constants and magnetic structure. In the case of the 122-compound, the lattice constants were taken from Ref. 13, and magnetic
structure was taken from Ref. 2, and for the case of the 1111-compound, they were taken from Ref. 6 and Ref. 4, respectively. From now on, we will refer to this method, i.e., GGA+U method with negative \( U \), as GGA−|\( U \)| method.

III. RESULTS AND DISCUSSION

The calculated magnetic moments obtained by a simple GGA calculations are about 2.02 \( \mu_B/\text{Fe} \) and 1.87 \( \mu_B/\text{Fe} \) for the 122- and 1111-compounds, respectively. These values are similar to those of previous publications (\( \sim 2.6 \mu_B \)\(^5\) and \( \sim 1.6 \mu_B \)\(^6\) for the 122- and 1111-compounds, respectively), however, they are still much larger than those of experiments. They were reduced to be 0.87 \( \mu_B/\text{Fe} \) and 0.38 \( \mu_B/\text{Fe} \) obtained by using GGA−|\( U \)| method with \( U = -0.09 \text{ Ry} \) and \( -0.10 \text{ Ry} \), respectively, which are in excellent agreement with the experimental ones.\(^2,4\)

To understand these changes, the differences between the symmetry-decomposed occupation numbers of \( d \)-orbitals obtained by using the GGA and GGA−|\( U \)| methods are summarized in Table I. For the 122-compound the application of negative \( U \) results in the reduction of the majority-spin \( d \)-electron occupation number by \( \sim 0.55 \) and increase of the minority-spin \( d \)-electron occupation number by \( \sim 0.58 \) resulting in a decrease of 1.13 \( \mu_B \) of the total magnetic moment. The increase in minority-spin \( d \)-electron occupation number is more significant in the \( t_{2g} \) orbitals (\( \sim 0.37 \)) than that of the \( e_g \) orbitals (\( \sim 0.21 \)). Almost the same number of electrons are decreased in majority-spin bands for the \( t_{2g} \) and \( e_g \) bands by 0.29 and 0.26 electrons, respectively. Since the \( t_{2g} \) orbitals are composed of the \( d_{xy}, \ d_{xz} \) and \( d_{yz} \) orbitals, and the \( e_g \) orbitals are composed of the \( d_{(x^2-y^2)} \) and \( d_{z^2} \) orbitals, the increased minority-spin \( d \)-electron are almost evenly distributed to all 5 \( d \)-orbitals, while the electrons per orbital in the majority-spin \( e_g \) orbitals (0.13) are more severely decreased than those of the \( t_{2g} \) orbitals (0.097). This difference may cause the symmetry changes of the spin-density plots, which will be discussed later. The similar arguments can be applied to the case of the 1111-compound.

These redistributions of the symmetry-decomposed \( d \)-orbital occupation numbers (\( d \)-OONs) calculated by using the GGA−|\( U \)| method is very similar to the case of those of Fe\(_3\)Al alloy upon transition from the high-spin to low-spin states.\(^14\) As can be seen in the last row of Table I, the reduction of the majority-spin \( d \)-OON by \( \sim 0.54 \), and the increase of
TABLE I. Differences between the symmetry-decomposed occupation numbers of $d$-orbitals obtained by using GGA and GGA−$|U|$ methods ($\Delta n_{eg}^{\uparrow} \equiv n_{eg}^{\text{GGA−}|U|} - n_{eg}^{\text{GGA}}$, and so on). The change of symmetry-decomposed occupation numbers of $d$-orbitals upon transition from high-spin to low-spin states in Fe$_3$Al alloy are also included for the reference.

|       | $\Delta n_{eg}^{\uparrow}$ | $\Delta n_{eg}^{\downarrow}$ | $\Delta n_{t_{2g}}^{\uparrow}$ | $\Delta n_{t_{2g}}^{\downarrow}$ |
|-------|----------------------------|----------------------------|----------------------------|----------------------------|
| 122   | −0.26                      | 0.21                       | −0.29                      | 0.37                       |
| 1111  | −0.33                      | 0.27                       | −0.39                      | 0.43                       |
| Fe$_3$Al | −0.26                   | 0.10                       | −0.28                      | 0.48                       |

the minority-spin $d$-OON by $\sim$0.58, result in a total magnetic moment decrease of 1.22 $\mu_B$ in Fe$_3$Al alloy upon the transition from the high-spin to low-spin states. Therefore, we may think that the magnetic states of Fe atoms in the 122- and 1111-compounds are similar to the case of low-spin state of Fe$_3$Al alloy.

There are two crystallographically different atomic sites for Fe atoms in Fe$_3$Al alloy; i) Fe$_I$ atoms and ii) Fe$_{II}$ atoms. Fe$_I$ atoms are surrounded by 4 Fe$_{II}$ atoms and 4 Al atoms, and the surrounding atoms are located at the corners of a cube centered at the Fe$_I$ atom. On the other hand, Fe$_{II}$ atoms are surrounded by 8 Fe$_I$ atoms. The Fe$_I$ atom exhibits the transition from the high-spin to low-spin states at high pressure, while the magnetic moment of Fe$_{II}$ atom remains almost unchanged.

The 4 Al atoms surrounding a Fe$_I$ atom form a tetrahedron. It is very similar to the tetrahedral cages formed by As ligand atoms in the 122- and 1111-compounds. According to the crystal-field theory, the 5 $d$-orbitals will be split into the $t_{2g}$ and $e_g$ orbitals if the transition metal is surrounded by 4 ligand atoms forming a tetrahedral cage. Since the ligand atoms of tetrahedral cage are directly contacted with one of the lobes of $t_{2g}$ orbitals, these orbitals have high electron-electron repulsion, resulting in a higher energy than the $e_g$ orbitals. Since the amount of direct contact is not very large, the energy splitting is not very significant compared with the case of octahedral cages. If the energy difference ($\Delta E_l$) between $t_{2g}$ and $e_g$ orbitals is smaller than the pairing energy ($\Delta E_p$), then two electrons with opposite spins prefer to form a electron pair because the pairing reduces the total energy and, thus, the electrons do not obey the Hund’s rule. The pairing reduces the magnetic moments and the transition metal-ligands complex (TMLC) is in the low-spin state. In the
majority of cases, however, $\Delta E_t < \Delta E_p$. Therefore, most of tetrahedral TMLCs are in the high-spin state.

The transition from high-spin state to low-spin state at high pressure can be understood by the fact that a decreased lattice constant results in pushing the bands above (below) the Fermi level ($E_F$) toward the higher (lower) energy region.\textsuperscript{16,17} It implies that $\Delta E_t$ increases as the pressure is applied, favoring the pairing of electrons and, hence, the transition to the low-spin state.

In our case, the situation is not that simple. Figure 1 clearly exhibits the tendency of redistribution of the symmetry-decomposed $d$-OONs of both compounds. Majority-spin bands move upward, while minority-spin bands move downward for both $t_{2g}$ and $e_g$ orbitals, and all $t_{2g}$ and $e_g$ orbitals are split into two band groups for both majority- and minority-spin bands. To show this tendency of redistribution of the symmetry-decomposed $d$-OONs more clearly a schematic diagrams of symmetry decomposed Fe $d$-DOS of metamagnetic Fe$_3$Al alloy is presented in Fig 2. For the $e_g$ majority-spin bands only the upper-band group is located near $E_F$, while the both band groups of minority-spin bands are far from $E_F$. Therefore, $d$-OONs of $e_g$ orbitals do not change significantly for majority spin, while there are almost no change in $d$-OONs of $e_g$ orbitals for minority spin upon transition to the low-spin state. The situation of the case of $t_{2g}$ orbitals is quite different from that of the $e_g$ orbitals. The upper majority-spin bands of $t_{2g}$ orbitals are located just below $E_F$, and the lower minority-spin bands of $t_{2g}$ orbitals are located just above $E_F$ for the high-spin state. Upon transition to the low-spin state, $d$-OONs for majority-spin (minority-spin) $t_{2g}$ orbitals decreases (increases) significantly, resulting in a significant reduction of magnetic moment.

This redistributions of $d$-OONs can be clearly manifested in spin-density plots. Before discussing the spin densities of the Fe-based pnictide compounds, we present spin-density plots for the high-spin and low-spin states of metamagnetic Fe$_3$Al alloy in Fig. 3. The distribution of spin density plotted on the (110) plane (left panel) around the Fe$_1$ atom is symmetric and exhibits no significant directionality in the high-spin state, while that for the low-spin state exhibits a strong directionality. Especially, the strong directionality appears along the $z$-axis. For the high-spin state $d$-OONs of five $d$-orbitals are almost identical to each other, while those of $e_g$ orbitals are significantly smaller than those of $t_{2g}$ orbitals for the low-spin state. Therefore, the directionality appeared along the $z$-axis is evident, reflecting the deficiency of $d_{z^2}$ orbital in the low-spin state. The same arguments can be applied to
FIG. 1. (Color online.) Symmetry-decomposed Fe $d$-DOS of the 122- and 1111-compounds.

FIG. 2. (Color online.) Schematic diagrams of symmetry-decomposed Fe $d$-DOS of metamagnetic Fe$_3$Al alloy.

the plots on the (001)-plane (see the right panel of Fig. 3). In the low-spin state the spin density exhibits strong directionality along the $x$- and $y$-axes, reflecting the deficiency of $d_{(x^2-y^2)}$ orbitals.

To see if the same trend can be found in the Fe-based pnictide compounds, Fig. 4 presents the spin-density plots of the 1111-compound on the (010) and (100) planes. Unlike the case of the metamagnetic Fe$_3$Al alloy, in calculations with simple GGA there is no symmetric distribution of spin density on the (010) plane, in which the magnetization is in the plane. In the GGA$-|U|$ calculation the spin density exhibits clear 4-fold symmetry, while it is slightly 2-fold in the simple GGA calculation. For the (100) plane, in which the magnetization is out of the plane, the situation becomes opposite. It exhibits almost perfect 4-fold symmetry in the simple GGA calculation, while it becomes slightly 2-fold symmetric in the the GGA$-|U|$
FIG. 3. (Color online.) Spin-density plots of the Fe$_3$Al alloy on the (110) and (001) planes for (top) fictitious Fe$_2$Al alloy (see text), (middle) for high-spin state, and (bottom) for the low-spin state. Thick arrows indicate the direction of magnetization.

calculation. Very similar arguments can be applied to the case of the 122-compound.

Since the transition from high-spin state to low-spin state occurs at high pressure, the distance between the Fe atom and ligand atom, $d_{\text{Fe}-\text{Lig.}}$, may play a crucial role. For the Fe$_3$Al alloy $d_{\text{Fe}-\text{Lig.}} = 4.48$ a.u.$^{14}$ in the low-spin state, while those for the 122- and 1111-compounds are 4.53 a.u. and 4.46 a.u., respectively. Since all $d_{\text{Fe}-\text{Lig.}}$'s are in almost the same distances, we calculated the spin densities of a fictitious 1111-compound with the expanded lattice constant, bearing $d_{\text{Fe}-\text{Lig.}} = 4.7$ a.u., which is the same as that of Fe$_3$Al alloy in the ambient pressure. As can be seen in the top row of Fig. 4, the spin-density plots do not exhibit a symmetric distribution of spin density. Rather, it is more 2-fold symmetric for the (010) plane and more 4-fold symmetric for the (100) plane. Although there are only 4 As atoms, forming a tetrahedral cage, around the Fe atoms in Fe-based pnictide compounds, there are 4 Al atoms, forming a tetrahedral cage, plus 4 Fe$_{\text{II}}$ atoms, also forming a tetrahedral cage, around the Fe$_{\text{I}}$ atom. To compare the results of the Fe$_3$Al alloy with those of Fe-based pnictide compounds, it is necessary to remove the effects of surrounding 4 Fe$_{\text{II}}$ atoms. Therefore, we calculated the spin density of another fictitious Fe$_2$Al alloy, in which the Fe$_{\text{II}}$ atoms are removed from the Fe$_3$Al alloy. The results are
FIG. 4. (Color online.) Spin-density plots of the 1111-compound on the (010) and (100) planes for (top) fictitious compound with expanded lattice constant (see text), (middle) for a simple GGA calculation, and (bottom) for GGA$-|U|$ calculation. Thick arrows indicate the direction of magnetization.

almost identical to those of the fictitious 1111-compound with the expanded lattice constant (see the top row of Fig. 3).

The symmetric distribution of spin density in the high-spin state of the Fe$_3$Al alloy can be attributed to the existence of 4 Fe$_{II}$ atoms. Since the 4 Fe$_{II}$ atoms form another tetrahedral cage, they can attract spin density into themselves from the Fe$_{I}$ atom, resulting in a symmetric distribution of spin density in the high-spin state. The effects of the existence of 4 Fe$_{II}$ atoms can be further manifested by the fact that the symmetry directions in the spin-density plot on the (001) plane for the low-spin state are 45° rotated from those of fictitious Fe$_2$Al alloy.

According to our calculational results, the LDA, GGA or GGA$+U$ with positive $U$ can not properly predict the magnetic states of the Fe-based pnictide superconductors. Rather, the GGA$-|U|$ method can. In Ref. 9 it was argued that the negative $U$ correction can be considered as an unexpectedly well screening on $d$-orbitals in Fe atoms. If the screening is strong enough or over, then we can reach a situation that the intra-band repulsion becomes smaller than the inter-band one. In such a case, an effectively attractive force may result in.
IV. SUMMARY

We have calculated the electronic structures, DOS, occupation numbers and spin-density of 3$d$ Fe of BaFe$_2$As$_2$ and LaFeAsO in the orthorhombic, AFM phases by using GGA and GGA$-|U|$. We found that, in high-$T_c$ iron-based superconducting compounds, the use of GGA with negative $U$ with similar values ($-0.09$ Ry and $-0.10$ Ry) give the well-matched results with experimental magnetic moment per Fe atom. By comparing the differences of DOS, symmetry-decomposed $d$-OONs and spin densities between simple GGA and GGA$-|U|$ calculations, the magnetic state of the iron-based pnictide compounds are very similar to the case of the low-spin state of metamagnetic Fe$_3$Al alloy. To further address the validity of negative $U$ more researches, such as direct calculation of the onsite Coulomb interaction $U$ and the exchange iteration $J$ from the first-principles calculations, are needed.

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