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Structural origin of the anomalous temperature dependence of the local magnetic moments in the CaFe_2As_2 family of materials

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We report a combination of Fe $K\beta$ x-ray emission spectroscopy and Density Functional reduced Stoner Theory calculations to investigate the correlation between structural and magnetic degrees of freedom in $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. The puzzling temperature behavior of the local moment found in rare earth-doped CaFe_2As_2 [H. Gretarsson, *et al.*, *Phys. Rev. Lett.* **110**, 047003 (2013)] is also observed in $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. We explain this phenomenon based on first-principles calculations with scaled magnetic interaction. One scaling parameter is sufficient to describe quantitatively the magnetic moments in both $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ($x = 0.055$) and $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$ at all temperatures. The anomalous growth of the local moments with increasing temperature can be understood from the observed large thermal expansion of the c -axis lattice parameter combined with strong magnetoelastic coupling. These effects originate from the strong tendency to form As-As dimers across the Ca layer in the CaFe_2As_2 family of materials. Our results emphasize the dual local-itinerant character of magnetism in Fe pnictides.

It is generally believed that superconductivity in Fe-based materials (FeBS) is related to magnetic fluctuations. [1, 2] However, from the very beginning two schools were formed as regarding the best description of magnetism in these systems. One described the Fe moments as soft and itinerant and related magnetic interactions to the Fermi surface properties. [3–5] The other assumed localized moments not unlike those in cuprates that interact via superexchange-type interactions. [6, 7] At a later stage it was proposed that the truth is in-between, namely that the moments are substantially localized, and large, but they are nonetheless soft (can easily change their amplitude, not just direction), strongly coupled to the lattice (the amplitude strongly depends on the pnictogen's position), formed by itinerant electrons, and are greatly reduced by fluctuations. [8–12]

CaFe_2As_2 and its derivatives are an odd case among the Fe-based superconductors (FeBSs). Under pressure the parent compound collapses into a new structure, with a much shorter c -axis lattice parameter and smaller As-As distance. [13] The crystal structure of CaFe_2As_2 at an ambient pressure, like that of all other FeBSs, is very well described by the density functional theory (DFT) calculations, *if the moments are allowed to grow to their DFT values*, which can be more than a factor of two larger than the measured *ordered* moments. In those FeBSs in which long-range order is suppressed by means other than pressure, the crystal structure is still predicted correctly by the magnetic DFT, and not by its nonmagnetic variant. This strongly suggests that sizeable local moments

are present also in FeBSs which do not show long-range magnetic order.

Conversely, the high-pressure collapsed tetragonal (cT) structure of CaFe_2As_2 is accurately described by *non-magnetic* DFT calculations, in agreement with the fact that the local moments are quenched in this phase. [14] This magnetic collapse in CaFe_2As_2 has a structural origin, namely the reduced As-As distance across the Ca layer, and is now fully understood on the basis of DFT calculations. [15–18] In practice, below a critical bond length, the p_z orbitals of As tend to form covalent bonds with the As atoms sitting above or below it. This pushes anti-bonding π states away from the Fermi level, increasing the effective valence of Fe, and reinforcing both Fe-As in-plane and the As-As out-of-plane bonds. Experiments also find that the magnetic moments in CaFe_2As_2 are very sensitive to this As-As distance. [19, 20] Besides pressure, structural and magnetic transitions can be modulated through rare-earth [21] or phosphorous [22] substitutions.

In this work we will show that in these compounds not only the ordered moments, but also the local moments are exceptionally soft, and their counterintuitive growth with increasing temperature is due to the negative chemical pressure exerted upon Fe by the lattice expansion.

Some of us had shown before that the shape of the Fe $K\beta$ emission line in x-ray emission spectroscopy (XES) can be used to measure the local moment in FeBSs. [23–25] In this paper, we employ this technique to study the temperature dependence of the magnetic moment in

$\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ ($x = 0$, $x = 0.033$ and $x = 0.055$), combined with high-quality X-Ray diffraction data, and show that the anomalous increase of the magnetic moment with temperature correlates with a strong c -axis expansion. DFT calculations as a function of the lattice parameter, including an effective fluctuation-induced renormalization of the magnetic moment, [26, 27] quantitatively reproduce the increase of the local moment in this compound, as well as in the previously measured $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$. [24] This unambiguously demonstrates that the observed effect is not related to thermal *excitations* but to thermal *expansion*, combined with the unique softness of the Fe moments in CaFe_2As_2 .

The XES measurements were performed at the Cornell High-Energy Synchrotron Source (CHESS) on the bending magnet beamline C1. Incident energy of 9 keV (1% bandwidth) was selected from a multilayer monochromator. To measure the Fe $K\beta$ emission line, we used five Ge(620) 4" spherical analyzers (1 m radius) and a Vortex detector in quasi-Rowland circle geometry. X-ray diffraction measurements were performed using a Cu tube source with a Ge(111) monochromator. Samples were aligned within a four-circle Huber diffractometer. The temperature dependence of the c -axis was determined by monitoring the (008) Bragg peak. Data was collected on cooling using a closed-cycle refrigerator. Details of the growth of the single-crystal samples have been reported before. [28]

The ground state of $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ has been shown to be very sensitive to small inhomogeneity in doping and crystal growth conditions; [22, 29] we thus carefully characterized all our samples using x-ray diffraction. In Fig. 1 (a) the thermal evolution of the c -axis lattice constant in $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ can be seen. Both the parent compound and the $x = 0.033$ sample exhibit a first-order tetragonal(T)- to orthorhombic(O)-phase transition (T_O) around 165 K and 130 K, respectively. Upon increasing x further, T_O gets suppressed and eventually superconductivity appears for $x \sim 0.04$. [22] At $x = 0.055$ superconductivity disappears and a sharp transition into the collapsed-tetragonal(cT) phase is seen at 80 K (T_{cT}). For comparison we also include data on $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$ from Ref. 24. This compound stays in the T-phase over the entire temperature range and thus provides “a bridge” between the $x = 0.033$ and $x = 0.055$ samples.

Fig. 1 (a) already reveals the unique feature of CaFe_2As_2 materials, an enormous lattice constant change with temperature. Even for the samples that do not exhibit the cT-phase transition (e.g. $x = 0.033$), the c -axis contraction ($\sim 100 \times 10^{-5}$ Å/K) in the T-phase is already three times larger than what we have observed in the related compound BaFe_2As_2 ($\sim 35 \times 10^{-5}$ Å/K). [30] Interestingly, this rate of contraction is not seen in the magnetically ordered O-phase, emphasizing the important role of magnetism in these materials.

In order to investigate if this large change in the c -axis

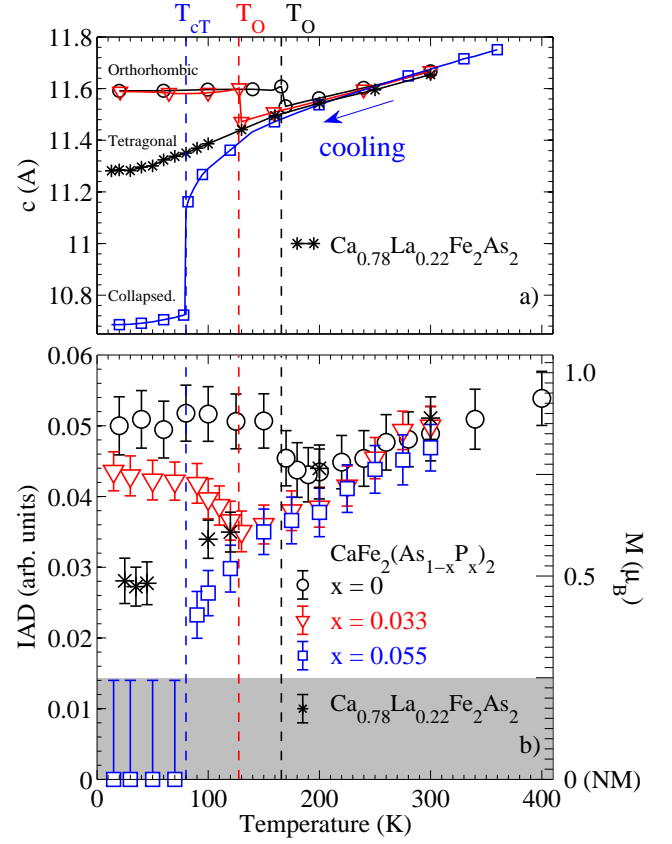


FIG. 1: (Color online) (a) Temperature dependence of the c -axis lattice parameter in $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Both $x = 0$ (black open circles) and $x = 0.033$ (red open triangles) samples go through tetragonal- to orthorhombic-phase transition (T_O) around 165 K and 130 K, respectively. In the $x = 0.055$ (blue open squares) an abrupt transition into collapsed-tetragonal phase is seen at 80 K (T_{cT}). (b) The temperature dependence of the IAD values for the same samples derived from their XES spectra. On the right-hand side is the magnetic moment of Fe (M) derived as described in text. Data for $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$ (black stars) – Ref. 24 – are also shown for comparison.

lattice parameter is coupled to the magnetic moment of Fe, we carried out Fe $K\beta$ ($3p \rightarrow 1s$) XES experiment. By applying the integrated absolute difference (IAD) analysis [31] on the shape of the emission line information on the size of the Fe magnetic moment can be obtained (see Supplemental Material for details). As in our previous work, [23, 24] the reference spectra for low-spin and high-spin were FeCrAs and $\text{K}_2\text{Fe}_4\text{Se}_5$, respectively. In Fig. 1 (b) the temperature dependence of the IAD values for all samples can be seen. Since the IAD is found to be linearly proportional to the magnetic moment of Fe (M) [32] we can add to the plot a right-hand axis showing the local moment scale, as determined from the IAD values of FeCrAs and $\text{K}_2\text{Fe}_4\text{Se}_5$. The detection limit of the IAD technique is shown as a shaded area. [24] By

comparing our results on $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ with the one obtained for $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$ we notice a similar temperature behavior of the local moment. At room temperature all samples have local moments around $0.8 \mu_B$, which upon cooling gradually decreases. The $x = 0.055$ sample shows the strongest effect, going from $\approx 0.8 \mu_B$ at $T = 300$ K, to $0.4 \mu_B$ at 100 K, and in the cT-phase it drops to zero. A similar trend can be seen in the T-phase for both the parent compound and $x = 0.033$, although to a lesser extent. Interestingly, in their magnetically ordered O-phase an increase in the moment is observed which gradually becomes temperature independent upon further cooling. This upturn of the local moment is expected also in DFT calculations, because the orthorhombic distortion enhances the magnetic moment, enhancing the xz/yz orbital imbalance. [33]

Our observation in Fig. 1 highlights the similarities between the evolution of the c -axis lattice parameter and the measured magnetic moment for both $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ and $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$. In particular, both M and c strongly depend on temperature in the T-phase, but not in the antiferromagnetic O-phase, demonstrating a strong entanglement between the structural and magnetic degrees of freedom.

The unusual thermal sensitivity of the c -axis lattice parameter in CaFe_2As_2 and its derivatives, combined with the well-known sensitivity of the magnetic moments in Fe pnictides to the Fe-As and As-As distances [34, 35], hints at the importance of the lattice geometry and thermal expansion. In order to investigate a possible *structural* origin of the anomalous behavior of the magnetic moment, we performed first-principles calculations of the magnetic moment as a function of the experimental, temperature-dependent lattice parameters for both La-doped and P-doped ($x = 0.055$) samples from Refs. 21, 22. [36, 38, 39, 41]

In order to correct the well-known tendency of standard local (spin) density approximation - L(S)DA - and generalized gradient approximation (GGA) exchange and correlation (xc) functionals to overestimate the size of the magnetic moment in Fe pnictides, we used the Reduced Stoner Theory (RST) introduced by some of us in Ref. 27. In practice, we introduced a scaling parameter $0 < s < 1$ for the spin-dependent part of the exchange and correlation functional, which accounts for the reduction of the magnetic moment due to spin fluctuations, in the spirit of Moriya's self-consistent theory. [26] The value of s in a given material indicates the importance of spin fluctuations: $s = 1$ reproduces the standard exchange and correlation functional (i.e. no additional fluctuation effects are included), while for $s = 0$ fluctuations are so strong that magnetism is entirely suppressed. [27] Importantly, while the original Moriya's theory only deals with the ordered moment, by integrating over all fluctuations with all frequencies, one expects the same approach, but with reduced renormalization (smaller $1 - s$) to work also for

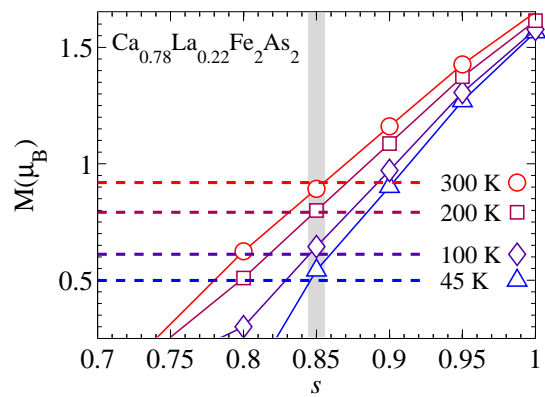


FIG. 2: (Color online) Magnetic moment M of $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$ as a function of the DFT-RST scaling parameter s for different temperatures (solid lines). The horizontal dashed lines show the experimental values of the magnetic moment for different temperatures taken from Ref. 24. Best agreement with experimental values is obtained using $s = 0.85$ (gray vertical line).

the local moments. Obviously, the scaling parameter in this case should depend on the time scale of the experiment probing the local moments; since in our experiment the time scale is independent of doping and temperature, we should be able, if this theory is correct, to explain the experiment using the same s for all samples and temperatures.

With this in mind, we have fixed s so as to reproduce the magnetic moment at the highest temperature ($T = 300$ K) for the La-doped sample, and found that without changing s the full temperature dependence of the magnetic moment for all measured samples could be reproduced.

In Fig. 2 we show the scaling effect for $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$. For $s = 1$, corresponding to standard LSDA calculations, the magnetic moment is almost temperature-independent, but for smaller s the moment acquires a stronger T-dependence, until magnetism is entirely suppressed below $s \approx 0.75$. The value of $s = 0.85$ reproduces experimental data at all temperatures nearly perfectly. This is even more clearly seen in Fig. 3 (a), where the magnetic moments for $s = 0.85$ and $s = 1$ are plotted as a function of temperature.

Fig. 3 (b) shows the same calculations for the P-doped samples at $x = 0.055$ (blue squares in Fig. 1 (b)). Experimentally, this sample turns into a non-magnetic collapsed tetragonal phase below $T_{cT} = 80$ K; the complete set of structural parameters and internal coordinate of the As is published in Ref. 22. As can be seen in Fig. 3 (b), the standard DFT overestimates M and underestimates its temperature dependence, although it correctly converges to a nonmagnetic ground state in the cT-phase

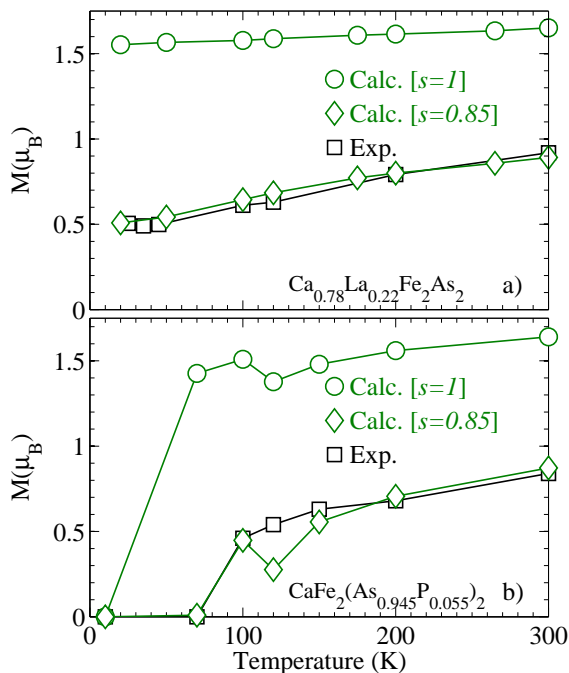


FIG. 3: (Color online) Magnetic moment as a function of temperature in the DFT-RST calculations using $s = 0.85$ (diamonds) compared with the experimental data (squares) of (a) $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$ (Ref. 24) and (b) $\text{CaFe}_2(\text{As}_{0.945}\text{P}_{0.055})_2$. The hollow circles indicate conventional LSDA results (equivalent to DFT-RST with $s = 1.00$). See also [43] and Supplemental Material for additional discussion.

($T = 10$ K). The same $s = 0.85$ as used for the La-doped compound reproduces remarkably well the experimental behavior. [43] Interestingly, we had not been able to describe with a single s the behavior of the ordered moment near the doping-induced quantum critical point (QCP) in BaFe_2As_2 . [44] This is understandable, because (i) a QCP generates much stronger fluctuations than a first-order structural collapse and (ii) more fluctuations contribute to renormalization of the ordered moment than to the local one.

In DFT, the origin of the magnetic collapse of the 122 structure is a subtle balance between the energy gain induced by lattice collapse, discussed in a seminal paper by Hoffmann and Zheng, [18] and the magnetic energy gained in the uncollapsed phase. The magnetic stabilization energy in Fe pnictides is discussed in detail in Ref. 45, using a simplified non-self-consistent version of reduced Stoner theory. This quantity depends in a non-trivial way on the value of the magnetic moment and on the details of the electronic structure, and a discussion is beyond the scope of the present paper. Two observations are however in place: (a) an anti-ferromagnetic (AFM) ground state can be stabilized only if d_{xy} electronic states are present at the Fermi level in the non-magnetic DFT band structure; [17] (b) the transition from the uncollapsed to the collapsed tetragonal phase results in a rela-

tive shift of the d_{xy} states with respect to other d states, but the change in occupation is so small ($\Delta n_{xy} \simeq 0.1$ e/unit cell) that it does not make sense to talk of a spin-state transition.

A pronounced temperature-dependence of a magnetic moment is often associated with some thermal excitations. With this in mind, the experimental data on $\text{Ca}_{0.78}\text{La}_{0.22}\text{Fe}_2\text{As}_2$, were fitted in Ref. 24 with a model assuming thermally excited low-high spin transitions, similar to the strongly correlated insulator LaCoO_3 [46]. This model implies narrow Fe d levels that could form two nearly degenerate magnetic states, whose relative occupation changes with temperature. An essential part of this model is an assumption that some or all electrons form localized narrow states, separated by a crystal field comparable with the Hund's rule coupling, so that localized electrons on a site can form two nearly degenerate states, a singlet and a triplet. An alternative version of the same model instead of using temperature to mix these two states utilizes an empirical magnetoelastic coupling. A proper tuning of the model ensured a good description of the experimental data. [24, 47] However, the fundamental assumption of this model does not seem to be applicable to CaFe_2As_2 . First, as opposed to LaCoO_3 , in CaFe_2As_2 the bandwidths for all orbitals are large, and, most importantly, all the crystal field splittings are much smaller than either the Hund's rule coupling J or the bandwidths. Thus, in actuality the materials appear to be in a completely different regime, where the softness of the magnetic moment is derived not from an accidental degeneracy of two ionic states (*i.e.*, from a competition between the Hund's rule and crystal field) but from the competition between the Hund's rule and kinetic energy. Our approach is aimed at capturing exactly this competition. The fact that with one single parameter we were able to describe two different, albeit similar material, testifies that this is the correct physics.

In conclusion, in this work we have addressed the issue of the intriguing and counterintuitive growth of local magnetic moments with temperature in the CaFe_2As_2 family of materials. We have shown that this phenomenon is present not only in the La-doped system, [24] but also in $\text{CaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, suggesting that it is universal for all Ca-based 122 materials, and ruling out explanations requiring fine parameter tuning. [48] Using density functional theory, we found that in both materials, again counterintuitively, the observed strong temperature dependence is not related to any thermally excited process, but is a consequence of the anomalously large thermal expansion along c , combined with strong magnetoelastic coupling, both due to As-As interaction across the (relatively thin) Ca layer. Therefore cooling the sample is equivalent to applying pressure on it. This finding emphasizes the dual character of magnetism in the parent materials of Fe-based superconductors, where sizable local moments are nonetheless soft and exhibit many traits

of itinerant magnetism.

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