CaFe$_2$As$_2$: a springboard to investigating Fe-pnictide superconductivity

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We present detailed electronic structure calculations for CaFe$_2$As$_2$. We investigate in particular the ‘collapsed’ tetragonal and orthorhombic regions of the temperature-pressure phase diagram and find properties that distinguish CaFe$_2$As$_2$ from other Fe-pnictide compounds. In contrast to the tetragonal phase of other Fe-pnictides the electronic structure in the ‘collapsed’ tetragonal phase of CaFe$_2$As$_2$ is found to be strongly 3D. We discuss the influence of these properties on the formation of superconductivity and in particular we find evidence that both magnetic and lattice interactions may be important to the formation of superconductivity. We also find that the Local Spin Density Approximation is able to accurately predict the ordering moment in the low temperature orthorhombic phase.

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I. INTRODUCTION

The recent discovery of superconductivity in the doped iron pnictide compounds and subsequent improvement in $T_c$ has generated significant interest in uncovering the mechanisms responsible for this novel superconductivity. In the 1,2,2 class of Fe-pnictide compounds including (Ca,Ba,Sr,Eu)Fe$_2$As$_2$, superconductivity has been shown under pressure tuning for (Ba,Sr,Eu)Fe$_2$As$_2$ with transition temperatures as high as 32K. There have been several reports of the presence of superconductivity in the phase diagram of CaFe$_2$As$_2$ as it is pressure tuned from the orthorhombic phase into the collapsed tetragonal phase at low temperatures. The determination of the presence of superconductivity has recently been shown to be more complex by measurements made using a Helium pressure medium. It has also been suggested that superconductivity results from the presence of a mixed phase intermediate between the collapsed tetragonal and orthorhombic phases. Therefore, CaFe$_2$As$_2$ may be a material that is near the border for the formation of superconductivity and as a result its electronic and magnetic structure have the potential to provide critical information regarding the superconductivity of these compounds.

The Temperature-Pressure phase diagram for CaFe$_2$As$_2$ is unusual amongst Fe-pnictide compounds and is shown schematically in Fig. 1. The presence of the ‘collapsed’ tetragonal phase at low temperatures with the application of modest pressures distinguishes this compound from other members of the 1,2,2 family. The low temperature orthorhombic antiferromagnetic phase that occurs at low pressures is common to the 1,2,2 class and is thought to result from the formation of spin density wave (SDW) itinerant magnetism. At high temperatures CaFe$_2$As$_2$ exists in a tetragonal structure and is non-magnetic.

In the calculations reported here we seek to consider the electronic structure of CaFe$_2$As$_2$ throughout the three key parts of the phase diagram. We investigate the mechanisms for the novel phase transitions and superconductivity of this compound. We also present predictions for future quantum oscillation studies that may experimentally verify the electronic structure.

II. STRUCTURE AND METHOD

The electronic structures were determined by the Full-Potential LAPW method implemented in WIEN2K. In all cases $R_{\text{MT}}^{\text{min}} K_{\text{max}} = 8$ was used. We have used the Local Spin Density Approximation (LSDA) for the correlation functional except where otherwise stated. We
have used the experimental lattice parameters reported for each part of the phase diagram. Further details will be discussed as is relevant to each calculation. Fermi surfaces were visualized with XCrysDen\textsuperscript{11}.

In the following sections we consider each part of the phase diagram in turn. First, we present the results for the ambient pressure tetragonal phase. These results place CaFe$_2$As$_2$ in a background from which it may be referenced to other Fe-pnictide systems. We then consider the collapsed tetragonal phase at $P=0.63$ GPa and contrast this electronic structure with the high temperature tetragonal phase. Finally, we consider the antiferromagnetic orthorhombic state and investigate the prediction of the magnetic moment in this phase. With each of these elements of the phase diagram in place, we are then in a position to qualitatively discuss their interplay in determining the magnetic order and possible mechanisms for superconductivity in the system.

### III. THE HIGH TEMPERATURE TETRAGONAL PHASE

The crystal structure of the high temperature tetragonal phase of CaFe$_2$As$_2$ is in the $I4/mmm$ tetragonal space group with lattice parameters $a = 3.912\AA$ and $b = 11.667\AA$\textsuperscript{12}. Calculations of the electronic structure of CaFe$_2$As$_2$ in this phase have previously been presented for comparison with X-ray photoelectron spectra\textsuperscript{13}. Here, we present details, in particular the form of the Fermi surface, that are important as a point of comparison between CaFe$_2$As$_2$ and other Fe-pnictide systems as well as for comparison with CaFe$_2$As$_2$ in its collapsed tetragonal structure. We have calculated the electronic structure using a $31 \times 31 \times 31$ k-point grid. The resulting Fermi surface is shown in Fig. 2(a). During the calculation we relaxed the lattice position of the As atom, $z_{\text{As}}$, from its experimental position of $z_{\text{As}} = 0.3665$ to $z_{\text{As}} = 0.353(0)$ under the LSDA. The Fermi surface obtained is similar to that found in previous calculations for (Ba,Sr)Fe$_2$As$_2$\textsuperscript{28,14}. It is intriguing to note the similarity between this Fermi surface and that of MgB$_2$ which also possesses two concentric warped cylinders at the zone corners as well as a flat 3D pocket in a similar position to the flared section of the dumbbell surface. The primary difference is the lack of a further 3D pocket about $\Gamma$ which occurs in MgB$_2$, but not in CaFe$_2$As$_2$. In MgB$_2$ it is the two outer cylinders which couple to the lattice to form superconductivity\textsuperscript{15}.

### IV. THE ‘COLLAPSED’ TETRAGONAL PHASE

In the collapsed tetragonal phase the crystal maintains the $I4/mmm$ symmetry of the high temperature tetragonal phase, but undergoes a dramatic reduction in the $c$-axis lattice parameter of approximately 6% while simultaneously the in-plane dimension increases by approximately 2%. The unit cell is effectively squashed. At $P=0.63$ GPa the lattice parameters are $a = 3.9780(1)\AA$ and $b = 10.6073(7)\AA$\textsuperscript{12}. We have calculated the electronic structure for this phase using a $39 \times 39 \times 39$ k-point grid. The resulting Fermi surface is shown in Fig. 2(b). In Table I we also present the quantum oscillation frequencies and associated band masses for $B$ parallel to $c$-axis. Experimental comparison with these values has the ability to verify the electronic structure obtained in our calculations and the experimental mass enhancement can indicate the strength of correlations in the system.

A critical observation of this investigation is the dra-
superconductivity as reported by Lee et al. found here for CaFe$_2$. The conventional magnetic unit cell is the same as that of the crystal structure, but the symmetry is reduced due to the magnetic order. We have evaluated the electronic and magnetic structure for the experimentally determined magnetic order using both the Generalized Gradient Approximation of Perdew–Burke–Ernzerhof (GGA) and the LSDA correlation functionals. For all calculations in this antiferromagnetic phase we have used 23 × 23 × 10 k-points in the Brillouin zone.

First, we applied the GGA to the AFM structure. Relaxing the As position within the AFM calculation results in, $z_{\text{As}} = 0.3659$, which matches the experimental value closely, but the predicted moment of $1.84 \mu_B$/Fe overestimates the experimental value by a factor of more than 2. Overestimates of this scale for the magnetic moment in Fe-pnictides while applying the GGA have been widely reported.

Secondly, we applied the LSDA to the antiferromagnetic structure while relaxing the GGA to the AFM structure. The forces and magnetic moments were determined under the Local Spin Density Approximation. The main figure shows the region about $F_Z = 0$ where the As position is relaxed into its equilibrium structure. The inset is a view of this plot over a wider scale of $z_{\text{As}}$. The solid horizontal line indicates where the force $F_Z = 0$. The dashed lines in the main figure are to illustrate the value of the moment in $\mu_B$/Fe that occurs when $F_Z = 0$.

V. THE ORTHORHOMBIC PHASE

In the low temperature and pressure region of its phase diagram CaFe$_2$As$_2$ is antiferromagnetic (AFM) in the $Fmmm$ orthorhombic structure. The lattice parameters are $a=5.506(2)$Å, $b=5.450(2)$Å, and $c=11.664(6)$Å and $z_{\text{As}} = 0.36642(5)$. The magnetic moment is $0.80(5) \mu_B$/Fe. The conventional magnetic structure while relaxing the value $z_{\text{As}}$. We find that the relaxation of the As coordinate is significant, from $z_{\text{As}} = 0.3664$ experimentally to $z_{\text{As}} = 0.3567$. In Fig. 3 we have plotted both the force on the As atom, $F_z$, and the magnetic moment of Fe as a function of its relaxation to the plane of the Fe atoms. Very importantly, this figure shows that the moment approaches $0.81 \pm 0.02 \mu_B$/Fe as $F_z$ tends towards zero i.e. when the As is in its crystallographic equilibrium position. This is in close agreement with the experimental reported moment of $0.80(5) \mu_B$/Fe. To confirm this result we have applied the same method to SrFe$_2$As$_2$ and BaFe$_2$As$_2$.

![FIG. 3: (Color online) Plot of the force on the As atom(black) and the magnetic moment of Fe(red) versus the lattice parameter $z_{\text{As}}$ in CaFe$_2$As$_2$. The forces and magnetic moments were determined under the Local Spin Density Approximation. The main figure shows the region about $F_Z = 0$ where the As position is relaxed into its equilibrium structure. The inset is a view of this plot over a wider scale of $z_{\text{As}}$. The solid horizontal line indicates where the force $F_Z = 0$. The dashed lines in the main figure are to illustrate the value of the moment in $\mu_B$/Fe that occurs when $F_Z = 0$.](image-url)
TABLE II: Comparison between the magnetic moment of 1,2,2 compounds predicted by the LSDA when the As position is relaxed in the antiferromagnetic phase and the experimental value\textsuperscript{15,20,21,22,23,24}.

| Compound     | LSDA $\mu (\mu_B)/Fe^a$ | Experimental $\mu (\mu_B)/Fe$ |
|--------------|--------------------------|-----------------------------|
| CaFe$_2$As$_2$| 0.81$\pm$0.02 0.3567    | 0.80(5) 0.36612(5)           |
| SrFe$_2$As$_2$| 0.97$\pm$0.03 0.3507    | 0.94(4) 0.3612(3)            |
| BaFe$_2$As$_2$| 0.86$\pm$0.02 0.3444    | 0.87(3) 0.35406(7)           |

\textsuperscript{a}The errors given are calculated from the convergence of the force on the As atom.

\textsuperscript{b}More recent measurements\textsuperscript{23} have found $\mu = 1.01 \mu_B/Fe$.

VI. SUMMARY AND CONCLUSIONS

The phase diagram of Fig. 1 illustrates that the CaFe$_2$As$_2$ Fermi surface changes dramatically through magnetic and structural phase transitions. This is suggestive that both magnetic and lattice interactions should be considered in the formulation of any model of superconductivity in this compound.

The greater three dimensionality of the collapsed phase Fermi surface suggest that pairing due to magnetic interactions may be weaker and this may explain the lower superconducting $T_c$, or absence of superconductivity, in CaFe$_2$As$_2$ when compared to (Ba,Sr,Eu)Fe$_2$As$_2$ under pressure.

Predictions for quantum oscillation experiments on the collapsed tetragonal phase have been given. We have also demonstrated that the magnetic moment in the AFM orthorhombic phase may be accurately calculated under the LSDA if the As coordinate is relaxed within an AFM calculation.
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