1-22-2009

Strong Coupling of the Fe-Spin State and the As-As Hybridization in Iron-Pnictide Superconductors from First-Principle Calculations

Taner Yildirim

National Institute of Standards and Technology; University of Pennsylvania, taner@seas.upenn.edu

Follow this and additional works at: http://repository.upenn.edu/mse_papers

Part of the Materials Science and Engineering Commons

Recommended Citation


Suggested Citation:


© 2009 The American Physical Society

http://dx.doi.org/10.1103/PhysRevLett.102.037003

This paper is posted at ScholarlyCommons. http://repository.upenn.edu/mse_papers/197

For more information, please contact repository@pobox.upenn.edu.
Strong Coupling of the Fe-Spin State and the As-As Hybridization in Iron-Pnictide Superconductors from First-Principle Calculations

Abstract
From first-principles calculations, we unravel surprisingly strong interactions between arsenic ions in iron pnictides, the strength of which is controlled by the Fe-spin state. Reducing the Fe-magnetic moment weakens the Fe-As bonding, and in turn, increases As-As interactions, causing giant reduction in the c axis. For the CaFe$_2$As$_2$ system, this reduction is as large as 1.4 Å. Since the large c reduction has been recently observed only under high pressure, our results suggest that the iron magnetic moment should be present in Fe-pnictides at all times at ambient pressure. Finally, the conventional electron-phonon coupling in the collapsed phase of CaFe2As2 gives a maximum $T_c$ of 0.6 K and cannot explain the ~12 K superconductivity observed in some experiments. Implications of these findings on the mechanism of superconductivity in iron pnictides are discussed.

Disciplines
Engineering | Materials Science and Engineering

Comments
Suggested Citation:

© 2009 The American Physical Society
http://dx.doi.org/10.1103/PhysRevLett.102.037003

This journal article is available at ScholarlyCommons: http://repository.upenn.edu/mse_papers/197
Strong Coupling of the Fe-Spin State and the As-As Hybridization in Iron-Pnictide Superconductors from First-Principle Calculations

T. Yildirim

1 Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA
2 NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

(Received 4 August 2008; published 22 January 2009)

From first-principles calculations, we unravel surprisingly strong interactions between arsenic ions in iron pnictides, the strength of which is controlled by the Fe-spin state. Reducing the Fe-magnetic moment weakens the Fe-As bonding, and in turn, increases As-As interactions, causing giant reduction in the c axis. For the CaFe$_2$As$_2$ system, this reduction is as large as 1.4 Å. Since the large c reduction has been recently observed only under high pressure, our results suggest that the iron magnetic moment should be present in Fe-pnictides at all times at ambient pressure. Finally, the conventional electron-phonon coupling in the collapsed phase of CaFe$_2$As$_2$ gives a maximum $T_c$ of 0.6 K and cannot explain the ~12 K superconductivity observed in some experiments. Implications of these findings on the mechanism of superconductivity in iron pnictides are discussed.

PACS numbers: 74.25.Jb, 67.30.hj, 74.25.Kc, 75.30.Fv

The recent discovery of superconductivity at $T_c$’s up to 55 K in iron pnictide systems [1–5] has sparked enormous interest in this class of materials. So far, two types of materials have been discovered. The first one is the rare-earth pnictide oxide layered systems, REOFeAs, which is denoted as “1111” [2–6]. The second class is the so-called “122” systems with the chemical formula MFe$_2$As$_2$ ($M$ = Ca, Sr, etc.) [6–10]. The 122 systems are simpler in terms of their crystal structure due to absence of REO layers. The crystal structure of CaFe$_2$As$_2$ is shown in the inset to Fig. 1.

The pressure-induced superconductivity in these systems is particularly interesting [11–13] because it provides a new avenue for investigation of the mechanism of the high-$T_c$ superconductivity. Very recently, a high pressure neutron scattering study has reported that the CaFe$_2$As$_2$ system undergoes a surprising transition to a “collapsed-tetragonal phase” (cT-phase) under applied pressure in which the c parameter is reduced from 11.7 to 10.6 Å [1]. Motivated by this interesting report, in this Letter, we present a detailed first-principles study of Fe-pnictides with many surprising results.

We discovered that the optimized c-lattice parameter of CaFe$_2$As$_2$ varies by about 1.5 Å depending on the magnetic configuration considered. Such a giant coupling of spin-state of an ion with its lattice is almost unheard of and deserves detailed investigation. Reducing Fe-moment by about 1/2 gives lattice parameters that are quite close to high pressure data [1]. Hence, the collapsed-phase does not necessarily mean the total loss of Fe magnetism as suggested in Ref. [1] but could be due to large reduction of the Fe-moment. We explain this strange behavior by noting that in iron pnictide systems there are significant As-As hybridization (both intra and interplane arsenic ions) whose strength is controlled by the Fe-spin state. Reducing the Fe-spin state reduces the Fe-As bonding, which in turn, increases the As-As bonding and causes the observed huge reduction in the lattice parameters. This effect is maximized in the case of Ca122 system due to close proximity of two arsenic ions in adjacent Fe-planes (see Fig. 1). We argue that since there is no observation of large c axis reduction during the normal to superconducting phase transition in iron pnictides, the iron magnetic moment should be present at all times at ambient pressure. Otherwise, one should have seen a large reduction in the c axis as recently reported from high-

![FIG. 1 (color online). Total energy as the Ca122 tetragonal phase goes to collapsed-tetragonal phase without any energy barrier during nonspin polarized structural optimization. The insets show the initial (T-Phase) and final (cT-phase) Ca122 structures with relevant bond-distances (in Å) and angles (in degrees).](image-url)
pressure neutron scattering experiments [1]. Hence, it
seems that the Fe-magnetic moment in its paramagnetic
state (i.e., no long-range order but nonzero Fe-site mo-
moment) is either required for the superconductivity or at least
is not detrimental to the superconductivity.

The first-principles calculations were performed within
the plane-wave implementation of the Perdew-Burke-
Ernzerhof (PBE) generalized gradient approximation
(GGA) to density functional theory as implemented in
the PWSCE package [14]. The details of the parameters
used in the calculations can be found in Refs. [15,16]. In
order to get a general understanding of the iron pnictides,
in this study, we consider one example of each class of
pnictides: namely CaFe$_2$As$_2$, for the 122 system with
the smallest Ca-ion available and the BaFe$_2$As$_2$ with the
largest metal Ba. For the 1111 system, we consider LaOFeAs.
Since in our calculations, we consider two Na and two Ca are
ordered. For each given system, we have performed full
structural optimization including the lattice parameters and
the atomic positions. We consider our optimization is
converged when the maximum force on each atom is less
than 0.005 eV/Å and the pressure is less than 0.1 kbar. We
have performed the full structural optimization for non-
magnetic (NM), i.e., “nonspin polarized,” checkerboard
antiferromagnetic (AF1) and stripe (AF2) spin configurations.
Our results are summarized in Table I. As expected,
the ground state for all four systems is the stripe AF2 phase
and the optimized parameters are in good agreement with
the experimental data at ambient conditions.

The most striking and surprising finding listed in Table I
is the giant dependence of the optimized c-lattice parameter
on the spin configuration considered. For the case of
CaFe$_2$As$_2$, we note that AF1 configuration is the next
stable state (after the AF2), but the c-value is significantly
reduced: 11.63 Å versus 10.60 Å for AF2 and AF1 spin
configurations, respectively. The difference is even larger,
when the Fe-magnetism is ignored (i.e., nonspin polarized
calculations). The optimized c-value for NM-state is
10.39 Å, which is 1.34 Å shorter than the experimental
value at ambient pressure. We note that the optimized
lattice parameters, $a = 5.65$ Å and $c = 10.6$ Å for the
AF1 phase, are in reasonable agreement with the neutron
data ($a = 5.8$ Å and $c = 10.6$ Å) [1]. Hence, based on
this result, it is premature to conclude that the observed exper-
imental cT-phase is due to the complete disappearance of
the Fe-magnetism but as we shall see below, it is closely
related to the magnitude of the Fe-spin.

In Fig. 1, we show that the T-phase directly collapses
into the cT-phase without any energy barrier if the
Fe-magnetic moment is ignored. During the c axis col-
lapse, there is significant and comparable decrease in the
height of the Fe-As and As-Ca-As planes, indicating that
the whole lattice almost uniformly shrinks. Since there is
no energy barrier between the T-phase and the cT-phase,
as soon as we lose the Fe-magnetic moment for some reason,
we should see the expected c-lattice reduction. Since this
does not seem to happen in the superconducting samples,
it is tempting to conclude that we have the Fe-moment
present in the superconducting phase. This is a quite im-
portant result by itself to understand the mechanism of the
high $T_c$ superconductivity observed in iron pnictides.

In order to get a better understanding of the cT-phase,
we have performed electronic band structure calculations and
studied the projected atomic density of states. Our results
for the T-phase agree well with previous calculations [20–
23]. Figure 2 shows that despite to the 1.4 Å c reduction,
the band structure and the PDOS of both phases are sur-
prisingly similar. The main difference between the two
phases is that most of the bands are shifted in lower energy
in the cT-phase which is expected since the cT-phase has
the lower energy. This downward shift of the bands is most
obvious in the band structure plot along the Γ $-$ M direc-
tion as shown in Fig. 2. In the T-phase, there were several
states above the Fermi level which crosses the $E_F$ along the
M $-$ Γ direction. This results in a larger density of states at
the Fermi level. However, for the case of cT-phase, we note
that most of the bands just above $E_F$ in the T-phase are now
just below the $E_F$ in the cT-phase, and there is only one
band which crosses the $E_F$ along the Γ $-$ M direction. This
explains why $N(E_F)$ is reduced in the cT-phase. The other
and probably the most important difference is the change in

<p>| TABLE I. Various optimized structural parameters for NM, AF2, and AF1 spin configurations, respectively. The experimental data are taken from Refs. [8,17–19]. |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d_{FeAs}$</th>
<th>$M_Fe$</th>
<th>$E$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaFe$_2$As$_2$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NM</td>
<td>5.63</td>
<td>5.63</td>
<td>10.39</td>
<td>0.36251</td>
<td>2.309</td>
</tr>
<tr>
<td>AF1</td>
<td>5.65</td>
<td>5.65</td>
<td>10.60</td>
<td>0.36440</td>
<td>2.338</td>
</tr>
<tr>
<td>AF2</td>
<td>5.61</td>
<td>5.48</td>
<td>11.61</td>
<td>0.36695</td>
<td>2.367</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.68</td>
<td>5.68</td>
<td>11.73</td>
<td>0.3665</td>
<td>2.370</td>
</tr>
<tr>
<td><strong>BaFe$_2$As$_2$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NM</td>
<td>5.59</td>
<td>5.59</td>
<td>10.52</td>
<td>0.36284</td>
<td>2.31</td>
</tr>
<tr>
<td>AF1$^a$</td>
<td>5.59</td>
<td>5.59</td>
<td>10.52</td>
<td>0.36284</td>
<td>2.31</td>
</tr>
<tr>
<td>AF2</td>
<td>5.43</td>
<td>5.53</td>
<td>12.05</td>
<td>0.36536</td>
<td>2.382</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.42</td>
<td>5.42</td>
<td>11.86</td>
<td>···</td>
<td>···</td>
</tr>
<tr>
<td><strong>LaOFeAs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NM</td>
<td>5.64</td>
<td>5.64</td>
<td>8.59</td>
<td>0.35944</td>
<td>2.332</td>
</tr>
<tr>
<td>AF1</td>
<td>5.69</td>
<td>5.69</td>
<td>8.71</td>
<td>0.35128</td>
<td>2.393</td>
</tr>
<tr>
<td>AF2</td>
<td>5.67</td>
<td>5.73</td>
<td>8.72</td>
<td>0.34860</td>
<td>2.409</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.70</td>
<td>5.70</td>
<td>8.737</td>
<td>0.3479</td>
<td>2.407</td>
</tr>
</tbody>
</table>

$^a$The AF1 configuration goes to NM for Ca$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$. 
Fe-plane. Hence, this overlap of the As-As along the cT-axis makes this system quite isotropic and far from being layered system. According to bond-population analysis, the As-As bond strength increased almost twice in the cT-phase. Because of close proximity of the As ions in adjacent Fe-layers, the observation of the As-As interaction is probably not that surprising. What is surprising is to see that there is almost the same type of hybridization between two arsenic ions on the same Fe-plane as shown in the right panel of Fig. 3.

Since we have shown that the As ion above the Fe-plane has a strong overlap with the As ion below the same iron plane, their interaction is automatically increased as the Fe-As interaction decreases due to decrease in the Fe-moment which changes the chemistry of the Fe ion. Therefore, we have now a mechanism which explains why the As ion z values get shorter with the decreasing Fe-moment. Our mechanism also explains why we see a smaller reduction in the c-axis for the LaOFeAs than the 122 system as listed in Table I. The reduction in the c-axis in the LaOFeAs system is due to the intraplane As-As interaction only since there are no two adjacent FeAs planes to interact to with each other as in the case of Ca122. Our theory also predicts that for larger ions like Ba, we should see less c reduction because the As-As distance between two adjacent planes is now larger due to larger ionic radius of Ba. In Table I, we also show that similar c reduction with Fe-spin occurs in the doped Na0.5Ca0.5Fe2As2 system as well.

In order to convince the reader further that the spin-state of the iron is the key parameter that controls the As-As bonding in these systems, we have performed fixed-spin calculations for CaFe2As2, and the results are shown in Fig. 4. We consider ferro spin configuration to show that the spin-structure is a secondary effect, and the main effect is the on-site Fe-spin state. As we see from Fig. 4, when the Fe-moment is zero, the c axis is the smallest consistent with the strongest As-As interaction (because As-Fe bonding is weak for nonmagnetic Fe). As the Fe moment becomes significant, the Fe-As interaction gets stronger, and, therefore, the As-As distance starts to increase to optimize the Fe-As bonding. Ironically, at the Fe-moment of $\mu_B = 2.2$, we have the ideal tetragonal arrangement of the four As ion around each iron during which the two As-Fe-As angles are equal. At this point, the low- to high-Fe spin transition is obvious during which the a-axis is reduced while c axis is increased significantly.

Since our results suggest that Fe-magnetism is either totally lost or reduced by half in the cT-phase, one wonders if the observed \(~12\) K superconductivity in the vicinity of the collapse cT-phase of CaFe2As2 [13] can be explained by conventional electron-phonon (e-ph) coupling? In order to address this question, we have calculated phonon spectrum and Eliashberg function from linear response theory [14]. We used basically the same method and the equivalent parameters that are used in Ref. [25] for LaOFeAs.
results are summarized in Fig. 5 and very similar to those for LaOFeAs. We obtained a value of electron-phonon coupling $\lambda = 0.23$ and the logarithmically average frequency $\omega_{\text{log}} = 218$ K, which gives $T_c = 0.6$ K using the Allen-Dynes formula with $\mu^* = 0$ (i.e., an upper bound for $T_c$). Hence, the mechanism of superconductivity in the cT-phase of CaFe$_2$As$_2$ is likely unconventional, and probably, it is the same as in the other iron pnictides. This finding together with our results summarized in Table I suggests that in the cT-phase, the Fe-magnetism is not totally lost with pressure, but it is partially reduced. Hence, it seems that there is an optimum strength of Fe-spin state that is required for high-$T_c$ superconductivity.

In conclusion, we have revealed surprisingly strong As-As interactions in iron pnictides. The strength of this interaction is controlled by the Fe-As chemical bonding. Reducing the Fe-moment reduces the Fe-As bonding, which in turn increases the As-As interaction along the $z$-axis, causing arsenic atoms on opposite sides of Fe-square lattice to move towards each other. This explains the high sensitivity of the $z$-atom positions and the large reduction of the $c$ axis with the loss of Fe-magnetic moment. We showed that under external pressure, the high Fe-spin AF2 structure (i.e., stripe phase) should transform to a new structure with low Fe-spin state and significantly reduced $c$ axis. We think that this could be the phase recently observed by high-pressure neutron scattering [1]. This is also consistent with our finding that the pressured induced $\sim 12$ K superconductivity cannot be explained by the conventional e-ph coupling. The Fe-magnetism is still needed for an unconventional mechanism. Since at ambient pressure, we do not observe large $c$ axis drops in the superconducting samples, we conclude that the Fe-magnetic moment should be present at all times in these systems, at least in 122 materials such as CaFe$_2$As$_2$. The giant coupling of the on-site Fe-magnetic moment with the As-As bonding that we have discovered here may provide a mechanism for the superconductivity.

The author acknowledges useful discussions with M. A. Green.

*танer@nist.gov