Microscopic origin of pressure-induced phase transitions in iron pnictide AFe$_2$As$_2$ superconductors: an ab initio molecular-dynamics study

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Using ab initio molecular dynamics we investigate the electronic and lattice structure of AFe$_2$As$_2$ (A=Ca, Sr, Ba) under pressure. We find that the structural phase transition (orthorhombic to tetragonal symmetry) is always accompanied by a magnetic phase transition in all the compounds, while the nature of the transitions is different for the three systems. Our calculations explain the origin of the existence of a collapsed tetragonal phase in CaFe$_2$As$_2$ and its absence in BaFe$_2$As$_2$. We argue that changes of the Fermi surface nesting features dominate the phase transitions under pressure rather than spin frustration or a Kondo scenario. The consequences for superconductivity are discussed.

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The discovery of iron pnictide superconductors with critical temperatures $T_c$ up to 57.4 K upon doping has strongly revived the interest in high-$T_c$ superconductivity. The undoped Fe-based parent compound undergoes at low temperatures a structural transition from tetragonal to orthorhombic symmetry accompanied by a magnetic phase transition to a stripe-type spin-density wave state. While the nature of these two transitions is different between LaFeAsO (1111 compound) and AFe$_2$As$_2$ (122 compound) with A=(Ba, Sr, Ca), superconductivity appears in both material classes only when the lattice distortion and magnetic ordering are suppressed, indicating a strong competition between the structural distortion, magnetic ordering and superconductivity in iron pnictides.

Recently, superconductivity in the parent compounds 1111 and 122 was reported under application of pressure. In LaFeAsO, resistivity measurements show superconductivity at $\approx 12$ GPa with $T_c = 21$ K. In BaFe$_2$As$_2$ superconductivity is found to appear gradually with increasing pressure while in SrFe$_2$As$_2$ the onset of superconductivity occurs abruptly. In CaFe$_2$As$_2$, detailed neutron and X-ray diffraction analysis shows that the system undergoes a first order phase transition from a magnetic orthorhombic to a nonmagnetic 'collapsed' tetragonal phase under pressure. The possible appearance of superconductivity in this 'collapsed' tetragonal phase is presently under debate. While various experiments give different values of critical pressures due to the fact that the phase transition is sensitive to possible nonhydrostatic pressure effects, Sn content in some samples, or the use of single crystals or polycrystalline material for structure determination, it is claimed that BaFe$_2$As$_2$ and SrFe$_2$As$_2$ do not manifest a 'collapsed' tetragonal phase at elevated pressure. Therefore, the fact that structurally similar compounds exhibit phase transitions of different nature urgently calls for a theoretical understanding. Moreover, it is still under intensive debate which is the driving mechanism of the collinear stripe-
FIG. 1: (Color online) Calculated changes of (a) volume, c/a ratio and magnetization (inset), (b) lattice parameters as a function of applied external pressure normalized to the critical pressure for CaFe$_2$As$_2$. The phase boundary between $F$mmm and $I4/mmm$ is indicated by the vertical dashed line.

verged to less than 0.01 meV/atom and the cell parameters to less than 0.0005 Å. The 3s3p3d (4s4p4d/5s5p5d) states in Ca (Sr/Ba) and the 3d4s4p states in Fe and As are treated as valence states. We checked our calculations with the FPLAPW method as implemented in the WIEN2k code. Very good agreement is found between these two methods. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) to DFT has been used.

Our findings can be summarized as follows: We show that CaFe$_2$As$_2$ undergoes a first order phase transition to a collapsed tetragonal phase with relative changes of lattice parameters, bond lengths and angles agreeing very well with the experimental observations. In particular our calculations can account for the measured expansion along the $ab$ plane at the critical pressure, which was not obtained in previous calculations. We also find an abrupt disappearance of magnetization at the critical pressure. For SrFe$_2$As$_2$ and BaFe$_2$As$_2$, where less is known about the details of the lattice structure and magnetization changes under pressure, we obtain a simultaneous structural (orthorhombic to tetragonal) and magnetic phase transition at high pressure. However, we observe a weak first-order phase transition for SrFe$_2$As$_2$ and a continuous phase transition for BaFe$_2$As$_2$ in contrast to the strongly first order phase transition in CaFe$_2$As$_2$. We explain the microscopic origin of these differences in terms of the different Fermi surface behavior under pressure. Finally, we argue that the existence of a magnetic transition from a striped AF state to a non-magnetic state under pressure is mainly driven by changes of the Fermi surface nesting rather than spin frustration or a Kondo scenario.

In Figs. 1(a) and (b) we present the calculated changes of the volume and lattice parameters of CaFe$_2$As$_2$ as a function of pressure. The volume and the lattice parameter $c$ decrease gradually with increasing pressure and show a discontinuous shrinkage at the critical pressure, where the system undergoes a structural phase transition from orthorhombic symmetry to a volume ‘collapsed’ tetragonal symmetry. Our results are in very good agreement with experimental data with a volume collapse of $\Delta V^\text{th} \approx 4.1\%$, $\Delta V^\text{exp} \approx 4\%$. Moreover, the magnetization sharply goes to zero as shown in the inset of Fig. 1(a). Surprisingly, however, the lattice parameters $a$ and $b$ show abrupt expansions at the phase boundary although otherwise they show a monotonous compres-
FIG. 3: (Color online) Comparison of the CaFe$_2$As$_2$ band structure and DOS in the ‘collapsed’ tetragonal phase obtained from (a) our optimized lattice structure at $P/P_c = 1.04$ and (b) the experimental lattice structure at $P_{\text{exp}}/P_c \approx 1.6$. In (a) the total DOS for the high $T$ tetragonal phase is also shown by the dashed (red) line.

sion in both phases. Such expansions, as also observed in experiments, were not detected in previous DFT calculations and have a fundamental physical origin. In the orthorhombic phase below the critical pressure, the system shows collinear AF ordering within $ab$ plane. At the critical pressure, the AF ordering is destroyed and the Pauli principle becomes more effective due to the appearance of more parallel Fe spins giving rise to a non-negligible lattice expansion along $a$ and $b$. As a consequence, the Fe-Fe bond length increases at the phase transition as observed in experiments, were not detected in previous DFT calculations and have a fundamental physical origin. In the orthorhombic phase below the critical pressure, the system shows collinear AF ordering within $ab$ plane. At the critical pressure, the AF ordering is destroyed and the Pauli principle becomes more effective due to the appearance of more parallel Fe spins giving rise to a non-negligible lattice expansion along $a$ and $b$. As a consequence, the Fe-Fe bond length increases at the phase transition as observed in Fig. 2 (b). In contrast, the As atoms move towards the Fe plane at the phase transition and the Fe-As bond length suddenly decreases with a relative shrinkage of $\Delta d_{\text{Fe-As}}^{\text{exp}} \approx 1.3\%$ in very good agreement with $\Delta d_{\text{Fe-As}}^{\text{exp}} \approx 1.2\%$. Accordingly, the angles of the tetrahedra are suddenly shifted away from the ideal tetrahedral value of 109.47° at the phase transition, while in the orthorhombic and in the high temperature tetragonal phase they are much closer to the ideal value (Fig. 2 (a)). The strong distortion of the tetrahedron enhances the crystal field splitting between $d_{x^2-y^2}$, $d_{xz}$, $d_{yz}$ and $d_{z^2}$, $d_{xy}$ (orbitals given in the $x \parallel a, y \parallel b, z \parallel c$

FIG. 4: (Color online) Calculated changes of (a) volume, $c/a$ ratio and magnetization (inset), (b) lattice parameters and (c) As-Fe-As angles as a function of applied external pressure normalized to the critical pressure for SrFe$_2$As$_2$. The phase boundary between $F_{\text{mmm}}$ and $I_{\text{4/mmm}}$ is indicated by the vertical dashed line.

local reference frame). This can be seen in the density of states (DOS) shown in Fig. 3 (a) where the two peaks just below (of $d_{x^2-y^2}$, $d_{xz}$, $d_{yz}$ character) and above (of $d_{z^2}$, $d_{xy}$ character) the Fermi level in the high temperature ambient pressure tetragonal phase (dashed (red) line) are further separated in the high pressure volume ‘collapsed’ tetragonal phase (solid (black) line).

One aspect of the calculations to be considered is that the calculated critical pressure $P_c = 5.25 \pm 0.25$ GPa is an order of magnitude larger than the experimental critical pressure $P_{\text{exp}} \approx 0.3$ GPa. The overestimation of $P_c$ in our calculations is a consequence of the well-known
FIG. 5: (Color online) Calculated changes of (a) volume, c/a ratio and magnetization (inset), (b) lattice parameters and (c) As-Fe-As angles as a function of applied external pressure normalized to the critical pressure for BaFe$_2$As$_2$. The phase boundary between $Fmmm$ and $I4/mmm$ is indicated by the vertical dashed line.

overestimation of volume and magnetic moment by GGA in the Fe pnictides at ambient pressure. Therefore in order to reach the experimental structure conditions we have to go to higher simulation pressures. This procedure is proven to be valid since, as discussed above, we can reproduce the experimentally reported structural features of the phase transition in CaFe$_2$As$_2$, as well as the electronic properties in both orthorhombic phase (not shown) and 'collapsed' tetragonal phase as shown in Figs. (a) and (b) where we present the comparison between the electronic structure obtained from the Car-Parrinello-derived lattice structure (at $P/P_c = 1.04$) and that obtained from the experimentally measured one (at 0.47 GPa, $P_{exp}/P_{exp} \approx 1.6$). We observe that the shapes of the total DOS are almost the same and only slight differences are found in details of the band structure. Therefore we can conclude that, although our calculations always overestimate the critical pressure, the phase transition and the physical properties in both phases can be quantitatively captured by our analysis.

In Fig. 4 and Fig. 5 we show the results for SrFe$_2$As$_2$ and BaFe$_2$As$_2$. We find that the structure and the magnetic phase transitions under pressure still occur simultaneously in these two compounds, but the nature of the phases is distinctly different from the CaFe$_2$As$_2$ case. SrFe$_2$As$_2$ shows smaller magnetization, volume, lattice and angles jumps at the critical pressure (see Fig. 4) compared to CaFe$_2$As$_2$ while we can hardly detect any discontinuity in BaFe$_2$As$_2$ (see Fig. 5). The simultaneous and abrupt change of the lattice structure and the magnetization in SrFe$_2$As$_2$ is again consistent with recent experimental findings, while our results in BaFe$_2$As$_2$ have not yet been completely confirmed experimentally. Here, the pressure is again normalized to the critical simulated pressure $P_c' = 9.5 \pm 0.5$ GPa for SrFe$_2$As$_2$ and $P_c' = 17.5 \pm 0.5$ GPa for BaFe$_2$As$_2$. The calculated critical pressure for SrFe$_2$As$_2$ and BaFe$_2$As$_2$ is about 2-3 larger than the experimental one, while for CaFe$_2$As$_2$ it
is around 20 times larger. This can be understood from the already mentioned overestimation of magnetic interactions and volumes in GGA calculations. Due to this, one would expect an (approximately constant) shift between the calculated and measured $P_c$, thus resulting in the large deviation for CaFe$_2$As$_2$ (where $P_c$ is small) and the better agreement for SrFe$_2$As$_2$ and BaFe$_2$As$_2$.

In order to understand the microscopic origin of the differences in behaviour between SrFe$_2$As$_2$, BaFe$_2$As$_2$, and CaFe$_2$As$_2$, we performed non-spin-polarized calculations with the optimized lattice structures and analyzed the band structures and Fermi surfaces. Below the critical pressure, we considered an average of lattice parameters $a$ and $b$ as a single lattice parameter in order to make the comparison of band structures of different phases (orthorhombic and tetragonal) possible within the same Brillouin zone. It has already been noticed that the tiny differences between $a$ and $b$ has no appreciable influence on the electronic structure.

In Figs. 6 and 7 we show $k_z=0$, $\pi/c$, and $2\pi/c$ Fermi surface cuts of CaFe$_2$As$_2$ and BaFe$_2$As$_2$ at three different pressures. As a function of pressure, the changes of the Fermi surface in both compounds is remarkably differ-
ent. Below $P_c$, CaFe$_2$As$_2$ shows with increasing pressure gradual shrinkages of the nested inner hole and electron cylinders around $(0,0,k_z)$ and $(\pi/a, \pi/a, k_z)$ respectively leading to a reduction of the nesting features at each $k_z$ (compare in Fig. 6 the rows at $P/P_c=0.1$ and $P/P_c=0.95$) and consequently a continuous reduction of the magnetization in the orthorhombic phase (inset of Fig. 1 (a)). As pressure increases to the critical region, the residual steep DOS at the Fermi level (Fig. 5) still forces the system to find a way to alleviate such an instability. However, the nested inner cylinders become too small to remove it by magnetic ordering. A sudden distortion of the tetrahedron is realized to lower the electronic energy by further splitting the Fe 3$d$ orbitals (see the dashed (red) DOS line in Fig. 6) at the pressure of increasing the lattice energy. Thus, as shown in Fig. 6, $P/P_c=1.05$ row, right above the critical pressure all the cylinders around $(0,0,k_z)$ completely vanish due to the splitting of Fe 3$d$ orbitals by lattice distortions in contrast to BaFe$_2$As$_2$ (see below), and accordingly, the magnetic ordering abruptly disappears (inset of Fig. 1 (a)).

In contrast, the BaFe$_2$As$_2$ Fermi surface shows a shrinkage of the hole cylinders around $(0,0,k_z)$ into hole pockets while the Fermi surface sheets around $(\pi/a, \pi/a, k_z)$ are changed insignificantly (see Fig. 5). Therefore, as the shrinkage occurs under pressure, the vanishing of Fermi surface nesting at the lower $k_z$-plane is partially compensated by the appearance of new nestings at a higher $k_z$-plane (e.g. Fig. 7 at $P/P'_c=0.17$ and $P/P'_c=0.97$), which prohibits the sudden change of magnetization since the nesting remains significant below the critical pressure (e.g. Fig. 7 at $k_z=2\pi/c$ and $P/P'_c=0.97$). Since lowering the total energy by magnetic ordering always prevails over abrupt lattice distortions, the sudden jump of the angles is suppressed as shown in Fig. 6 (c). The slow change of the Fermi surface topology as shown in Fig. 7 is consistent with the continuous reduction of magnetization as observed in the inset of Fig. 6 (a).

Fig. 9 presents the calculated noninteracting susceptibility $\chi(0)$ at $q=(\pi, \pi, 0)$ as a function of pressure within the constant matrix element approximation $^{13, 26, 29, 36}$ for all the three 122 compounds. The relation between the change of the Fermi surface nesting features at $q=(\pi, \pi, 0)$ and the phase transitions under pressure is clearly quantified with this magnitude. $\chi(0)$ at $q=(\pi, \pi, 0)$ is the response for the observed Fermi-surface-nesting-induced stripe-type antiferromagnetism and while it shows a continuous decrease at elevated pressures in BaFe$_2$As$_2$, abrupt reductions at the phase transition are detected in both CaFe$_2$As$_2$ and SrFe$_2$As$_2$, indicating that the phase transition for these two systems are of first order where a sudden disappearance of the Fermi surface nesting occurs. Moreover, we observe that the volume and lattice parameter discontinuities (Fig. 4 (a)) and the tetrahedron distortion (Fig. 4 (c)) right above the phase transition for SrFe$_2$As$_2$ are of the same nature as in CaFe$_2$As$_2$ but less pronounced. We conclude that the phase transition is of weak first order in SrFe$_2$As$_2$.

Finally, we find that the ground state energy of the stripe-ordered AF state is always far below that of the checkerboard-ordered one in the orthorhombic phase while that of the high-pressure tetragonal phase is non-magnetic, indicating that the phase transition under pressure for the three compounds is not driven by the competition between different magnetic ordering, i.e., spin frustration. Furthermore, the tiny crystal field splittings of the Fe 3$d$ states and strong itinerancy of all Fe 3$d$ electrons does not support the Kondo scenario $^{44}$ for the phase transitions under pressure.

In conclusion, we investigated the phase transitions in the iron pnictide 122 compounds under pressure within the framework of ab initio molecular dynamics. The results on CaFe$_2$As$_2$ agree very well with the experimental findings. We show that magnetic and structural phase transitions also appear concomitantly in SrFe$_2$As$_2$ and BaFe$_2$As$_2$. While they are weakly first order in SrFe$_2$As$_2$, the phase transition is continuous in BaFe$_2$As$_2$ which may be closely related to the different behavior of entering superconductivity between SrFe$_2$As$_2$ and BaFe$_2$As$_2$ observed experimentally $^{22}$. The remaining hole pocket as well as nesting features in BaFe$_2$As$_2$ may be related to the highest transition temperature $^{23}$ observed among 122 compounds due to the remaining spin fluctuations. Since the topology of the Fermi surface in the high pressure phase is quite different among these 122 compounds and LaOFeAs $^{41}$, the pairing mechanism may differ among these compounds although they belong to the same family of superconductors.

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