The discovery of high-Tc superconductivity in the iron oxypnictide LaO$_{1-x}$F$_x$FeAs is attracting a lot of attention, mostly because this class of materials is one of the first set of materials to have a high $T_c$, mostly because this class of materials is one of the first set of materials to have a high $T_c$, mostly because this class of materials is one of the first set of materials to have a high $T_c$. Understanding the magnetic ground-state of LaO$_{1-x}$F$_x$FeAs is the first crucial step towards uncovering the mystery of the role of magnetism in the onset of superconductivity. Determining magnetic ground states using first principles density functional theory (DFT) calculations is a routine procedure. In fact, one of the most complex and interesting aspects of magnetism in LaO$_{1-x}$F$_x$FeAs is its interplay with structural properties. At a temperature of 136 K the undoped parent compound undergoes a phase transition to a stripe antiferromagnetic (AFM) order which, additionally, is associated with a structural distortion from tetragonal to orthorhombic. The impact of doping upon structural and magnetic properties is only beginning to be understood; experiments differ on whether doping (greater than 5%) suppresses the structural phase transition. Furthermore, a recent experiment finds evidence of incommensurate order upon doping, indicating a rich interaction between structural and magnetic order as the parent compound is doped. Highly accurate ab-initio calculations can play a crucial role in elucidating this complex behaviour, and in the present work we shall address in detail the magnetic and structural properties of both doped and undoped LaOFeAs.

In order to keep the numerical analysis as accurate as possible, in the present work all calculations are performed using the state-of-the-art full-potential linearized augmented plane wave (FPLAPW) method, implemented within the Elk code. We have taken great care that all relevant calculational parameters are converged; in particular we use a $k$ mesh of $12 \times 12 \times 8$ shifted by $[0.5,0.5,0.5]$, and 188 states per $k$-point which ensures convergence of the second variational step. We found that using less well converged values of these parameters has a dramatic impact on the magnetic moment (such computational details can be seen in the supplementary material).

We first determine the magnetic ground state of the undistorted (tetragonal phase) parent compound LaOFeAs. That magnetism in this system is remarkably sensitive to calculational details is clear from the spread of moments obtained using the FP-LAPW method and experimental crystal structure, 0.87-2.20 $\mu_B$. This dramatic spread of results is presumably indicative of both a sensitive dependence of the magnetism upon calculational details, as well as a strong dependence on crystal structure.

Using state-of-the-art first-principles calculations we have elucidated the complex magnetic and structural dependence of LaOFeAs upon doping. Our key findings are that (i) doping results in an orthorhombic ground state and (ii) there is a commensurate to incommensurate transition in the magnetic structure between $x = 0.025$ and $x = 0.04$. Our calculations further imply that in this system magnetic order persists up to the onset of superconductivity at the critical doping of $x = 0.05$. Finally, our investigations of the undoped parent compound reveal an unusually pronounced dependence of the magnetic moment on details of the exchange-correlation (xc) functional used in the calculation. However, for all choices of xc functional an orthorhombic structure is found.

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In this regard it has been noted that both Fermiology \cite{16} as well as magnetic moment \cite{19} are strongly dependent on the \( z \) coordinate of the As atom. In the right hand panel of Fig.1 we show this dependence of the magnetic moment on the \( z \) coordinate of the As atom for the so-called stripe AFM phase \cite{15,19} (the proposed ground state structure of this system), for two common parameterizations \cite{20,21} of the local spin density approximation (LSDA). Clearly, this choice leads to a dramatic difference in the results. For instance, at the value of \( z_{\text{As}} \) obtained by optimizing with the generalised gradient approximation (GGA) (\( z_{\text{As}}^{\text{GGA}} = 0.638 \) a.u.), the difference in the moment per Fe atom calculated using two different parameterizations for LSDA is 0.44\( \mu_\text{B} \). It is further clear that only for a theoretically optimised \( z_{\text{As}} \) (GGA or LSDA) can a moment close to the experimental value be obtained. Taken together with the work of Mazin et al., where it was shown \cite{16} that only for \( z_{\text{As}}^{\text{GGA}} \) a Fermiology consistent with experiment could be found, these results indicate that a theoretical value of this parameter should be used. However, given this unusually strong dependence of magnetism upon the choice of exchange correlation functional, we adopt the strategy of calculating structural properties with the GGA, but then calculate magnetic properties via both the von Barth-Hedin (vBH) \cite{21} and Perdew-Wang (PW) \cite{20} parameterizations of the LSDA.

Given this, we now explore the phase space of possible magnetic structures consistent with experiments. To date, the commensurate collinear stripe and checkerboard structures have been investigated, with the stripe phase substantially lower in energy \cite{13,22}. Two crucial questions which then may be asked are: (i) when the constraint of commensuration is removed does the stripe phase remain the minimal energy structure? and (ii) what is the dependence of the moment on the underlying spin structure?

We here calculate spin spirals with \( \mathbf{q} \) around the \([1/2,0,0]\) (\( X \)) and \([1/2,1/2,0]\) (\( M \)) special points in the Brillouin zone. Two special cases of these are the commensurate stripe and checker-board phases, generated with wave vectors \( M \) and \( X \), respectively. Around the \( M \)-point, an alternative magnetic order is a spin spiral with a 90° phase difference between the two Fe sites, equivalent to a 2k structure at the \( M \)-point. Due to the inherent frustration of ordering at the \( M \)-point, this structure is also a candidate for the ground state \cite{22}. In the upper-left panel of Fig.1 are shown the moment per Fe atom for spin spiral vectors with \( \mathbf{q} \) near the \( M \) point for 1k type spin spiral. Remarkably, we find that for the vBH parameterization a magnetic solution exists only around the \( M \) point and even a small change in spiral \( \mathbf{q} \) from \([0.50,0.50,0.00]\) to \([0.62,0.62,0.00]\) results in a vanishingly small value of the moment (similar results were obtained using LMTO method in Ref. \cite{24}). The PW parameterization also results in a moment which falls strongly on moving away from the \( M \) point, but the value is non-zero over the whole BZ with a minimal value of 0.20\( \mu_\text{B} \) at the \( \Gamma \) point.

Turning to the energetics of these spirals (lower-left panel Fig.1), we find the 1k type spiral to be always lower in energy than the 2k type spiral (for clarity we show only the 2k result for vBH-LSDA). Interestingly, the global energy minima is not at the \( M \) point but instead at a spiral of \( \mathbf{q} = [0.52, 0.52, 0.00] \), a results which is independent of the functional chosen. The ground state of undistorted LaOFeAs is thus an incommensurate spin spiral. With the vBH LSDA this structure lowers the total energy by 0.5 meV per formula unit as compared to the previously supposed stripe ground state \cite{13,19} and gives a moment of 0.46\( \mu_\text{B} \). This energy difference and the moment are increased to 2 meV per formula unit and 0.92\( \mu_\text{B} \) respectively when the PW LSDA is used for determining both the \( z_{\text{As}} \) and the magnetic structural energies.

At a temperature of 150 K LaOFeAs undergoes a phase transition from the tetragonal to orthorhombic structure, closely associated with the onset of magnetism \cite{7,8,9,10,17,25,26}. Recently, this transition was explained as the system lowering magnetic frustration, rationalised by arguments based on a \( J_1-J_2 \) Heisenberg model. Here we shall take a different approach and explain the mechanism of this distortion without recourse to the \( J_1-J_2 \) model, which is unlikely to be appropriate for a weak itinerant magnet such as LaOFeAs.

In Fig. 2 (upper panel) is displayed the total energy of the non-magnetic state of LaOFeAs as a function of distortion angle, for both the vBH and PW parameterisations; clearly, a special feature is the very flat minima at 90°. Considering first the commensurate stripe phase we find that the moment (middle panel) increases with
increasing distortion angle. The gain in magnetic energy is then sufficient to shift the minimum of the total energy from 90° to 90.30° (lower panel) for the vBH and 90.50° for the PW LSDA, in good agreement with the measured value of 90.27°. Thus the vBH LSDA gives both the ground state moment and distortion in close agreement with experiment. On the other hand, the larger magnetic moment produced by the PW parameterisation simply results in a slightly larger distortion; reassuringly therefore, the qualitative behaviour is independent of the particular choice of functional.

Turning now to possible non-collinearity of spins in this distorted phase of LaOFeAs we find that, in contrast to the undistorted crystal, the commensurate stripe phase is the minimal energy structure in the distorted case (for both parameterizations of LSDA). We should stress that the analysis of the structural distortion presented here relies solely on the behaviour of the global moment with distortion and the concomitant increase in magnetisation energy, and is thus appropriate for the itinerant nature of LaOFeAs. In Ref. 17 the interesting suggestion was made that the cause of the distortion could be a release of the inherent magnetic frustration of the FeAs layers. Such a relaxation of frustration would, generally, be expected to lead to an increase in moment, and so this idea is also compatible with the picture presented here.

The electron doped material LaO$_{1-x}$F$_x$FeAs becomes superconducting 1, 8, 11, 27 at a critical doping of $x = 0.05$. A crucial question is whether magnetism persists up to the superconducting transition, i.e., is a competing ground state, or is lost before the onset of superconductivity. Experimentally, it is established that beyond $x = 0.075$ no magnetic order persists, however if magnetic order is entirely lost before the superconducting transition is still a point of discussion 8, 11, 28. It is also evident from recent experiments 11 that there exists a complex structural and magnetic behaviour with doping, the full nature of which has yet to be clarified. In fact, on the question of whether the distortion observed at $x = 0$ persists beyond the superconducting transition at $x = 0.05$, the current experimental data are contradictory: Refs. 11 and 28 find that distortion persist up to $x = 0.08$, while in Refs. 8, 11 no distortion is observed beyond the onset of superconductivity at $x = 0.05$. The magnetic state of of LaO$_{1-x}$F$_x$FeAs is also uncertain, with one experiment 11 finding evidence of an incommensurate structure for $x > 0$.

In order to clarify this situation we have determined the ground state for several doping concentrations, by minimising over both the distortion angle $\gamma$, see Fig. 4, and spiral vector $q$ (for 1k type spin configuration). To simulate doping a small amount of charge is added to the unit cell along with a compensating background, which ensures charge neutrality. Since the concentration of electrons is very small this approximation to the doping should be good. Indeed, the accuracy of this approximation has recently been demonstrated 29.

We first consider the overall behaviour of the magnetic moment with doping. This is shown in Fig. 3 for both the vBH and PW parameterisations of the LSDA. It is immediately apparent that the choice of functional simply leads to a scaling of the doping curve. However, only for the vBH LSDA do we find a behaviour that results in quantitative agreement with available experimental data for $x < 0.05$, i.e., less than the critical doping. However, a marked divergence between experiment and theory occurs after this point; while the theoretical data show a slowly vanishing tail the experimental data display a sudden decrease. Our calculations, therefore, imply that magnetic and superconducting order are competing ground states in the sense that magnetism does
not die before the onset of superconductivity. The sharp decrease in moment at $x = 0.05$ may then be brought about by the onset of superconductivity. The question of whether magnetism and superconductivity then coexist for a small doping range, or if the onset of superconductivity destroys entire the magnetic order, we cannot answer. On the other hand, one should note that the small moment itinerant magnetism of this system implies a strong role for spin fluctuations $[4, 6, 30]$, which is not correctly treated by the LSDA functional used in the present calculations. These may act to damp the slowly vanishing tail of the moment vs. doping seen in Fig. 3.

FIG. 4: (color online) Left panel shows the total energy (in meV per formula unit) as a function of distortion angle, for various dopings. Right panels show total energy (in meV per formula unit) as a function of spin-spiral q-vector for distorted (upper panel) and undistorted (lower panel) doped LaOF$_x$As.

We now turn to the important question of the impact of doping upon the crystal and magnetic ground state. Given that the vBH parameterised LSDA has shown good agreement with experiment for the magnetic moment, distortion and doping curve, we shall use this functional to explore this question. We first fix the magnetic structure to that of the commensurate stripe phase and, for each value of $x$, minimise the distortion angle. Remarkably, we find for all $x > 0$ a crystal distortion opposite ($\gamma < 90^\circ$) to that of the undoped parent compound (see Fig. 4(left panel)). Furthermore, subsequent minimisation of the spin spiral $\mathbf{q}$ reveals a stripe phase to incommensurate spin spiral transition ($\mathbf{q} = [0.54, 0.54, 0]$) between $x = 0.025$ and $x = 0.04$ (top right panel, Fig. 3). This opposite distortion upon doping can be understood as a mechanism the system adopts to lower the moment. The monotonic increase of the moment with $\gamma$, displayed in Fig. 2 for $x = 0$, is also found for all doping concentrations, and hence a crystal distortion of $\gamma < 90^\circ$ lowers the moment.

This finding of a commensurate stripe to incommensurate transition is in agreement with the experimental observation $[11]$ of Huang et al. We should note, however, that the small energy difference between the incommensurate and stripe structures (0.4 meV per formula unit) suggests that this may only be seen at the low temperature (8 K) experiments performed by Huang et al. Furthermore, in experiments a small increase in the parameter $z_{\text{expt}}$ is seen with doping, an effect we have not included in our calculations. As increasing this parameter results in an increase of moment, the likely effect of including this would be to shift the onset of moment lowering mechanisms ($\gamma < 90^\circ$ distortion and incommensurate order) to somewhat higher values of doping.

To summarize by the means of accurate $ab$-initio calculations we have given an explanation for the phase transition in LaOF$_x$As based on an itinerant magnetic picture in terms of an increase in spin polarisation brought about by crystal distortion. Furthermore, we have elucidated the impact of doping on the ground state; we find both that the doped material distorts, but with $\theta = 89.85$, and a stripe phase to incommensurate spin spiral transition takes place between $x = 0.025$ and $x = 0.04$. Most importantly, our calculations indicate that in this system magnetic order persists up to the onset of superconductivity.

Supplementary material
second-variational problem. In Fig. 5 are shown the results for magnetic moment per Fe atom, for undistorted undoped LaOFeAs as a function of the number of these first-variational eigenstates per $k$-point. The results are for the stripe anti-ferromagnetic phase. It is clear that ground state magnetic moment for this material is greatly sensitive to both the number of states per $k$-point as well as the number of $k$-points in the irreducible Brillouin-zone (IBZ).

The magnetism in this system is remarkably sensitive to calculational details is clear from Fig. 6. In this figure are shown the results of magnetic moments obtained using various approximations to the exchange-correlation functionals implemented within different full-potential as well as pseudo potential codes. The moments obtained using different methods and experimental As position, range from 0.87-2.20$\mu_B$ and the moments obtained using the theoretically optimized (GGA) As position range from 0.46-1.80$\mu_B$. On the other hand both Neutron diffraction and Mössbauer experiments report a value between 0.25-0.36$\mu_B$.

FIG. 6: (color online) Top panel shows the magnetic moment per Fe atom (in $\mu_B$), calculated using various methods, with As atoms at experimental position. Bottom panel shows the same but for As atom at theoretically optimized position, this position is obtained using GGA functional and by treating LaOFeAs non-magnetically.