

COULOMB CORRELATION EFFECTS IN LaFeAsO: AN LDA + DMFT(QMC) STUDY

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Received June 10, 2008

Effects of Coulomb correlation on the LaFeAsO electronic structure are investigated by the LDA + DMFT(QMC) method (combination of the local density approximation with the dynamic mean-field theory; impurity solver is a quantum Monte Carlo algorithm). The calculation results show that LaFeAsO is in the regime of intermediate correlation strength with a significant part of the spectral density moved from the Fermi energy to the Hubbard bands and far from the edge of the metal–insulator transition. Correlations affect iron *d*-orbitals differently. The t_{2g} states (xz , yz and $x^2 - y^2$ orbitals) have a higher energy due to crystal field splitting and are nearly half-filled. Their spectral functions have a pseudogap with the Fermi level position on the higher subband slope. The lower energy e_g set (xy and $3z^2 - r^2$ orbitals) have occupancies significantly larger than $\frac{1}{2}$ with typically metallic spectral functions.

PACS: 74.25.Jb, 71.27.+a, 71.30.+h

1. INTRODUCTION

The very recent report of superconductivity with the remarkable T_c of 26 K in LaFeAsO_{1-x}F_x [1] has stimulated an intense experimental and theoretical activity. Calculation of the electron–phonon coupling in this material has shown [2] that it cannot give such a high superconducting transition temperature T_c . That resembles the situation with high- T_c cuprates and raises a question about the strength of the Coulomb correlation effects in this material.

Recently, Haule et al. [3] reported results of the LDA+DMFT (the local density approximation combined with the dynamic mean-field theory) calculations of the electronic structure of an undoped LaFeAsO compound with the effective impurity model solved by the continuous-time quantum Monte Carlo method. According to [3], this system is in a strongly correlated regime. In the present work, we report results of the LDA+DMFT(QMC) calculations for LaFeAsO

with an effective impurity model solved by the standard quantum Monte Carlo method in the Hirsch–Fye algorithm. Our results confirm that correlations indeed have a sizable effect on the electronic structure of LaFeAsO. But the system is not at the edge of the metal–insulator transition. While Haule et al. [3] claim that the increase in the Coulomb parameter U from 4 eV to 4.5 eV takes the system to the insulating state, our calculations show that the solution is still clearly metallic even for $U = 5.0$ eV.

2. COMPUTATION DETAILS

The LDA band structure of LaFeAsO was calculated using the method of tight-binding linear muffin-tin orbitals in the atomic sphere approximation, TB-LMTO-ASA [4]. The crystal structure parameters were taken from Ref. [1]. The results agree well with the previously reported full-potential calculations [5]. In Fig. 1, the density of states (DOS) in the energy region of Fe 3*d*-bands is presented. The

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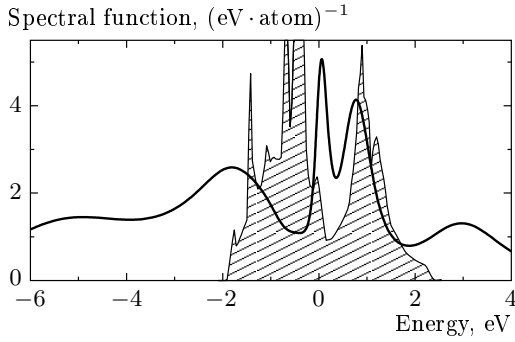


Fig. 1. The density of states obtained within the LDA (hatched area) and the spectral function from the LDA+DMFT scheme for $U = 4$ eV and $J = 0.7$ eV (solid line). Fermi energy is zero

Fermi level corresponding to 6 electrons per formula unit in a d -band is situated near a deep minimum between two subbands. These subbands have their origin in the bonding–antibonding separation due to a strong hybridization between d -states in FeAs layers.

Using eigenvalues and eigenfunctions from the LDA calculations for bands formed by Fe $3d$ -orbitals, we have calculated the Wannier functions via the projection procedure [6, 7]. The calculated Hamiltonian matrix $\hat{H}(\mathbf{k})$ in the basis of Wannier functions has the size 10×10 ($5d$ -orbitals per Fe ion and two Fe ions in the unit cell) and by construction has exactly the same eigenvalues as for the ten LDA bands formed by Fe $3d$ -orbitals.

This Hamiltonian was used in the LDA+DMFT [8] calculations (see Ref. [7] for a detailed description of the present computation scheme). The Coulomb interaction parameter value $U = 4$ eV and the Hund parameter $J = 0.7$ eV were set the same as in the previous LDA+DMFT calculations [3]. The effective impurity model for the DMFT was solved by the QMC method in the Hirsh–Fye algorithm [9]. Calculations were performed for the inverse temperature value $\beta = 10$ eV $^{-1}$. The inverse temperature interval $0 < \tau < \beta$ was divided into 100 slices; 4 million QMC sweeps were used in a self-consistency loop within the LDA+DMFT scheme and 12 million of QMC sweeps were used to calculate the spectral functions.

3. RESULTS AND DISCUSSION

The total spectral function calculated within the LDA+DMFT scheme in comparison with the total DOS obtained within the LDA approach are presented

in Fig. 1 (see also Fig. 3 for a wider energy range). Correlation effects are strong enough to move part of the spectral density from the Fermi energy to “shoulders” at -4 eV and $+4$ eV. But in contrast to the spectra in [3], where a strong Hubbard band at -4 eV is separated from the weak quasiparticle band by a deep wide depression in the $(-2$ eV, 0 eV) area, the main part of the spectral density in our results is still in the interval from -2 eV to $+2$ eV. In this energy range, the LDA+DMFT spectral function preserves the general shape of the LDA DOS with two subbands divided by a deep minimum. The essential result of correlation is the position of the Fermi energy, which has moved from the edge of the lower subband in the LDA DOS to the top of the upper subband. Exactly at the Fermi energy, a sharp peak has developed.

The crystal structure of LaFeAsO has the tetragonal symmetry [1]. The Green’s function for d -orbitals is diagonal with different matrix elements for each of the $3z^2 - r^2$, $x^2 - y^2$, xy orbitals and doubly degenerate elements for the xz , yz set of orbitals. The iron ion has a tetrahedral coordination of four As ions with a slight tetragonal distortion of the tetrahedron. In the tetrahedral symmetry group T_d , five d -orbitals must be split by the crystal field into a low-energy doubly degenerate set $3z^2 - r^2$, xy corresponding to the irreducible e_g representation¹⁾ and a high-energy triply degenerate set $x^2 - y^2$, xz , yz for the t_{2g} representation. We have calculated the Wannier functions energy and have found that the t_{2g} – e_g crystal field splitting parameter is very small, $\Delta_{cf} \approx 0.25$ eV. The slight tetragonal distortion of the tetrahedron leads to an additional splitting of the t_{2g} and e_g levels with the following values for orbital energies (the energy of the lowest $3z^2 - r^2$ orbital is taken as a zero): $\varepsilon_{3z^2-r^2} = 0.00$ eV, $\varepsilon_{xy} = 0.03$ eV, $\varepsilon_{xz,yz} = 0.26$ eV, $\varepsilon_{x^2-y^2} = 0.41$ eV. The intersite hybridization between d -orbitals is much stronger than the crystal field splitting (the total d -band width is about 4 eV). As a result, all five d -orbitals form a common d -band with the subbands originated not from the crystal field splitting, as in the case of octahedral coordinated oxides, but due to a strong bonding–antibonding separation (see Fig. 2). The xy -orbital that has lobes directed along the Fe–Fe bond in FeAs planes shows an especially strong bonding–antibonding separation.

In Fig. 2, we present the orbitally resolved spectral functions obtained from the LDA+DMFT calculation

¹⁾ The coordinate axes x, y in the LaFeAsO crystal structure are rotated through 45° from the standard tetrahedral notation, such that xy and $x^2 - y^2$ orbitals are interchanged.

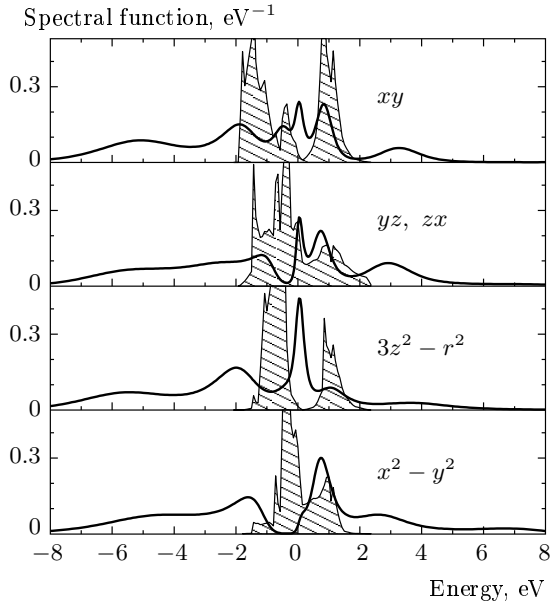


Fig. 2. Partial densities of states obtained within the LDA (hatched areas) and the LDA+DMFT partial spectral functions for $U = 4$ eV and $J = 0.7$ eV (solid lines). Fermi energy is zero. The set of e_g orbitals consists of xy and $3z^2 - r^2$ bands; the yz , zx , and $x^2 - y^2$ bands form the t_{2g} orbitals set (see also footnote 1)

with $U = 4.0$ eV and $J = 0.7$ eV. Comparison with the corresponding LDA partial DOS shows that different orbitals are affected by correlations in different ways. The $x^2 - y^2$ orbital curve has a nearly insulator shape with a pronounced pseudogap below the Fermi energy. The other t_{2g} orbitals xz, yz also show the presence of a pseudogap. For them, the Fermi energy is on the slope of the upper subband, and their general form is typical of a slightly electron-doped Mott insulator. The e_g set of d -orbitals ($3z^2 - r^2$ and xy) shows clearly metallic behavior with well-developed quasiparticle bands and no pseudogap.

The occupation numbers obtained from the LDA+DMFT calculations have the values $n_{xy} = 0.672$, $n_{yz}, n_{zx} = 0.565$, $n_{3z^2 - r^2} = 0.686$, and $n_{x^2 - y^2} = 0.512$. These values mean that one of t_{2g} states, the $x^2 - y^2$ orbital that has the highest crystal field energy ($\varepsilon_{x^2 - y^2} = 0.41$ eV), is nearly half-filled. The energy of the other t_{2g} states (xz, yz -orbitals) is 0.15 eV lower ($\varepsilon_{xz, yz} = 0.26$ eV) and these orbitals are slightly more occupied. The e_g set of d -orbitals ($3z^2 - r^2$ and xy), which have the lowest energy due to the crystal field splitting ($\varepsilon_{3z^2 - r^2} = 0$, $\varepsilon_{xy} = 0.03$ eV), have a significantly larger occupancy. This fact agrees with our analysis of orbitally resolved spectral

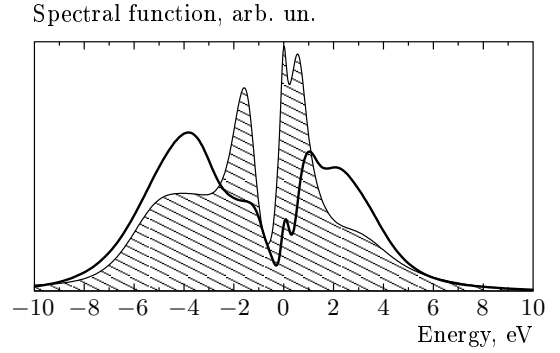


Fig. 3. Spectral function from the LDA+DMFT scheme for $U = 4$ eV (hatched area) and $U = 5$ eV (solid line). In both calculations, $J = 0.7$ eV. Fermi energy is zero

functions in Fig. 2. Half-filling of the $x^2 - y^2$ orbital ($n_{x^2 - y^2} = 0.512$) corresponds to a Mott-insulator shape of the spectral function. Deviation from half-filling for xz, yz orbitals ($n_{yz}, n_{zx} = 0.565$) results in a light electron-doped Mott insulator. The occupancies of e_g orbitals are much larger than the t_{2g} values, and the corresponding spectral functions are characteristic of correlated metal.

It was reported in Ref. [3] that “slightly enhanced Coulomb repulsion ($U = 4.5$ eV) opens the gap” such that the system is on the edge of the metal-insulator transition. We have repeated the LDA+DMFT(QMC) calculations with an even larger Coulomb parameter, $U = 5.0$ eV (the Hund parameter $J = 0.7$ eV). The resulting total spectral function is presented in Fig. 3 in comparison with the result for $U = 4.0$ eV. While increasing the U value leads to a spectral density redistribution from the peaks around the Fermi energy to the lower and upper Hubbard bands, the system still shows a clearly metallic character with a sharp peak at the Fermi energy. We therefore conclude that for $U = 4.0$ eV, the system is not close to the metal-insulator transition.

It is interesting to analyze the evolution of orbitally resolved spectral functions with different U values: $U = 5$ eV (Fig. 4) against $U = 4$ eV (Fig. 2). The t_{2g} states become fully insulating (the quasiparticle peak is now absent for xz, yz orbitals) and the Fermi level is positioned inside the gap for the $x^2 - y^2$ spectral function. But the e_g -set d -orbitals ($3z^2 - r^2$ and xy) still have a strong quasiparticle peak at the Fermi energy. That type of electronic structure with partial localization resembles the “orbitally selective Mott transition” effect that was proposed for the $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ com-

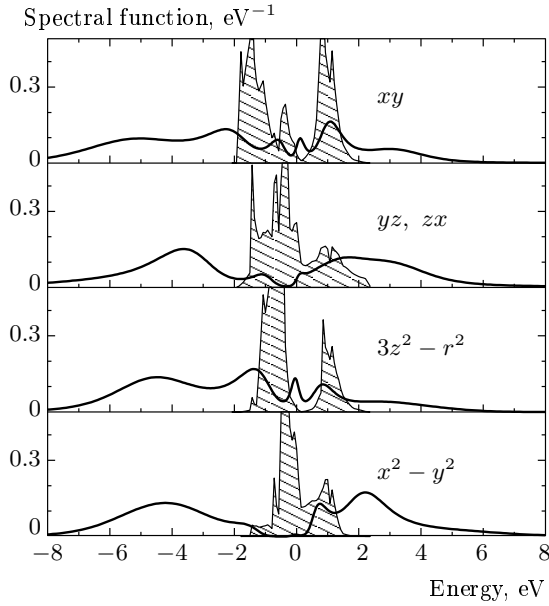


Fig. 4. Partial densities of states obtained within the LDA (hatched areas) and the LDA+DMFT partial spectral functions for $U = 5$ eV and $J = 0.7$ eV (solid lines). Fermi energy is zero

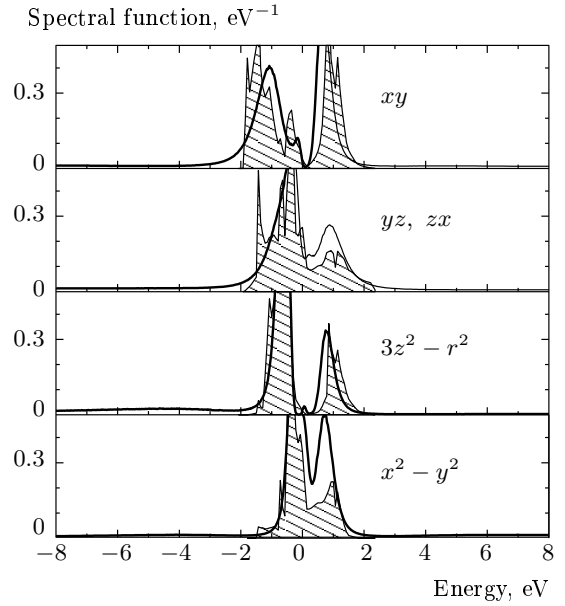


Fig. 5. Partial densities of states obtained within the LDA (hatched areas) and the LDA+DMFT partial spectral functions for $U = 4$ eV and $J = 0$ (solid lines). Fermi energy is zero

pound [10]. The Mott transition for the $x^2 - y^2$ spectral function is not 100% pure because a weak peak can be observed at the the Fermi level inside the gap. This peak is originated possibly due to the mixing of $x^2 - y^2$ orbitals with metallic e_g states. The evolution of orbital occupancies agrees with the better localization of the t_{2g} states in the $U = 5$ eV case: for (xz , $x^2 - y^2$) orbitals, the occupancy values decrease from (0.565, 0.512) to (0.535, 0.505) and for the e_g -set d -orbitals ($3z^2 - r^2$ and xy), the occupancies increase from (0.686, 0.672) to (0.750, 0.672).

We have found that elimination of the Hund parameter J from the calculation dramatically changes the effect of correlations on the electronic structure of LaFeAsO. The LDA+DMFT(QMC) calculations with $U = 4$ eV and $J = 0$ (Fig. 5) result in a very weakly correlated electronic structure with the quasiparticle renormalization amplitude $Z \approx 0.8$. The weakness of the correlations is evident, e. g., from the occupancies. The occupation numbers obtained from the LDA eigenvalues and eigenfunctions are $n_{xy} = 0.543$, $n_{yz}, n_{zx} = 0.601$, $n_{3z^2-r^2} = 0.753$, and $n_{x^2-y^2} = 0.502$. After the correlation effects are taken into account in the LDA+DMFT calculations with $U = 4$ eV and $J = 0$, the occupation numbers change to $n_{xy} = 0.540$, $n_{yz}, n_{zx} = 0.610$, $n_{3z^2-r^2} = 0.779$, and $n_{x^2-y^2} = 0.461$. These changes are relatively small, as is expected for

the weakly correlated regime, where the electron states are far from localization. The main influence on the occupancy changes is provided by crystal field effects: the e_g $d_{3z^2-r^2}$ states, which have the lower energy in the LDA, become more occupied, whereas the occupation of the higher t_{2g} orbital $d_{x^2-y^2}$ decreases. The occupations of t_{2g} orbitals (d_{yz} , d_{zx}) and the second e_g -orbital d_{xy} slightly change from their LDA values. Comparison with the corresponding LDA partial DOS shows that the shape of the curves is nearly unmodified by correlation effects preserving a clear bonding–antibonding separation into two subbands. At the same time, the band width decreases, as is expected for correlated quasiparticle bands. We can see very weak wide structures, which can be associated with the lower and upper Hubbard bands approximately 4 eV below and above the quasiparticle band around the Fermi level. This agrees with the results in Ref. [11], where the influence of a d -band degeneracy N_d on the critical values for the U/W ratio required for describing the metal–insulator transition was investigated. The critical U value was estimated in Ref. [11] as $U_c \approx \sqrt{N_d} U_c^0 - N_d J$, where U_c^0 is the critical U value for the nondegenerate Hubbard model. With the LDA band width value $W \approx 4$ eV and the Coulomb interaction parameter $U = 4.0$ eV, the ratio U/W is close to 1. With $J = 0$, the orbital degeneracy $N_d = 5$ would lead to the critical U value

increased by a factor of $\sqrt{5}$ or an effective decrease in the U/W ratio more than twice, thus resulting in the weakly correlated regime. But the value $J = 0.7$ eV is to compensate the increase in U_c due to the factor $\sqrt{5}$ and $U/W \approx 1$ should result in an intermediate-correlation-strength regime.

It is interesting to mention one of the conclusions in Ref. [12] here: to have the temperature dependence of the theoretical susceptibility $\chi(\tau)$ curve in agreement with experiment, the J value should not be greater than 0.35 eV. Such a small value of J , according to our comparison of the $J = 0.7$ eV and $J = 0$ cases, should lead to an even more weakly correlated regime than that described on the basis of Fig. 2.

4. CONCLUSIONS

Our LDA+DMFT(QMC) calculations show that LaFeAsO is in the intermediate-correlation-strength regime. Hubbard bands in the spectral function are well pronounced but still a major part of the spectral density is concentrated inside the bands in the vicinity of the Fermi level. The system is not close to the metal–insulator transition because a significant increase in the Coulomb interaction parameter does not lead to the insulating character of the energy spectrum of LaFeAsO.

The authors thank Jan Kuneš for his DMFT(QMC) computer codes used in the present calculations. Support by the Russian Foundation for Basic Research under Grant No. RFFI-07-02-00041, the Civil Research and Development Foundation together with the Russian Ministry of science and education through program Y4-P-05-15, the Russian president grant for young scientists MK-1184.2007.2, and the Dynasty Foundation is gratefully acknowledged.

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