Calculation of the specific heat of optimally K-doped BaFe$_2$As$_2$

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Abstract
The calculated specific heat of optimally K-doped BaFe$_2$As$_2$ in density functional theory is about five times smaller than that found in the experiment. We report that by adjusting the potential on the iron atom to be slightly more repulsive for electrons improves the calculated heat capacity as well as the electronic band structure of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. In addition, structural and magnetic properties are moved in the direction of experimental values. Applying the same correction to the antiferromagnetic state, we find that the electron–phonon coupling is strongly enhanced.

Keywords: optimally K-doped BaFe$_2$As$_2$, specific heat, semi-empirical density functional theory

(Some figures may appear in colour only in the online journal)

1. Introduction

The discovery [1] of superconductivity in LaFeAsO$_{1-x}$F$_x$ with a transition temperature of 26 K in 2008 triggered unprecedented interest and further research in iron-based superconductors. So far, superconductivity was found in four main families of iron-based compounds: 1111, 122, 111, and 11 [2, 3]. These iron-based materials have two phases in the normal state: one is a paramagnetic metal and the other is an antiferromagnetic metal. Superconductivity emerges in both the paramagnetic and antiferromagnetic metal phases via application of hydrostatic pressure or carrier doping of the parent materials. Hence, it is expected that understanding the electronic and magnetic structures of the metallic normal states of these systems is a needed ingredient for unraveling the origin of the superconductivity of iron-based materials.

Many experimental and theoretical studies have been made on the normal states of iron-based superconductors, and a consensus [4, 5] has been reached in these systems that the Coulomb interaction among the electrons is not strong enough to induce a Mott insulating phase. However, the Coulomb interaction plays an important role in determining the electric and magnetic properties. In the early stages of this research, theoretical insight into the properties of these materials was gained by calculations based on density functional theory (DFT) within the local density approximation (LDA) or generalized gradient approximation (GGA). However, LDA and GGA have some limitations in describing the normal states of iron-based superconductors. In a paramagnetic phase, the measured mass of low-energy quasiparticles [6] is 2–3 times larger than that calculated within LDA or GGA. In addition, the measured magnitude of the ordered moment in an antiferromagnetic phase [7, 8] is 2–3 times smaller than that obtained with LDA or GGA. Furthermore, LDA and GGA studies related to the specific heat of these materials are not consistent with the experimental data. The theoretical Sommerfeld coefficient [9–11] of optimally K-doped BaFe$_2$As$_2$ is about five times smaller than that found in the experimental data [12–16].

There have been many attempts to describe electronic correlations in these materials by combining LDA or GGA calculations with a dynamical mean-field theory (DMFT), quasiparticle self-consistent GW (QSGW), or the Gutzwiller method [17–20]. Using these methods, many of the electric and magnetic properties of correlated iron-based superconductors can be reproduced. For example, effective masses and Fermi surfaces (FSs) across all families of iron compounds are well described in the framework of DFT + DMFT [17] and QSGW [18], as well as ordered moments and the fluctuations of local moments within DFT + DMFT [17, 19]. However, a calculation of the electron–phonon coupling coefficient...
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\( \Sigma \sigma \int w_\sigma^c(r) \rho^c(r) \, dr = N_c \),

(2)

where \( w_\sigma \) acts as a weight function that defines the con-

strained property. The Kohn–Sham total energy is minimized

under the constraint from equation (2), by making the fol-

lowing functional stationary,

\[ W[\rho, V_c] = E[\rho] + V_c \left( \Sigma \sigma \int w_\sigma^c(r) \rho^c(r) \, dr - N_c \right) \]  

(3)

Here \( V_c \) is a Lagrange multiplier corresponding to the

constraint. Therefore, in the effective Hamiltonian of the CDFT

formalism, there is an additional potential \( V_c w_\sigma^c(r) \) coming

from the constraint. Since the GGA + A potential (equation (1)) has the same form as the constraint potential in the

CDFT approach, GGA + A method has the same effect as con-

straining the number of electrons around the iron atom.

2.1. Choice of A f(r) term

Now we discuss our choice of the correction term \( A f(r) \)

appearing in equation (1).

Following previous work on the FeSe monolayer [22] we

first choose \( f(r) = e^{-1.9r^2} \) in atomic units (Bohr radius) with the extent comparable with the size of the iron atom d-orbital.

Second, we tune \( A \) from 0 up to \( A_c \) until one of the properties of Ba_{0.6}K_{0.4}Fe_2As_2 agrees better with the experimental data.

We choose to tune the occupied bandwidth of the \( M \)-point electron pocket since it is severely overestimated in GGA (it is 130 meV in GGA while ~0–10 meV in the experiment [28, 29]). We find that using \( A_c = 1.3 \) R\( \)y has the desired effect of tuning the \( M \)-point bandwidth to about 4 meV.

Just as in [22] we find that the choice of \( f(r) \) is not very

important for physical properties as long as it is localized

on the iron atom and \( A \) is tuned for each choice of \( f(r) \). For example, using \( Af(r) = 2.2 e^{-1.7r^2} \) or \( Af(r) = 5.5 e^{-3.5r^2} \) results in nearly indistinguishable band structure of Ba_{0.6}K_{0.4}Fe_2As_2.

Using \( A = A_c \) improves not only the occupied bandwidth of the \( M \)-point electron pocket but other properties of Ba_{0.6}K_{0.4}Fe_2As_2 as well. For example, structural parameters relevant for superconductivity (arsenic height and iron-arsenic-ion angle) [30–33] are both moved in the direction towards experimental value. However, numerical values of these structural parameters match experimental values for \( A \) in between 0 and \( A_c \) and are thus overcorrected at \( A = A_c \). For example, going from GGA to GGA + A the arsenic height is increased from 1.30 Å to 1.44 Å while the iron-arsenic-ion angle is decreased from 112.5° to 105.9°. Another improvement is that the antiferromagnetic ground state is suppressed in GGA + A. See table 1 for more details. We confirmed that the modifications of structural and magnetic properties are insensitive to the choice of \( f(r) \).

Finally, using \( A = A_c \) the calculated heat capacity of Ba_{0.6}K_{0.4}Fe_2As_2 is more than three times larger as compared to the GGA value, and in good agreement with the experimental. We discuss heat capacity in more detail in section 4.

2. Methods

Our calculations are based on norm-conserving pseudopo-

tentials and the Perdew–Burke–Ernzerhof [25] functional as implemented in the SIESTA code [26]. Electronic wave-

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of Ba_{0.6}K_{0.4}Fe_2As_2 is near a magnetic phase transition, we also computed the heat capacity in the striped antiferromagnetic ground state, present in the parent compound. Just as in the nonmagnetic calculation, we again find an increased \( n^e \) (from 6 to 12 m\( \)mol\(^{-1} \) \( \text{K}^{-2} \)) when +A term is added. However, unlike in the nonmagnetic calculation, the increased \( n^e \) originates mostly from increase in the electron–phonon coefficient \( \lambda \).

The focus of this work is on the heat capacity and the elec-

tronic structure of Ba_{0.6}K_{0.4}Fe_2As_2. The microscopic origin for the success of the semi-empirical approach (+A) is left for future studies. We only note here that the success of this approach is not limited to Ba_{0.6}K_{0.4}Fe_2As_2, but that it also improves [22] calculated properties for a range of transition-metal compounds (KCuF_3, LaNiO_3, (La,Sr)_2CuO_4, SrTiO_3, and FeSe monolayer), and that this approach is similar in spirit to earlier empirical methods [23, 24]. For all the com-

pounds, the +A term modifies the \( d \)-levels of transition metals reducing the electron density near the transition metal sites. This implies that LDA/GGA might overestimate \( d \)-level filling in a transition-metal compounds.

\[ V_{\text{GGA}}(r) + A \sum_i f(|r - r_i|). \]  

(1)

Here \( f(r) \) is a positive dimensionless function peaked at the

nucleus of the iron atoms (\( r \)) and the extent of \( f(r) \) is compar-

rable with the size of \( d \) orbitals in the iron atoms. We discuss the choice of \( A \) and \( f(r) \) in section 2.1.

The GGA + A approach can be understood as a variant of the constrained DFT (CDFT) formalism [27]. The CDFT approach adds a general constraint to the density,
3. Electronic structure

Now we discuss the electronic structure of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ in GGA and GGA + A. In all of our calculations we perform a full structural relaxation for both forces on atoms and stresses on the cell. We used double zeta polarized basis and a charge density cutoff of 1200 Ry. The atomic positions are relaxed so that the force on each atom is less than 0.04 eV Å$^{-1}$. The relaxed structural parameters are given in table 1. We sample the Brillouin zone on a uniform 32 $\times$ 32 $\times$ 32 k-point mesh.

Figure 1 compares the electron density in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ in GGA and GGA + A. From panel b of the figure it is clear that including the +A term transfers some of the electronic density from the iron atom to the outer region. The maximal relative change in the electronic density is about 7 % and it occurs on a charge density peak near the iron atom.

Figure 2 compares the band structure and the Fermi surface in GGA and GGA + A. We compare these results to the experiment in section 3.1.

In the GGA case, as in a previous calculation, [9] there are three hole pockets at the zone center (Γ), and two electron pockets at the zone corner (M). However, the band structures and the Fermi surfaces in GGA + A are both quantitatively and qualitatively different in several respects. First, the occupied bandwidth of the M-point $d_{yz}$ and $d_{zx}$ electron pockets in GGA + A is 4 meV (figure 2(a)), while it is 130 meV in GGA. In addition, the effective mass of these pockets is increased by a factor of 3–4 in GGA + A and the shape of the Fermi pocket in GGA + A is more elongated towards the Γ and Z points.

Second, the area of the hole pockets at Γ and Z is changed in GGA + A. Specifically, in GGA + A the size of the $d_{xy}$ hole pockets at Γ and Z is increased by a factor of 4, so that it is larger than remaining two pockets. In addition, the $d_z$ hole pocket is not present at Z in GGA + A so that now there are only two hole pockets at the Z point (versus three hole pockets at Z in GGA). Therefore, a three-dimensional ellipsoidal Fermi surface exists at Γ in GGA + A.

3.1. Comparison with ARPES

Now we compare modifications in the band structure due to +A term with the currently available experimental data on Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ band structure.

First, in the angle-resolved photoemission spectroscopy (ARPES) experiment, three hole pockets are observed at the zone center and the largest pocket is shown to originate from $d_{xy}$ orbital [28] as in our GGA + A calculation. Second, large elongation of the M point pocket towards the Γ and Z points, we find using +A was experimentally observed in angle-resolved photoemission spectroscopy from [34]. Third, the presence of three-dimensional FS in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ was suggested from $c$-axis polarized optical measurements [35]. The optical experiment found that the $c$-axis data only exhibit a small difference across T$_c$. This indicates the existence of three-dimensional FS with a dispersive band along the $c$ axis.

4. Specific heat

In this section we discuss the calculated specific heat of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. The specific heat coefficient $\gamma_0$ is defined as,

$$\gamma_0 = (1 + \lambda)\gamma_0^*$$

Here $\gamma_0^*$ is the Sommerfeld coefficient proportional to DOS at the Fermi energy, and $\lambda$ is the electron–phonon coupling coefficient.

First we discuss the density of states in GGA and GGA + A. In GGA the DOS at the Fermi energy of nonmagnetic Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ is 4.4 states eV$^{-1}$ f.u.$^{-1}$ (the energy dependence of DOS is shown in figure 3). Similar value (3.1–5.5 states eV$^{-1}$ f.u.$^{-1}$) for DOS was found in previous calculations [9, 10].

|        | As height (Å) | Fe–As–Fe (°) | a (Å) | c (Å) | $\mu_0$ ($\mu_B$) | $\Delta E$ (eV) |
|--------|---------------|--------------|-------|-------|------------------|-----------------|
| GGA + A| 1.44          | 105.9        | 3.82  | 13.89 | 2.26             | −0.19           |
| GGA    | 1.30          | 112.5        | 3.89  | 13.26 | 2.91             | −0.33           |
| Experiment | 1.37          | 109.9        | 3.91  | 13.21 |                  |                  |

Table 1. A comparison of the arsenic height, iron-arsenic-iron angle, lattice constants ($a$ and $c$), magnetic moment ($\mu_0$) on iron atom, and the energy difference ($\Delta E$) per one iron atom between antiferromagnetic stripe and nonmagnetic ground state in GGA, GGA + A, and from experiment [21] in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. 

Figure 1. (a) The electron density of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ in the nonmagnetic state on a line between the nearest-neighbor (left) and next-nearest-neighbor (right) iron atoms within GGA (blue) and GGA + A (red). Difference between GGA and GGA + A is shown in panel (b). Densities of both semi-core (3s, 3p) and valence (3d, 4s) states are included in our pseudopotential calculation.
so the increase in $\lambda$ we find that within GGA + A method specific heat coefficient $\gamma_v$ equals 38 mJ mol$^{-1}$ K$^{-2}$, which is much closer to the experimentally measured values (40–50 mJ mol$^{-1}$ K$^{-2}$) than the GGA result (12 mJ mol$^{-1}$ K$^{-2}$).

4.1. Antiferromagnetic ground states

So far we discussed the specific heat in the nonmagnetic ground state of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, now we consider two antiferromagnetic ground states: striped and checkerboard. The striped case is especially important, since this is the experimentally determined ground state of the parent compound BaFe$_2$As$_2$. We study the alternative ground state (checkerboard) for a comparison with the striped phase.

The (single-)stripe order consists of ferromagnetically arranged chains of iron atoms, with antiferromagnetic alignment between neighboring chains. On the other hand, in the checkerboard antiferromagnetic order magnetic moments on all neighboring iron atoms in point in opposite directions. For easier comparison with the nonmagnetic calculations, in our magnetic GGA + A calculations we use the same value of $\lambda$, and the same function $f(r)$.

In the striped state, the peak in DOS occurring 50 meV below the Fermi level in GGA is shifted to 230 meV below the Fermi level when +A is included. However, there is no significant change in the value of DOS at the $E_F$ (figures 3(c) and (f)). However, in the checkerboard state within GGA + A we obtain the DOS at $E_F$ equal to 1.7 states eV$^{-1}$ f.u.$^{-1}$, which is about one sixth of the GGA result (see figures 3(b) and (e)). This suppression in the checkerboard state is due to the occurrence of a Jahn–Teller distortion in GGA + A, which is lowering the crystal symmetry from tetragonal to orthorhombic.

Even though within GGA + A DOS at $E_F$ is relatively small in the striped state (2.8 states eV$^{-1}$ f.u.$^{-1}$) the electron–phonon coupling is significantly larger than in the nonmagnetic case. We obtained $\lambda = 0.90$ (see table 2) in striped state which is ~60 % larger than in GGA. As we said earlier, DOS in striped state is nearly the same in GGA and GGA + A. Therefore, strong enhancement of $\lambda$ in GGA + A must originate from other sources, and not simply from increased DOS. However, the origin of this enhancement is not the focus of this paper, and it will be reported elsewhere.

5. Conclusion

Increasing the potential on iron atoms (making them slightly more repulsive for electrons) improves the relevant structural (such as arsenic height and iron-arsenic-iron angle), magnetic, and electronic properties of Ba$_{0.8}$K$_{0.2}$Fe$_2$As$_2$, as calculated within DFT. The main result of this paper is that with a corrected potential (+A) on iron atom, the heat capacity of Ba$_{0.8}$K$_{0.2}$Fe$_2$As$_2$ is increased more than threefold, in good agreement with experimental data. Applying the same correction to the magnetic states, we find that electron–phonon coupling is strongly enhanced. This observation might be crucial.
in understanding the superconducting properties of iron-based superconductors.

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References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Stewart G 2011 Rev. Mod. Phys. 83 1589
[3] Oh H, Moon J, Shin D, Moon C-Y and Choi H J 2011 Prog. Supercond. 13 65 (arXiv: 1201.0237)
[4] Andersen O K and Boeri L 2011 Ann. Phys. 523 8
[5] Dai P, Hu J and Dagotto E 2012 Nat. Phys. 8 709
[6] Lu D H et al 2008 Nature 455 81
[7] de la Cruz C et al 2008 Nature 453 899
[8] Gretarsson H et al 2011 Phys. Rev. B 84 100509
[9] Singh D J 2008 Phys. Rev. B 78 094511
[10] Shein I R and Ivanovskii A L 2008 JETP Lett. 88 107
[11] Hashimoto K et al 2010 Phys. Rev. B 82 014526
[12] Popovich P, Boris A V, Dolgov O V, Golubov A A, Sun D L, Lin C T, Kremer R K and Keimer B 2010 Phys. Rev. Lett. 105 027003
[13] Kant Ch, Deisenhofer J, Günther A, Schrettle F, Loidl A, Rotter M and Johrendt D 2010 Phys. Rev. B 81 014529
[14] Storey J G, Loram J W, Cooper J R, Bukowski Z and Karpiński J 2013 Phys. Rev. B 88 144502
[15] Rotundi C R, Forrest T R, Phillips N E and Birgeneau R J 2014 (arXiv: 1411.0116v2)
[16] Kim J S, Faeth B D and Stewart G R 2012 Phys. Rev. B 86 054509
[17] Yin Z P, Haule K and Kotliar G 2011 Nat. Mater. 10 932
[18] Tomczak J M, van Schilfgaarde M and Kotliar G 2012 Phys. Rev. Lett. 109 237010
[19] Hansmann P, Arita R, Toschi A, Sakai S, Sangiovanni G and Held K 2010 Phys. Rev. Lett. 104 197002
[20] Wang G-T, Qian Y, Xu G, Dai X and Fang Z 2010 Phys. Rev. Lett. 104 047002
[21] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[22] Coh S, Cohen M L and Louie S G 2015 New J. Phys. 17 073027
[23] Cohen M L and Heine V 1970 Solid State Phys. 24 37
[24] Wang L-W and Zunger A 1995 Phys. Rev. B 51 17398
[25] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[26] Sánchez-Portal D, Ordejón P, Artacho E and Soler J M 1997 Int. J. Quantum Chem. 65 453
[27] Dederichs P H, Blügel S, Zeller R and Akai H 1984 Phys. Rev. Lett. 53 2512
[28] Evtushinsky D V et al 2014 Phys. Rev. B 89 064514
[29] Neupane M et al 2011 Phys. Rev. B 83 094522
[30] Zhao J et al 2008 Nat. Mater. 7 953
[31] Lee C-H, Iyo A, Eiisaki H, Kito H, Fernandez-Diaz M T, Ito T, Kihou K, Matsuhata H, Braden M and Yamada K 2008 J. Phys. Soc. Japan 77 083704
[32] Kuroki K, Usui H, Onari S, Arita R and Aoki H 2009 Phys. Rev. B 79 224511
[33] Mizuguchi Y, Hara Y, Deguchi K, Tsuda S, Yamaguchi T, Takeda K, Kotegawa H, Tou H and Takano Y 2010 Supercond. Sci. Technol. 23 054013
[34] Malaeb W et al 2012 Phys. Rev. B 86 165117
[35] Cheng B et al 2011 Phys. Rev. B 83 144522
[36] Boeri L, Calandra M, Mazin I I, Dolgov O V and Mauri F 2010 Phys. Rev. B 82 020506
[37] Giustino F, Cohen M L and Louie S G 2007 Phys. Rev. B 76 165108
[38] Giannozzi P et al 2009 J. Phys.: Condens. Matter 21 395502