Giant Coupling of Fe-spin and the As-As Hybridization in Iron-Pnictides

T. Yildirim

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

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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 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 can not explain the $\sim 12$ K superconductivity observed in some experiments. Implications of these findings on the mechanism of superconductivity in iron-pnictides are discussed.

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The recent discovery of superconductivity at $T_c$'s up to 55 K in iron-pnictide systems 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, REOFes which is denoted as [1]1111.[2, 3, 4, 5]. The second class is the so called "122" systems with the chemical formula MFe$_2$As$_2$ (M=Ca,Sr, etc). 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 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 Å to 10.6 Å. 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 nearly close to high-pressure data. Hence, the collapsed-phase does not necessarily mean the total loss of Fe-magnetism as suggested in ref. 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 inter-plane 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 CaFe$_2$As$_2$ 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-pressure neutron scattering experiments. Hence it seems that the Fe-magnetic moment in its paramagnetic state (i.e. no long range order but non-zero Fe-site moment) is either required for the superconductivity or

![Diagram](image_url)

FIG. 1: (color online) Total energy as the Ca122 tetragonal phase goes to collapsed-tetragonal phase without any energy barrier during non-spin 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).
TABLE I: Various optimized structural parameters for NM, AF2, and AF1 spin configurations, respectively. The experimental data are taken from Refs[8, 14, 15, 16]. *The AF1 configuration goes to NM for Ca$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$.

|          | a   | b   | c   | d$_{Fe\_As}$ | M$_{Fe}$ | E (meV) |
|----------|-----|-----|-----|--------------|---------|--------|
| CaFe$_2$As$_2$ NM | 5.63 | 5.63 | 10.39 | 0.36251      | 2.309   | 0      |
| AF1      | 5.65 | 5.65 | 10.60 | 0.36440      | 2.338   | -16    |
| AF2      | 5.61 | 5.48 | 11.61 | 0.36695      | 2.367   | 2.2    |
| Exp.     | 5.68 | 5.68 | 11.73 | 0.3665      | 2.370   | 1.0    |
| Ca$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ NM | 5.59 | 5.59 | 10.52 | 0.36284      | 2.31    | 0      |
| AF1*     | 5.59 | 5.59 | 10.52 | 0.36284      | 2.31    | 0      |
| AF2      | 5.43 | 5.53 | 12.05 | 0.36536      | 2.382   | 2.4    |
| Exp.     | 5.42 | 5.42 | 11.86 |             | 0.0     | -97    |
| BaFe$_2$As$_2$ NM | 5.58 | 5.58 | 12.45 | 0.34790      | 2.319   | 0      |
| AF1      | 5.64 | 5.64 | 12.73 | 0.35231      | 2.382   | 2.1    |
| AF2      | 5.70 | 5.59 | 12.83 | 0.3549      | 2.408   | 2.4    |
| Exp.     | 5.52 | 5.52 | 13.02 | 0.3545      | 2.397   | 1.0    |
| LnOFeAs  NM | 5.64 | 5.64 | 8.59  | 0.35944      | 2.332   | 0      |
| AF1      | 5.69 | 5.69 | 8.71  | 0.35128      | 2.393   | 2.1    |
| AF2      | 5.67 | 5.73 | 8.72  | 0.34880      | 2.409   | 2.4    |
| Exp.     | 5.70 | 5.70 | 8.737 | 0.3479      | 2.407   | 0.35   |

The most striking and surprising finding listed in Table 1 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. non-spin 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 experimental c-T-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 c-T-phase without any energy barrier if the Fe-magnetic moment is ignored. During the c-axis collapse, 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 c-T-phase, as soon as we loose 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 important result by itself to understand the mechanism of the high Tc superconductivity observed in...
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 agrees well with previous calculations [20, 21, 22, 23]. Fig. 2 shows that despite the 1.4 Å c-reduction, the band structure and the PDOS of both phases are surprisingly 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 direction 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 the peak shape of the states near 3 eV below E_F. Visual inspection of these orbitals indicate that there is significant As-As hybridization in this system. The As-As hybridization becomes more significant in the cT-phase. This observation is quite unexpected and as we shall see below it actually explains the mystery why the Fe-spin state has a huge effect on 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 1. The reduction in the c-axis in the LaOFeAs system is due to the intra-plane 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 are now larger due to larger ionic radius of Ba. In Table 1, we also show that similar c-reduction with Fe-spin occurs in the doped Na_{0.5}Ca_{0.5}Fe_{2}As_{2} 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 CaFe_{2}As_{2} 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 non-magnetic 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 ions 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 $\sim 12$ K superconductivity in the vicinity of the collapse cT-phase of CaFe$_2$As$_2$ 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\[17\]. We used basically the same method and the equivalent parameters that are used in Ref\[23\] for LaOFeAs. Our 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 $\omega_{a=0} = 218$ 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 1 suggest that in the cT-phase the Fe-magnetism is not totally lost with pressure and but it is partially reduced. Hence it seems that there is an optimum strength of Fe-spin state that is required for high-Tc 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 can not 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.

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\* Electronic address: taner@nist.gov

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