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Vladislav Borisov
Goethe University

Paul C. Canfield
Iowa State University and Ames Laboratory, canfield@ameslab.gov

Roser Valentí
Goethe University

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Abstract
By performing pressure simulations within density functional theory for the family of iron-based superconductors AeAFe_4As_4 with Ae=Ca, Sr, Ba and A=K, Rb, Cs we predict in these systems the appearance of two consecutive half-collapsed tetragonal transitions at pressures P_c1 and P_c2, which have a different character in terms of their effect on the electronic structure. We find that, similar to previous studies for CaKFe_4As_4, spin-vortex magnetic fluctuations on the Fe sublattice play a key role for an accurate structure prediction in these materials at zero pressure. We identify clear trends of critical pressures and discuss the relevance of the collapsed phases in connection to magnetism and superconductivity. Finally, the intriguing cases of EuRbFe_4As_4 and EuCsFe_4As_4, where Eu magnetism coexists with superconductivity, are discussed as well in the context of half-collapsed phases.

Disciplines
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Trends in pressure-induced layer-selective half-collapsed tetragonal phases in the iron-based superconductor family \( \text{AeFe}_4\text{As}_4 \)

Vladislav Borisov,1,*  Paul C. Canfield,2,3 and Roser Valentí1
1Institute of Theoretical Physics, Goethe University Frankfurt am Main, D-60438 Frankfurt am Main, Germany
2Ames Laboratory US DOE, Iowa State University, Ames, Iowa 50011, USA
3Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

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By performing pressure simulations within density functional theory for the family of iron-based superconductors \( \text{AeFe}_4\text{As}_4 \) with \( \text{Ae} = \text{Ca, Sr, Ba and } A = \text{K, Rb, Cs} \) we predict in these systems the appearance of two consecutive half-collapsed tetragonal transitions at pressures \( P_1 \) and \( P_2 \), which have a different character in terms of their effect on the electronic structure. We find that, similar to previous studies for \( \text{CaKFe}_4\text{As}_4 \), spin-vortex magnetic fluctuations on the Fe sublattice play a key role for an accurate structure prediction in these materials at zero pressure. We identify clear trends of critical pressures and discuss the relevance of the collapsed phases in connection to magnetism and superconductivity. Finally, the intriguing cases of \( \text{EuRbFe}_4\text{As}_4 \) and \( \text{EuCsFe}_4\text{As}_4 \), where Eu magnetism coexists with superconductivity, are discussed as well in the context of half-collapsed phases.

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I. INTRODUCTION

The so-called 122 Fe-based pnictides [Fig. 1(b)] (\( \text{AFe}_2\text{As}_2 \), \( \text{AeFe}_2\text{As}_2 \), \( \text{EuFe}_2\text{As}_2 \)) with A alkali and \( \text{Ae} \) alkaline-earth cations crystallize at room temperature in a body-centered tetragonal \( \text{ThCr}_2\text{Si}_2 \) structure (\( 14/mmm \))[1,2], where As sites from the neighboring Fe-As blocks face each other across the \( A \) or \( \text{Ae} \) plane. The As-As interlayer distance in these systems can be then tuned by either mechanical or chemical pressure down to sufficiently small values, allowing the formation of As-As \( p_\perp \) bonds. This is accompanied by a structural phase transition to a collapsed tetragonal (cT) phase where the \( c/a \) ratio is significantly reduced due to a dramatic contraction of the \( c \)-lattice parameter and a slight expansion of the \( a \)-lattice parameter. This process is known to suppress superconductivity or/and long-range “stripe” magnetic order [Fig. 1(d)] due to the crossover to a more three-dimensional structure and the loss of spin fluctuations and local Fe moments caused by a compression of Fe-As bonds [3]. In the 122 materials, the transition to a cT phase affects the whole structure leading to As-As \( p_\perp \) bond formation across each cation spacer layer.

In contrast, a half-collapsed tetragonal (hcT) phase transition was recently reported for the 1144 material \( \text{CaKFe}_4\text{As}_4 \) [4] [Fig. 1(c)], where the periodic arrangement of Ca and K spacer layers produces two different kinds of As sites [5–7] and the tetragonal structure (\( P4/mmm \)) shows a layer-selective collapse upon application of pressure. First, at 4 GPa, the As-As \( p_\perp \) bonding across the Ca layer induces a cT transition with disappearance of superconductivity while a second collapsed transition across the K layer was predicted around \( \sim12 \) GPa. Furthermore, Ref. [4] showed that “hedgehog” [spin-vortex, Fig. 1(e)] magnetism had to be invoked in the pressure-dependent density functional theory (DFT) simulations to predict the observed structural transitions. This magnetic order has been recently measured upon electron-doping \( \text{CaKFe}_4\text{As}_4 \) [8].

The rare-earth-based \( \text{EuRbFe}_4\text{As}_4 \) and \( \text{EuCsFe}_4\text{As}_4 \) are also attracting growing attention due to the coexistence of Eu magnetism and bulk superconductivity as reported in Refs. [10–13]. However, the exact nature of the Eu magnetic order and its effect on the superconductivity remain to be elucidated, as well as possible \( \text{Eu}^{2+} \) to \( \text{Eu}^{3+} \) transitions previously observed for 122 systems [14]. The interactions between the localized Eu spins are expected to be sensitive to the lattice parameters and, in this respect, the half-collapse transition might influence the ground state, which stimulates a detailed study.

Predicting the appearance of possible cT transitions in \( \text{ThCr}_2\text{Si}_2 \)-structured intermetallic compounds is not only of relevance for the superconducting and magnetic properties of these materials but also for their potential superelastic behavior as has been recently shown [15].

In this paper, we systematically study via DFT calculations possible pressure-induced hcT transitions in a series of previously synthesized 1144 systems [5] with the following combinations of the spacer cations: \( \text{CaRb, CaCs, SrRb, SrCs, and BaCs,} \) as well as \( \text{EuRb and EuCs} \). We discuss the tendencies expected for the transition pressures in relation to the nature of the spacer cations, the underlying Fe-moment fluctuations, and possible magnetism in Eu for the latter two systems.

1We note that the exact crystal structure of \( \text{BaCsFe}_4\text{As}_4 \) is not completely clarified and this material can probably exist both in the 122 and in the 1144 forms due to a smaller difference in the cation radii, compared to other 1144 systems. Nevertheless, we include the 1144 phase of \( \text{BaCsFe}_4\text{As}_4 \) in our simulations to reveal general trends in the 1144 family of iron pnictides.

*Corresponding author: borisov@itp.uni-frankfurt.de

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Structural transitions under pressure are simulated using the projector-augmented wave method [16,17] as implemented in the VASP code [18–20] within the GGA exchange-correlation approximation [21]. For the two systems with Eu, strong correlations for the 4f states were included using two different GGA+U schemes [22,23]. Convergence of the properties of interest is achieved for a \((5 \times 5 \times 5)\) \(k\)-mesh and an energy cutoff of 600 eV. Increase of the cutoff up to 800 eV changes the \(c\)-lattice parameter by \(\sim 0.05\) Å and the critical pressure by less than 0.5 GPa (see Fig. 8 in Appendix B), which is an acceptable accuracy for studying the pressure-structure trends in the 1144 systems.

At low pressures, the structural prediction is done while imposing a “frozen” spin-vortex configuration of Fe moments Fig. 1(e), which simulates, to a first approximation, the imposing a “frozen” spin-vortex configuration of Fe moments in the 1144 systems. In general, the 1144 phase of \(\text{AeFe}_4\text{As}_4\) is stable when the difference in the ionic radii \(\Delta r = |r(\text{A}) - r(\text{A})|\) is larger than 0.3 Å. Possible Fe magnetic orders are shown in (d) stripe order and (e) “hedgehog” or spin-vortex order.

II. METHODS

Structural transitions under pressure are simulated using the projector-augmented wave method [16,17] as implemented in the VASP code [18–20] within the GGA exchange-correlation approximation [21]. For the two systems with Eu, strong correlations for the 4f states were included using two different GGA+U schemes [22,23]. Convergence of the properties of interest is achieved for a \((5 \times 5 \times 5)\) \(k\)-mesh and an energy cutoff of 600 eV. Increase of the cutoff up to 800 eV changes the \(c\)-lattice parameter by \(\sim 0.05\) Å and the critical pressure by less than 0.5 GPa (see Fig. 8 in Appendix B), which is an acceptable accuracy for studying the pressure-structure trends in the 1144 systems.

At low pressures, the structural prediction is done while imposing a “frozen” spin-vortex configuration of Fe moments Fig. 1(e), which simulates, to a first approximation, the effect of spin fluctuations, as shown in our previous work on \(\text{CaKFe}_4\text{As}_4\) [4,24]. The assumption of a particular underlying Fe magnetism is necessary for a correct prediction of the \(c\)\(T\) transition, even if the actual system doesn’t show any long-range magnetic order. Purely nonmagnetic calculations in Fe-based superconductors fail to reproduce the correct structural parameters [25–29]. For \(\text{EuRbFe}_4\text{As}_4\) and \(\text{EuCsFe}_4\text{As}_4\), we impose the fully ferromagnetic order along the [100] direction on the Eu sublattice, in addition to the Fe spin vortex. For selected pressures, the striplike order within each Eu layer is compared to the ferromagnetic one in terms of the enthalpy to identify possible first-order transitions related to Eu spins. Such antiferromagnetic order appears not to affect the optimized structure though.

III. RESULTS (ZERO PRESSURE)

For all systems studied here, we find that the assumption of a spin-vortex-type magnetism in our DFT calculations is crucial to reproduce the experimental structure at zero pressure as shown in Fig. 3 where the measured \(c\)- and \(a\)-lattice parameters are compared with the optimized ones. In contrast, \(c\) is severely underestimated by \(\sim(0.5–1.0)\) Å and \(a\) is overestimated by 2% in nonmagnetic calculations (dashed lines in Fig. 3). We note, however, that the theoretical values for the \(c\) parameter still

FIG. 2. (a), (b) Characteristic evolution of the non-spin-polarized band structure [31] and (c), (d) the energy position \(E\) of the antibonding As-As \(p_z\) orbital relative to the Fermi energy \(E_F\) across a \(hcT\) transition in \(\text{AeFe}_4\text{As}_4\) (\(\text{BaCsFe}_4\text{As}_4\) data are taken here as an example). Upon the first \(hcT\), only the As-As \(p_z\) antibonding band from the As facing the smaller cation layer, in this case \(\text{Ae}\) (blue lines), shifts abruptly above the Fermi level (plot c), while the band from As facing the larger cation layer (orange lines) remains occupied. This suggests that As-As bonds are strongly formed across the \(\text{Ae}\) layer. The second \(hcT\) at higher pressures is identified in the same fashion and, in contrast to the first \(hcT\), reveals a smooth shift of the corresponding As bands across the Fermi level (plot d).

Once the optimized 1144 structures under pressure are obtained, the electronic bands are calculated using the all-electron full-potential localized orbitals basis set (FPLO) code [30] with the GGA exchange-correlation functional (GGA\(+U\) for Eu-based systems). The critical pressure for a \(hcT\) transition is captured by monitoring the energy position of the antibonding As-As \(p_z\)-based molecular orbitals, which shift towards the Fermi level with increasing pressure. At the transition, these bands shift abruptly above the Fermi level [compare Figs. 2(a) and 2(b)] and the corresponding As-As \(p_z\) bonds are enhanced. This criterion was successfully applied to several \(\text{AeFe}_2\text{As}_2\) systems (\(\text{Ae} = \text{Ca, Sr, Ba}\) [3,26–28,32,33], as well as to \(\text{CaKFe}_4\text{As}_4\) [4]. As shown in Figs. 2(c) and 2(d), the As band shift corresponding to the second \(hcT\) phase at higher pressures is smoother than the one corresponding to the first \(hcT\) phase.
FIG. 3. Correlation between the zero-pressure $a$- and $c$-lattice parameters and the sum of the ionic radii $r_1 + r_2$ of the spacer cations ($r_1$ for $Ae$ and $Eu$ and $r_2$ for $A$ cations) for different 1144 iron pnictides. The measured (circles) and theoretical values (triangles) are shown for each system. Filled symbols indicate the parameters of the Eu-based systems and the star shows the low-temperature data for CaKFe$_4$As$_4$ [6]. The theory prediction is obtained using GGA and the spin-vortex configuration of Fe moments, following previous work [4], from which the data for CaKFe$_4$As$_4$ is taken for this plot. Dashed lines show results of purely nonmagnetic calculations.

deviates by (0.1–0.3) Å from the experimental result, where smaller deviations are observed for compounds with larger spacer cations. One possible source of discrepancy is the fact that the 1144 crystal structures were measured at room temperature [5], while DFT calculations formally correspond to the zero-temperature case, suggesting that thermal expansion can partially explain the observed deviations. For example, the thermal effect in the $c$ parameter of CaKFe$_4$As$_4$ can be as large as 0.16 Å when going from room temperature down to a few kelvins [6], so that the overall agreement between theory and experiment for this compound is acceptable (compare circles and triangle symbols in Fig. 3).

IV. FIRST HALF-COLLAPSED TETRAGONAL TRANSITION

Assuming a spin-vortex magnetic configuration, we performed pressure simulations for all 1144 materials over a wide range of pressures. The observed evolution of the in-plane, $a$, and out-of-plane, $c$, lattice parameters with applied pressure is qualitatively similar in all cases, despite large variations in their absolute values (see Figs. 4 and 5 as well as Figs. 9–13 in Appendix C). At the first hcT transition, the $c$ parameter and the As-As interlayer distances ($d_{As-As}$) across the cation plane where the collapse is happening decrease abruptly, while the in-plane parameter $a$ shows an upturn. The As-As antibonding orbitals lie above the Fermi level as illustrated in Figs. 2(b) and 2(c). As a matter of fact, the As-As distance right after the first hcT is very similar for all 1144 compounds and varies between (2.8–2.9) Å (Table I), which agrees with the chemical nature of cT transitions in these materials.

The estimated critical pressure for the first half-collapsed tetragonal transition ($P_{hcT}$ in Table I) shows clear trends as a function of the cation sizes. For all CaAFE$_4$As$_4$ ($A = K, Rb, Cs$) systems, the first hcT is observed near 5 GPa, which agrees with the fact that the As-As $p_z$ bonding is happening across the Ca layers in all three systems. When $Ae = Ca$ is replaced by Sr, $P_{hcT}$ is shifted to larger values, up to 14–15 GPa for $A = Rb$ and up to 18 GPa for $A = Cs$. Similar critical pressures for the first hcT are found here for Eu-based 1144 systems, which can be expected based on almost identical ionic radii of Sr and Eu (Table I). The maximal critical pressure $P_{hcT}$ of 34 GPa is found for BaCsFe$_4$As$_4$ with the largest alkaline-earth interlayer cation (Ba). From Table I, it can be observed that for a given $Ae$ cation, increasing the size of the A cation shifts the first hcT phase to higher pressures. Similar to the 122 pnictides, the half-collapsed transitions in the 1144 systems are more...
abrupt for smaller spacer cations and become broadened for cations with larger ionic radii.

One point to discuss is the consequences of invoking a spin-vortex Fe magnetic order for the structural relaxations under pressure even though these systems at zero pressure do not manifest magnetic order associated with the Fe site. This assumption may lead to slightly underestimated $P_{c1}$. Whereas we have discussed above the importance of introducing this “frozen” magnetic order, the calculations show, on top of the structural collapse, a “magnetic collapse” that is absent in the real system. Such a collapse may happen simultaneously to the structural collapse or at slightly different pressures as it is the case for CaRbFe$_4$As$_4$, CaCsFe$_4$As$_4$, or BaCsFe$_4$As$_4$ (see the grey area in Figs. 9, 10, and 13). This result may be interpreted in terms of the hcT transition being a broad transition smeared by spin fluctuations.

For the special cases of EuRbFe$_4$As$_4$ and EuCsFe$_4$As$_4$ we find the first hcT transition to occur across the Eu layer at a $P_{c1}$ of about 12.5 GPa and 14 GPa, respectively (Figs. 4 and 5). This prediction shows a rather good agreement with the most recent experimental study of pressure effects in EuRbFe$_4$As$_4$ and EuCsFe$_4$As$_4$ [13]. In our simulations, Eu magnetism [34] persists up to the highest studied pressure slightly above the second collapse. No drastic changes of the Eu oxidation state are observed in the whole pressure range. However, from the enthalpy analysis, we observe that the Eu order in EuRbFe$_4$As$_4$ transforms from FM to AFM near 3 GPa, but gets back to FM at higher pressures. In contrast, EuCsFe$_4$As$_4$ remains ferromagnetic in the whole pressure range (0–50) GPa, although the energy splitting between the two magnetic states varies significantly in between. These findings motivate a more detailed study including Eu with different $q$ vectors, which would clarify the ground state of the 4f-subsystem in these superconductors.

TABLE I. Predicted critical pressures $P_{c1}$ and $P_{c2}$ and As-As interlayer distances $d_{As-As}$ for the two hcT transitions in the 1144 series (data for CaKFe$_4$As$_4$ is taken from Ref. [4]). Note that the values provide indicative trends for the real systems. The ionic radii $r_1$ and $r_2$ are provided for the $Ae$ and $A$ species and Eu [same data in Fig. 1(a)]. The accuracy of the provided critical pressures lies within 0.5 GPa, as determined by the smallest pressure step and convergence of the simulations. Superconducting $T_c$ from Refs. [5,10] is shown for each compound together with the zero-pressure As height asymmetry $\eta_0 = \eta(P = 0)$ defined below by Eq. (1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$ (K)</th>
<th>$\eta_0$ (%)</th>
<th>$r_1$ (Å)</th>
<th>$P_{c1}$ (GPa)</th>
<th>$d_{As-As}$ (Å)</th>
<th>$r_2$ (Å)</th>
<th>$P_{c2}$ (GPa)</th>
<th>$d_{As-As}$ (Å)</th>
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<tr>
<td>CaKFe$_4$As$_4$</td>
<td>33.1</td>
<td>1.47</td>
<td>1.12</td>
<td>4</td>
<td>2.82</td>
<td>1.51</td>
<td>12.4</td>
<td>3.00</td>
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<tr>
<td>CaRbFe$_4$As$_4$</td>
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<td>1.48</td>
<td>1.12</td>
<td>5.25</td>
<td>2.79</td>
<td>1.61</td>
<td>26</td>
<td>2.95</td>
</tr>
<tr>
<td>CaCsFe$_4$As$_4$</td>
<td>31.6</td>
<td>1.54</td>
<td>1.12</td>
<td>5.8</td>
<td>2.79</td>
<td>1.74</td>
<td>58</td>
<td>2.81</td>
</tr>
<tr>
<td>SrRbFe$_4$As$_4$</td>
<td>35.1</td>
<td>0.76</td>
<td>1.26</td>
<td>14.5</td>
<td>2.88</td>
<td>1.61</td>
<td>24</td>
<td>2.95</td>
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<tr>
<td>SrCsFe$_4$As$_4$</td>
<td>36.8</td>
<td>0.72</td>
<td>1.26</td>
<td>18</td>
<td>2.78</td>
<td>1.74</td>
<td>48.5</td>
<td>2.88</td>
</tr>
<tr>
<td>BaCsFe$_4$As$_4$</td>
<td>26.0</td>
<td>0.43</td>
<td>1.42</td>
<td>34</td>
<td>2.91</td>
<td>1.74</td>
<td>39</td>
<td>2.97</td>
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<tr>
<td>EuRbFe$_4$As$_4$</td>
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<td>12.5</td>
<td>2.82</td>
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<td>1.74</td>
<td>48.5</td>
<td>2.87</td>
</tr>
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V. SECOND HALF-COLLAPSED TETRAGONAL TRANSITION

At higher pressures, the studied 1144 systems undergo a second hcT transition in our simulations. In our previous work...
on CaKFe$_4$As$_4$, we predicted the second structural collapse to occur around 12 GPa [4]. Here, we find that the second critical pressure $P_{c2}$ correlates with the size of the corresponding spacer cation (A = K, Rb, Cs), similar to the first hcT phase, where $P_{c1}$ rapidly increases in the series Ca, Sr, Eu, Ba. The lowest pressure for the second hcT is expected for CaKFe$_4$As$_4$, whereas the highest one (58 GPa) is found for CaCsFe$_4$As$_4$. For that reason, the second hcT transition might be difficult to access experimentally.

Interestingly, the second hcT transition has a relatively smaller effect on the lattice parameters (only a small kink is observed for $a$ and $c$) and is detected in our first-principles calculations again based on the analysis of the As-As 4$p_z$ orbital bonding, as demonstrated in Fig. 2. The characteristic As-As distance $d_{As−As}$ across the $A$ layer is around (2.8–3.0) Å after the collapse (Table I), which is on average slightly larger than $d_{As−As}$ across the $Ae$ layer at $P_{c1}$. The smallest critical $d_{As−As}$ of 2.81 Å is found for CaCsFe$_4$As$_4$, which correlates with the highest critical pressure $P_{c2}$ of 58 GPa. It should be emphasized that, for all studied 1144 systems, the Fe moments are fully suppressed long before the second hcT transition and play no role for this transition. The purely chemical nature of the second half collapse becomes then even more apparent.

VI. As HEIGHT ASYMMETRY

The main difference between the well-known 122 and the new 1144 (AeFe$_4$As$_4$) compounds is the broken glide-plane symmetry in the latter case, which creates two types of As sites. This asymmetry of As tetrahedra in the 1144 systems was found to play a leading role for the emergence of spin-vortex magnetism under electron doping [8]. We can characterize this structural property by the parameter

$$\eta = \frac{h(A) − h(Ae)}{h(A) + h(Ae)} \times 100\%,$$

with $h(Ae)$ and $h(A)$ being the As heights on the side of the $Ae$ and $A$ spacer layers, respectively [Fig. 6(a)].

We find that $h(A)$ is always larger than $h(Ae)$ for all studied 1144 pnictides. Also, the largest As height asymmetry at zero pressure is found for CaAFe$_4$As$_4$ ($\eta \approx 1.5\%$), while the asymmetry gradually decreases towards 0.4% in the series $Ae = Ca, Sr, Ba$. As evident from Table I, this fact is directly related to the difference in the ionic radii of the $Ae$ and $A$ cations.

Upon increasing pressure, the As height asymmetry $\eta$ grows continuously until the first hcT transition is reached where it shows a clear upturn [Fig. 6(b)]. The Fe magnetic collapse in the calculation is always accompanied by a sudden increase of the asymmetry parameter $\eta$, while the second hcT transition slightly reduces the asymmetry. These trends are observed for all studied systems.

Since a large As height asymmetry favors the “hedgehog” spin-vortex magnetic order in CaKFe$_4$As$_4$ [8] and increases under pressure for the studied 1144 systems [example in Fig. 6(b)], we can argue that pressure can stabilize the spin-vortex state relative to the usual stripe phase. On the other hand, BaCsFe$_4$As$_4$ is predicted here to have a more symmetric As-Fe-

![FIG. 6. (a) Definition of two different As heights in 1144 compounds. (b) As height asymmetry Eq. (1) vs pressure for EuRhFe$_4$As$_4$ and EuCsFe$_4$As$_4$. The critical pressures $P_{c1}$ and $P_{c2}$ for both hcT are indicated by the vertical dashed (EuRb) and dotted (EuCs) lines. Similar qualitative behavior is observed for other 1144 systems.](image)

As block than other 1144 systems and, for that reason, is likely to be closer to stripe order than the other 1144 compounds.

VII. CONCLUSION

We performed first-principles DFT simulations under pressure of various members of the 1144 family of Fe-based superconductors and found clear trends in the appearance of layer-selective hcT transitions as well as changes in the electronic properties of these systems. First of all, the critical pressures $P_{c1}$ and $P_{c2}$ for both consecutive hcT transitions increase rapidly with the cation size of the respective spacer layers. This agrees with the already known features of collapse in AFe$_2$As$_2$ systems ($Ae = Ca, Sr, Ba$) [27,32,35–38] and EuFe$_2$As$_2$ [14,39]. Second, even though the systems considered don’t show magnetic long-range order at the Fe sites, it is necessary to include Fe spins in a certain magnetic arrangement in simulations to correctly predict the structure in the low-pressure range. Depending on the chosen chemical composition, the Fe moments either survive or vanish across the structural collapse. In the case of BaCsFe$_4$As$_4$, the local Fe moments are suppressed even before the formation of As-As bonds.

Based on our calculations, the critical value for the As-As distance leading to a structural collapse varies between (2.8–3.0) Å, depending on the spacer cation size. The initial As-As distance at zero pressure determines then the critical pressure necessary for a structural transition. Finding ways of bringing the 1144 systems closer to the critical As-As separation already at zero pressure will eventually allow the observation of half-collapsed phases at ambient pressure in this class of materials.
For instance, the critical pressures at which the half collapses happen can be significantly reduced in uniaxially compressed systems as has been already observed in 122 systems [27,36,40], making the observation of this structural transition, in principle, possible for some of the explored compounds. Also, study of cT phases in other 1144 systems based on trivalent and monovalent spacer cations that were newly suggested to be stable at ambient pressure [41,42], e.g., LaKFe4As4 and EuKFe4As4, might be another promising research direction.

For the EuRbFe4As4 and EuCsFe4As4 systems, the character of the half-collapsed transition and the critical pressures are similar to the Sr-based systems, which is explained by almost identical ionic radii of Eu and Sr 2+ cations. The Eu magnetism is stable across both collapse transitions, with the 4f moments staying close to the expected value of 7\(\mu_B\). Very recent experimental observations [13] seem to confirm the predicted pressure trends. In addition, our simulations suggest that the ordering vector of Eu may change under pressure in the EuRbFe4As4 system.

In view of the novel magnetism discovered recently in electron-doped CaKFe4As4 [8], the rest of the 1144 family is worth studying in terms of their magnetic properties. CaRbFe4As4 and CaCsFe4As4 have the largest As height asymmetry and are therefore promising candidates for a spin-vortex magnetic crystal with a high ordering temperature. Search for other 1144 materials with a larger difference in the two cation sizes, leading to a stronger asymmetry between the As sites, appears to be a natural next step. In contrast, 1144 systems with bigger cations, such as BaCsFe4As4, have a more symmetric structure and are likely to be closer to stripe order than more asymmetric 1144 compounds. The motivation to look for further spin-vortex ordered Fe-based systems is the recently proposed relation of this magnetic order to the strong unconventional superconductivity in 1144 systems.

Furthermore, this is a unique example of a noncollinear double-\(Q\) magnetic order in iron pnictides and presents an important part of their general phase diagram [8].

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APPENDIX A: ROLE OF LOCAL Fe MOMENTS

As emphasized in the main text, the presence of local Fe moments is a necessary ingredient of our simulations, since otherwise the predicted structures would have a largely underestimated \(c\)-lattice parameter, which, in case of CaRbFe4As4, even leads to the formation of As-As bonds near Ca already at zero pressure, confirmed by the band structure analysis (Fig. 7). We have also performed some test calculations with Fe magnetic orders other than spin vortex and found that the best agreement with structural parameters from experiment is achieved assuming a spin-vortex arrangement of Fe moments.

APPENDIX B: ACCURACY OF STRUCTURE OPTIMIZATION

Regarding the accuracy of our pressure simulations, as mentioned in the main text and illustrated in Fig. 8, the increase of the energy cutoff from 600 eV to 800 eV leads to rather small changes in the lattice parameters, which do not affect the general trends in the 1144 family.

APPENDIX C: STRUCTURE-EVOLUTION UNDER PRESSURE

The pressure-dependence of the in-plane (\(a\)) and out-of-plane (\(c\)) lattice parameters along with the As-As distances

![ FIG. 7. Comparison of the As-4\(p_z\) orbitals for CaRbFe4As4 structures relaxed at zero pressure (a) using the spin-vortex Fe order or (b) nonmagnetically. In the latter case, the As-As bonds across Ca are already formed, as opposed to the former structure, which emphasizes the importance of spin-vortex fluctuations in 1144 systems. For both relaxed geometries, the band structure is non-spin-polarized [31]. The color code is the same as in Fig. 2.](image)

![ FIG. 8. Comparison of the calculated pressure-dependent \(c\)-lattice parameter of CaCsFe4As4 for two different energy cutoff values 600 eV and 800 eV.](image)
FIG. 9. Pressure evolution of (a) lattice parameters \(a = b\) and \(c\), (b) volume and \(c/a\) ratio, and (c) As-As distances across both hcT transitions for CaRbFe\(_4\)As\(_4\). The critical pressures of the two half-collapsed transitions are marked by vertical dashed lines and the pressure range between the first hcT and the subsequent collapse of Fe moments is indicated by shading.

FIG. 10. Pressure evolution of (a) lattice parameters \(a = b\) and \(c\), (b) volume and \(c/a\) ratio, and (c) As-As distances across both hcT transitions for CaCsFe\(_4\)As\(_4\). The critical pressures of the two half-collapsed transitions are marked by vertical dashed lines and the pressure range between the first hcT and the subsequent collapse of Fe moments is indicated by shading.

FIG. 11. Pressure evolution of (a) lattice parameters \(a = b\) and \(c\), (b) volume and \(c/a\) ratio, and (c) As-As distances across both hcT transitions for SrRbFe\(_4\)As\(_4\). The critical pressures of the two half-collapsed transitions are marked by vertical dashed lines. Here, the first hcT and the collapse of Fe moments occur simultaneously.
transitions for BaCsFe$_4$As$_4$. The critical pressures of the two half-collapsed transitions are marked by vertical dashed lines. Here, the first hcT and the collapse of Fe moments occur simultaneously.

across both collapse transitions is summarized for all studied 1144 systems in Figs. 4, 5, and 9–13. At the first half collapse, the qualitative behavior is the same for all CaFe$_2$As$_2$ compounds, but for SrRbFe$_4$As$_4$ and SrCsFe$_4$As$_4$ the structural collapse transition overlaps with the suppression of Fe moments. BaCsFe$_4$As$_4$ seems to be an extreme case, since it shows the magnetic collapse first and then undergoes an actual half collapse at a somewhat higher pressure.


[31] Although it is absolutely necessary to include Fe magnetic order in the structural optimization, the subsequent analysis of As orbitals relevant to the half-collapsed tetragonal transition can be successfully done based on a nonmagnetic band structure, since the As sites are barely spin-polarized by the neighboring Fe moments. The only exceptions are EuRbFe4As4 and EuCsFe4As4 single crystals as seen by 57Fe Mössbauer spectroscopy, Phys. Rev. B 90, 085110 (2014).

[32] Please note that in our simulations we didn’t consider more complex cases of Eu magnetism than ferromagnetism and striplike antiferromagnetism.


[39] C. Tresca and G. Profeta, Compressed tetragonal phase in XFe2As2 (X = Na, K, Rb, Cs) and in the alloy Na0.5K0.5Fe2As2, Phys. Rev. B 95, 165129 (2017).


