LDA + Negative $U$ Solves a Puzzle of too Large Calculated Magnetic Moment in Iron-based Superconductor LaFeAsO$_{1-x}$F$_x$

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A puzzle in the iron-based superconductor LaFeAsO$_{1-x}$F$_x$ is that the magnetic moment obtained by first-principle electronic structure calculations is unexpectedly much larger than the experimentally observed one. For example, the calculated value is $\sim 2.0 \mu_B$ in the mother compound, while it is $\sim 0.3 \mu_B$ in experiments. We find that the puzzle is solved within the framework LDA + $U$ by expanding the $U$ value into a slightly negative range. We show $U$ dependence of the obtained magnetic moment in both the undoped $x = 0.0$ and doped $x = 0.125$. These results reveal that the magnetic moment is drastically reduced when entering to the slightly negative range of $U$. Moreover, the negative $U$ well explains other measurement data, e.g., lattice constants and electronic DOS at the Fermi level. We discuss possible origins of the negative $U$ in these compounds.

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Very recently, iron based novel superconductors have attracted much attention, since its discovery may open another pathway toward the room temperature superconductor. Consequently, the superconducting critical temperature has exceeded 50K within just a few months since the start of the high-temperature race [1]. At the same time, several theoretical mechanisms have been proposed [2].

Here, we summarize the experimental results accumulated since the discovery. The typical undoped mother compound LaFeAsO shows an antiferromagnetic spin density wave (SDW) ordering after the lattice structural transition from the tetragonal to the orthorhombic structure at $\sim 150K$ when decreasing the temperature [3, 4]. The SDW disappears with doping carriers via chemical substitution of a part of O by F, and the superconducting phase instead emerges from $x \sim 0.05$ in LaFeAsO$_{1-x}$F$_x$. Thus, the superconductivity has a close relationship to the magnetism and the lattice distortion. In addition, the optical absorption, photoemission and NMR studies reported that a large pseudo-gap 19 meV $\sim 100$ meV opens even above the superconducting transition $T_c$ [3, 5]. These imply an anomalous DOS suppression at the Fermi level by development of an order or other reasons. However, the clear origin still remains unsolved.

Besides the above measurement activities, the new material discovery has stimulated first-principle electronic structure calculations [7, 8, 9, 10]. Initially, inconsistent results on the magnetic structure were suggested. But, there is now a good agreement between the calculations and the experiments in respect of the magnetic and the related lattice structures. The antiferromagnetic SDW is confirmed to be the lowest energy state, in which the orthorhombic structure is stabilized by optimizing the lattice structure under the SDW magnetic order [5]. However, it is noted that there remains a big puzzle in the magnetic moment on an Fe atom in the SDW state. The moments calculated with the local-density approximation (LDA) and the generalized gradient approximation (GGA) are $\sim 1.0 \mu_B$ (LDA) to $\sim 2.0 \mu_B$ (GGA) [8], which is much larger than experimental data $0.2 \sim 0.35 \mu_B$ obtained by the powder neutron scattering [8], Mössbauer effect [11], and muon spin relaxation [12]. Normally, the moment over-estimation in LDA(GGA) calculation is almost rare. This clearly implies that the calculations lack an unknown effect peculiar to the compounds or requires a particular correction. For example, we immediately notice that spin fluctuations always suppress the moment and two-dimensionality due to layered materials somewhat enhances the fluctuation. However, $S \sim 2$ is too large to be reduced to about $\sim 1/5$ times only by the fluctuations. Thus, this puzzle may be crucial for elucidating the superconducting mechanism.

The Coulomb repulsion effect inside the local Fe $d$-orbit is listed as a missing effect. The effect is approximately treated within “LDA + $U$”, $U(=U_{\text{eff}})$ of which is theoretically decomposed into $U_{\text{eff}} = U - J$, where $U$ is the on-site Coulomb repulsion (Hubbard $U$) and $J$ is the atomic-orbital intra-exchange energy (Hund’s parameter) in the “simplified” framework [13]. We vary the single parameter $U_{\text{eff}} = U - J$ from a large positive value to a slightly negative one and also calculate electronic structures in another “separable” framework for $U$ and $J$ [14] in order to identify which parameter is more essential. We find that a slight negative $U_{\text{eff}}$ well explains the experimental results.

The on-site Hubbard $U$ employed in the electronic structure calculations is usually a positive value. The positiveness promotes the localized character of $d$-electrons and enhances the magnetic moment in the cases of magnetically ordered compounds. Since the parameter $U$ is treated within the mean-field level in the stan-
dard LDA+ $U$, more sophisticated methods coupled with DMFT and QMC have been also suggested [15, 16]. However, we point out that one cannot expect a drastic moment reduction irrespective of the use of such advanced methods as long as the positive large $U$ is taken into account. In contrast, we extend the parameter $U_{\text{eff}}$ range to a negative one. Although the negative case is not popular, it occurs in the following two cases. The Hubbard $U$ itself is negative, and the intra-exchange $J$ is effectively larger than the Hubbard $U$. The former case has been suggested by many authors in various theoretical models as discussed later. Besides such explicit reasons, a slightly negative Hubbard $U$ simply may compensate the energy calculation errors in the LDA calculations. However, there has been just a few works taking the negative on-site Hubbard $U$ into account within the LDA+ $U$ framework to our knowledge [17, 18]. On the other hand, the latter case [20] may be also possible in the present compounds since $J$ is suggested to be large [19] while $U$ is reported to be effectively smaller than our naive expectation [21, 22]. These facts require that one flexibly chooses $U_{\text{eff}}$ in the present compounds at least.

In this study, we employ the VASP code [23] in which the projector augmented-wave (PAW) method [24, 25] is implemented, and the lattice and the electronic structures are optimized by choosing GGA + $U$. The stabilities of some different magnetic structures are examined by comparing their total energy. The typical lowest-energy state at $U = 0$ for the mother compound is shown in Fig. 1 whose magnetic structure is equivalent with Ref. [3]. For the mother compound ($x = 0$), we actually adopt the La$_4$Fe$_4$As$_4$O$_4$ cell that have space group symmetry $Ibam$, in order to realize SDW antiferromagnetic state as in Fig. 1. In the case of the doped compound ($x = 0.125$), we use the super cell as shown in Fig. 1, where one of O atoms is replaced by F. In our calculation, the energy cut-off for the plane-wave set is set to 500 eV, the convergence condition for electronic self-consistent loop is less than $10^{-5}$ eV in the total energy difference, and the structure relaxation loop is repeated until all forces on ions are smaller than 0.02 eV/Å. The grids for $k$ points are taken as $6 \times 6 \times 6$ and $4 \times 4 \times 2$ for the undoped and doped compounds, respectively.

Let us show numerical calculation results. Firstly, we focus on the mother compound LaFeAsO. Figure 2(a) shows $U_{\text{eff}}$ dependence of the energy difference between the non-magnetic and the stable SDW states, and Fig. 2(b) displays $U_{\text{eff}}$ dependence of the magnetic moment in the SDW state. At $U_{\text{eff}} = 0$ where several calculations were previously made, the moment is $\sim 2.0 \mu_B$ and the energy difference is $\sim 90$ meV per LaFeAsO cell. These values are consistent with the previous results [3, 8, 13], in which the lattice structure is optimized and the orthorhombic one is observed to be stable. For $U_{\text{eff}} > 0$, the effect of $U_{\text{eff}}$ further develops the moment value. As expected, the positive $U_{\text{eff}}$ stresses the localized character of d-orbital electrons, and overemphasizes the inconsistency with the experiments. On the other hand, the moment decreases with decreasing $U_{\text{eff}}$ and coincides with the experimental results at a negative $U_{\text{eff}}$ region. In addition, we note that the energy difference becomes very small around $U_{\text{eff}} = -1$, as in Fig. 2(a).
This indicates that SDW state becomes not so strongly stable as that at $U_{\text{eff}} = 0$.

Figure 3(a) displays $U_{\text{eff}}$ dependence of lattice constants, $a$, $b$, and $c$ for the mother compound. The experimental values are shown by horizontal dashed lines. In this paper, $b$ is the direction along which the antiferromagnetic ordering grows. In the positive $U_{\text{eff}}$ range, the increase of $U_{\text{eff}}$ brings separations from the experimental results for $a$ and $b$, while they show good agreements with experimental ones in the slightly negative range.

From the results as seen in Fig. 2 and Table I, it is found that the slightly negative $U_{\text{eff}}$ well explains the experimental results. Here, we check which parameter ($U$ or $J$) is more essential in reproducing the experimental results by using the separable framework. Table I is a comparison between $U = -1.0(J = 0)$ and $J = 1.0(U = 0)$ for the magnetic moment and the lattice constants. These results indicate that $U = -1.0$ is slightly closer to the experiments but it is not a conclusive difference. Moreover, the lattice constants obtained by the optimization do not differ significantly in both cases. We point out that a clear-cut determination is impossible here within the present framework.

Next, let us turn to the doped compound. The calculations are made on the supercell as shown in Fig. 1, where one of O atoms is replaced by F and $x = 0.125$ in LaFeAsO$_{1-x}$F$_x$. At the doping value, the compound shows the superconducting ground state. The dashed lines of Fig. 2(b) show $U_{\text{eff}}$ dependence for the magnetic moment value in the doped compound. The data calculated at $U_{\text{eff}} = 0$ still shows the stability of the SDW state, which is equivalent with the previous literatures. Then, the energy difference ($\sim 90$ meV) is too large to replace the SDW state by the non-magnetic ordered one even in the doped one. Also, the increase of $U_{\text{eff}}$ in the positive range enhances the stability of the SDW state, which is inconsistent with the experimental results. On the other hand, the negative $U_{\text{eff}}$ diminishes the moment resulting in the disappearance of the SDW, and the system recovers to the tetragonal lattice structure by the optimization. The behavior of the lattice constants is also similar to the undoped case as seen in Fig. 3(b). At the negative range, the calculated values except for $c$ show good agreements with experimental ones.

This table summarizes the magnetic moment and lattice constants obtained in the present work. The results indicate that SDW state becomes not so strongly stable as that at $U_{\text{eff}} = 0$.

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The discovery of cuprate High-$T_c$ superconductors has been published on several metal oxides. A famous idea originates from the charge disproportionation on the cation.
sites, which has been mainly discussed in doped superconductors based on BaBiO$_3$, in which CDW occurs close to the emergence of its superconductivity [27]. In addition, the overscreening effects on the Coulomb interaction coupled with the strong correlation (due to the low carrier density) have been proposed in the context of high-$T_c$ superconductivity mechanism [28]. If the overscreening, i.e., the attractive interaction effectively works between two electrons, then unusual softening of electronically coupled longitudinal optical (LO) phonon compared to transverse optical (TO) one has been predicted. In fact, there are several reports which confirm the LO-TO frequency inversion due to the drastic LO softening in high-$T_c$ superconductor as well as other various metal oxides [29]. Thus, the negative Hubbard $U$ is now not rare. But, since the effect is counterintuitive, more experimental and theoretical tasks are required. On the other hand, the idea that $J$ is relatively effective in fixing $U_{\text{eff}}$ may be very simple and acceptable. In this iron based superconductors, the Hubbard $U$ may be rather small because Fe related five bands are entangled within their wide band-width. In fact, there are some experimental reports which support it [21, 22].

In conclusion, we calculated electronic structure of iron based typical superconducting compound LaFeAsO$_{1-x}$F$_x$ using the framework LDA+$U$ with expanding the range of $U(= U_{\text{eff}} = U - J)$ from the positive to the slightly negative range. Consequently, we found that the calculated magnetic moment, the lattice constants, and the pseudo-gap feature shows good agreements with the experimental results in the negative $U_{\text{eff}}$ range. We discussed some negative origin of $U_{\text{eff}}$ in the superconductor.

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FIG. 4: The electronic density of states DOS for (a) $U_{\text{eff}} = 2$, (b) $U_{\text{eff}} = 0$, and (c) $U_{\text{eff}} = -1$ in the undoped compound. $E = 0$ corresponds to the Fermi energy.
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[28] See, e.g., M. Tachiki, M. Machida, and T. Egami, Phys. Rev. B 67, 174506 (2003).

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