What is the minimal model of magnetic interactions in Fe-based superconductors?

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Using noncollinear first-principles calculations we perform a systematic study of the magnetic order in several families of ferropnictides. We find a fairly universal energy dependence on the magnetization order in all cases. Our results confirm that a simple Heisenberg model fails to account for the energy dependence of the magnetization in couple of ways: first a biquadratic term is present in all cases and second the magnetic moment softens depending on the orientation. We also find that hole doping substantially reduces the biquadratic contribution, although the antiferromagnetic stripe state remains stable within the whole range of doping concentrations, and thus the reported lack of the orthorhombicity in Na-doped BaFe$_2$As$_2$ is probably due to factors other than a sign reversal of the biquadratic term. Finally, we discovered that even with the biquadratic term, there is a limit to the accuracy of mapping the density functional theory energetics onto Heisenberg-type models, independent of the range of the model.

I. INTRODUCTION

Fe-based superconductors are only the second family, after cuprates, of known high-$T_c$ superconductors (HTSC). The parent compounds of these materials exhibit magnetic ordering at low temperatures, and in their phase diagrams the magnetic phase is proximate to the superconducting phase. The two orders are intimately related as the superconductivity emerges when magnetism is suppressed, for instance, by doping. Therefore, it is generally believed that magnetic fluctuations in these systems are the likely driver of the pairing mechanism.$^{1,2}$ Magnetic order is also accompanied (with a notable exception discussed later) by a structural phase transition, and there are compelling arguments that this is also driven by magnetism: (1) density functional calculations quantitatively reproduce the observed orthorhombic distortions, including the amplitude and the counterintuitive sign, and also reproduce a qualitatively different distortion in FeTe$^3$ (2) the same calculations fail to produce any distortion in the absence of magnetism. The seemingly counterintuitive fact that the structural instability sometimes occurs at a temperature slightly above the magnetic transition is in fact consistent with this concept, because long range magnetic order is sufficient, but not necessary, for breaking the global $C_4$ symmetry: it is enough to unequally populate magnetic fluctuations with different $k$-vectors. These can be described as fluctuating domain walls in an itinerant picture$^4$ or as “order-from-disorder” in the local-moment picture (see Refs. $^5$-$^8$ for a review, see Ref. $^8$). This picture is also consistent with observations of fluctuations breaking charge$^9$ and spin$^{10}$ $C_4$ symmetry locally well above the Néel temperature.

The local-moment picture has the advantage of being analytically solvable and simple; Heisenberg-like models are a popular way to approach the magnetism of Fe-based HTSCs. This can be considered a reasonable approach since, with a sufficient number of parameters, any sort of magnetic interaction can be mapped onto a local moment model. The simplest possible model is a Heisenberg-type interaction between the first and second nearest
neighbors. This model has the desired property that symmetry breaking always occurs above the Néel temperature, although this splitting diminishes as the magnetic interaction becomes more three dimensional. While the model replicates some physical properties of Fe-based HTSCs, there is a serious problem that is often overlooked. The essential physics of this approach can be described as follows: an Fe plane can be viewed as a bipartite lattice where the only interaction within each sublattice is the second nearest neighbor exchange $J_2$, while the only interaction between the sublattices is $J_1$. As illustrated in Fig. 1, exchange interaction constant $J_2$, if $J_2 > J_1/2$, generates a checkerboard antiferromagnetic (AFM) pattern in each sublattice, while the interaction between the sublattices cancels completely, which holds not only for an arbitrary $J_1$, but for any Heisenberg interaction of an arbitrary range. In Ref. 5 it was shown that, after integrating out quantum fluctuations, a nearest neighbor biquadratic term of the form $K(S_i \cdot S_j)$ appears in the effective Hamiltonian, with $K > 0$ and of the order $10^{-4} J$. This lifts the infinite degeneracy of the ground state, leaving a double degenerate state of ferromagnetic stripes running along one of the two crystallographic directions with AFM alternation, matching the ground state of the ferropnictides of interest. However, the small amplitude of $K$ is unphysical, making this result purely academic and not applicable to any real material.

There is another profound problem with the Heisenberg model. Even though it formally generates the correct ground states for ferropnictides, it fails to explain the double stripe structure of FeTe: to do so requires introducing the third nearest neighbor exchange $J_3$, which is found to be of the same order as $J_1$ and $J_2$, a result inconsistent with the superexchange picture. Even worse, in order to fit both the ground state and the spin wave spectra, one needs to split the nearest neighbor exchange into two inequivalent parameters, $J_{1a}$ and $J_{1b}$. The two parameters end up being different from each other, sometimes even changing sign. This implies that not only do the exchange constants change qualitatively from compound to compound, but that they have a strong, counterintuitive dependence on temperature; the inequivalent parameters $J_{1a}$ and $J_{1b}$ above the Néel temperature, become equivalent as required by symmetry, i.e. $J_{1a} = J_{1b}$. This bizarre and inconsistent behavior is the death knell for using the superexchange theory to model the Fe-based HTSCs, as there is no plausible physical mechanism that can explain the dramatic temperature dependence of the superexchange constants.

Density functional theory (DFT) calculations, when mapped onto the same Heisenberg model, yield similar exchange constants, including the splitting of the nearest neighbor exchange. This indicates that DFT is correct in its description of the Fe-based HTSCs (it can quantitatively explain the spin wave spectrum, for example), suggesting that this methodology can be used to resolve the exchange constants conundrum. In fact the necessary calculations have been reported at a very early stage, yet were largely overlooked. Instead of an unphysical model with only superexchange terms, the same DFT calculations can be mapped with good accuracy onto an isotropic ($J_{1a} = J_{1b}$) Heisenberg model which includes a biquadratic term (formally the same as found in Ref. 3 with an amplitude of $K \sim J_1, J_2$). Moreover noncollinear DFT calculations with one magnetic sublattice rotated with respect to the other, see Fig. 1, can only be mapped onto this model. It was then shown that this biquadratic, isotropic Hamiltonian with temperature-independent parameters is an excellent model of the magnetic properties of Fe-based HTSCs at any temperature, including the spin wave spectra. The model also is consistent with an orthorhombic transition occurring above the magnetic one.

These discoveries yielded a much more robust description of the magnetic behavior of the Fe-based HTSCs, which includes a consistent explanation of the orthorhombic distortion. Instead of a minuscule “order from disorder” term appearing to drive the physics of these systems, we have a sizable biquadratic term on the mean field level. So what is missing at this point? To date, there is no body of information about the biquadratic term. Important questions include: how variable is it from compound to compound? How does it depend on doping? Can it change sign, leading to a noncollinear ground state while preserving tetragonal symmetry? At the present moment only some answers are available. In Ref. 14 only two compounds were studied, and the uncontrollable atomic spheres approximation was used. While there is no question that the obtained results were qualitatively correct, their quantitative accuracy remained unclear. Beyond that, in Ref. 10 it was demonstrated that the biquadratic term depends on the details of a material’s band structure. Using accurate full potential DFT calculations with linear muffin tin orbitals, it was shown that the biquadratic term is negative in stoichiometric KFe$_2$Se$_2$, a hypothetical material. The term is also dependent on the size of the local Fe moment (or, equivalently, the Fe-As/Se bond-length distance), again indicating the necessity for accurate calculations. Finally, the ultimate question that can be posed is whether the total energy is mappable onto the pair interaction at all, linear or quadratic in $S_i \cdot S_j$. This is always taken for granted, but there is no a priori reason for that to be true in an itinerant system.

In DFT, the change in energy between different magnetic patterns accumulates via integration over the entire occupied portion of the Fe band, which extends several eV below the Fermi energy. Profound orbital reordering induced by magnetism leads to the observed stripe order being lower in energy compared to other patterns, and by extension affects the exchange constants obtained by mapping. These complex changes in the electronic structure are responsible for the anisotropy in the $J$–only model and for the large biquadratic term in the $J – K$ model, and also for the longer range interactions in FeTe.
This contrasts with the simplistic superexchange model where both $K$ and $J_3$ appear only as higher order terms and must be much smaller than $J_1$ and $J_2$.

Resolving the incomplete understanding of the biquadratic term has become even more important after an intriguing experimental report that the orthorhombic distortion becomes even more important after an additional parameter is not fixed and could change upon doping. The authors favor the plausible explanation that the biquadratic term changes sign in that region, generating the non-collinear structure shown in Fig. 1 of Ref. [19]. An alternative explanation would be that the magnetoelastic coupling that drives the orthorhombic distortion becomes small and the (still existing) C$_2$ symmetry breaking goes undetected.

The former explanation, that the biquadratic term changes sign upon doping, was supported by the calculations of Chubukov and Eremin [20] who derived a biquadratic term in the linear response regime. The problem with this approach is that it contradicts the DFT finding that the energy associated with magnetic interaction accumulates over a large energy window, and that the local moments of Fe remain large throughout the entire phase diagram. On the other hand, knowing that magnetic ordering has a strong effect on the density of states and the orbital composition of the Fe bands, it is plausible that the sign of the biquadratic interaction parameter is not fixed and could change upon doping. As previously discussed, the results of Ref. [16] show that for the hypothetical KFe$_2$Se$_2$ compound, which can be viewed as a case of extreme hole doping, the biquadratic term does indeed change sign.

Our goal in this paper is to make a systematic investigation of the biquadratic interaction in representative Fe-pnictide and Fe-chalcogenide families to address the variability of the biquadratic interaction. For this investigation, we use the all-electron, full-potential Linear Augmented Plane Waves (FLAPW) method. We find that the biquadratic parameter can vary within large limits, but that it does not change sign in the accessible ranges of doping. We conclude, in particular, that the observed lack of an orthorhombic distortion in the Na-doped BaFe$_2$As$_2$ compound in Ref. [19] is likely due to the inaccessibility of the tetragonal symmetry breaking by the experimental tools used in that work.

### II. METHODS

We investigate the magnetic order in representative compounds from different families of the iron-based superconductors: FeSe for the 11 family; LiFeAs and NaFeAs for the 111 family; BaFe$_2$As$_2$, BaFeCoAs$_2$, CaFe$_2$As$_2$, SrFe$_2$As$_2$, KFe$_2$As$_2$, and KFe$_2$Se$_2$ for the 122 family; and LaFeAsO for the 1111 family. The magnetic order is modeled using the $J_1 - J_2 - K$ model Hamiltonian,

$$H = J_1 \sum_{nn} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{nn} \mathbf{S}_i \cdot \mathbf{S}_j - K \sum_{nn} (\mathbf{S}_i \cdot \mathbf{S}_j)^2.$$  (1)

We use the experimentally determined crystal structures when available; for the hypothetical material KFe$_2$Se$_2$ we used the lattice constants from Ref. [16]. A summary of the symmetry groups, lattice constants, and Fe-Fe and Fe-As(Se) bond lengths for all the materials is found in Table I. The FeAs(Se) planes are stacked along the c-axis separated by a non-magnetic filler plane, except for the 11 compound FeSe which consists only of FeSe planes. The Fe layers form a two-dimensional square lattice and the ground state magnetic order has been confirmed both experimentally and theoretically to be AFM stripe order, as schematically represented in Fig. [1] (stripe order corresponds to $\theta = 0$ or $\theta = 180^{\circ}$). In all cases in order to accommodate the AFM stripe pattern we double the cell in the xy-plane ($\sqrt{2} \times \sqrt{2}$).

In order to study the biquadratic coupling we allow the angle $\theta$ between the two Fe sublattices to vary. The angle $\theta$, as depicted in Fig. [1] gradually interpolates between two equivalent stripes states with $q = (1,0)$ and $q = (0,1)$. According to the biquadratic model in Eq. (1) the angular energy dependence $\Delta E(\theta) = E(\theta) - E(0)$ of the 11, 111, and 1111 families is predicted to be,

$$\Delta E(\theta) = 4K \sin^2 \theta.$$  (2)

The 122 family belongs to a centered symmetry group, and therefore rotating $\theta$ by $180^\circ$ takes the system from one stripe pattern to another, inequivalent one. The two differ by the stacking order along c and the energy difference is proportional to the interplanar exchange constant $J_{\perp}$. Taking this into account, the angular energy dependence for the 122 family is,

$$\Delta E(\theta)_{122} = 4K \sin^2 \theta - 16J_{\perp} \sin^2 \left( \frac{\theta}{2} \right).$$  (3)

This splits the degeneracy of $\theta = 0$ and $\theta = 180^\circ$ states by $16J_{\perp}$.

In order to calculate the angular energy dependence we perform fully noncollinear first-principles calculations using the ELK code [22]. ELK implements density functional theory (DFT) within a FLAPW basis set with local orbitals. In our calculations we use the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [23]. ELK allows constrained magnetic moment calculations where the moment direction and/or magnitude can be fixed. To study the effect of hole doping on BaFe$_2$As$_2$, we use the virtual crystal approximation (VCA) in the standard way, in which homogeneous doping is achieved by replacing the Ba atoms with fictitious atoms of fractional nuclear charge between those of Ba and Cs. The density of states (DOS) around the Fermi energy of BaFe$_2$As$_2$ is

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TABLE I. Summary of the crystallographic symmetry groups, lattice structure (lattice constants \( a \) and \( c \), and fractional coordinates \( z \) of the non-magnetic planes), Fe-Fe/Fe-As(Se) bond lengths, the fitted parameters of Eqs. 2 & 3 and the energy change due to the softening of the magnetic moment for all the studied compounds.

| Compound          | Sym. Group | \( a \) (Å) | \( c \) (Å) | \( z_{\text{As,Se}}^\text{E}(z_{\text{Li,Na}},\text{La}) \) (frac.) | \( d_{\text{Fe-Fe}} \) (Å) | \( d_{\text{Fe-As(Se)}} \) (Å) | \( M(0) \) (\( \mu_B \)) | \( K \) (meV) | \( J_\perp \) (meV) | \( E(0)|\mu(0)| - E(0)|\mu(0)| \) (meV) |
|-------------------|------------|-------------|-------------|----------------------------------------------------|-----------------|-----------------|----------------|---------|-----------|-------------------------------|
| FeSe              | P4/nmm     | 3.803       | 6.084       | 0.2708 (-)                                          | 2.689           | 2.516           | 2.72           | 9.67    | -0.04     |                                |
| LiFeAs            | P4/nmm     | 3.793       | 6.366       | 0.2365 (0.6541)                                     | 2.682           | 2.421           | 1.85           | 9.75    | 4.21      |                                |
| NaFeAs            | P4/nmm     | 3.949       | 7.040       | 0.2028 (0.6460)                                     | 2.793           | 2.437           | 2.18           | 15.43   | 7.30      |                                |
| LaFeAsO           | P4/nmm     | 4.037       | 8.742       | 0.1513 (0.6415)                                     | 2.854           | 2.413           | 2.09           | 13.24   | 4.97      |                                |
| SrFe$_2$As$_2$    | I4/mmm     | 3.930       | 12.324      | 0.3604 (-)                                          | 2.779           | 2.390           | 1.94           | 10.57   | 0.79      | 2.78                          |
| CaFe$_2$As$_2$    | I4/mmm     | 3.896       | 11.683      | 0.3665 (-)                                          | 2.755           | 2.376           | 1.83           | 9.39    | 1.33      | 1.58                          |
| KFe$_2$As$_2$     | I4/mmm     | 3.842       | 13.860      | 0.3525 (-)                                          | 2.716           | 2.389           | 2.46           | 6.36    | 0.40      | 9.48                          |
| KFe$_2$Se$_2$     | I4/mmm     | 3.914       | 14.037      | 0.3434 (-)                                          | 2.767           | 2.355           | 2.47           | 3.29    | -0.05     | 0.48                          |
| BaFe$_2$As$_2$    | I4/mmm     | 3.942       | 13.021      | 0.3545 (-)                                          | 2.791           | 2.397           | 1.99           | 10.84   | 0.23      | 3.33                          |
| Ba$_{0.9}$Na$_{0.1}$Fe$_2$As$_2$ | I4/mmm | 3.942 | 13.021 | 0.3545 (-) | 2.791 | 2.397 | 1.99 | 10.84 | 0.23 | 3.33 |
| Ba$_{0.8}$Na$_{0.2}$Fe$_2$As$_2$ | I4/mmm | 3.942 | 13.021 | 0.3545 (-) | 2.791 | 2.397 | 1.99 | 10.84 | 0.23 | 3.33 |
| Ba$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$ | I4/mmm | 3.942 | 13.021 | 0.3545 (-) | 2.791 | 2.397 | 1.99 | 10.84 | 0.23 | 3.33 |
| Ba$_{0.6}$Na$_{0.4}$Fe$_2$As$_2$ | I4/mmm | 3.942 | 13.021 | 0.3545 (-) | 2.791 | 2.397 | 1.99 | 10.84 | 0.23 | 3.33 |
| Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ | I4/mmm | 3.942 | 13.021 | 0.3545 (-) | 2.791 | 2.397 | 1.99 | 10.84 | 0.23 | 3.33 |
| Ba$_{0.4}$Na$_{0.6}$Fe$_2$As$_2$ | I4/mmm | 3.942 | 13.021 | 0.3545 (-) | 2.791 | 2.397 | 1.99 | 10.84 | 0.23 | 3.33 |
| BaFe$_{0.5}$Co$_{0.5}$As$_2$ | I4/mmm | 3.942 | 13.021 | 0.3545 (-) | 2.791 | 2.397 | 1.99 | 10.84 | 0.23 | 3.33 |

Convergence was checked as a function of the size of the k-point mesh. Different size Monkhorst-Pack k-point grids were used for the different families of compounds: 9 \( \times \) 9 \( \times \) 8 for 11; 9 \( \times \) 9 \( \times \) 8 for 111; 8 \( \times \) 8 \( \times \) 9 for 122; and 6 \( \times \) 6 \( \times \) 4 for 1111 respectively. Due to the small energy differences the energy convergence criterion was set to \( 10^{-7} \) Ha.

III. RESULTS AND DISCUSSION

We checked the relative energies of the different magnetic orders. In all cases we obtained that in the FM configuration the magnetic moment collapses and this configuration is much higher in energy than the AFM configurations. The energy of the checkerboard AFM configuration was found to be higher in energy than the AFM stripe ground state; hole doping decreased the relative energy difference, although the AFM stripe state remained as the ground state configuration.

The angular dependence of the energy difference \( \Delta E(\theta) = E(\theta) - E(0) \) for different compounds is plotted in Fig. 2(a). It is clear that biquadratic coupling is present in all of these compounds. We fitted these results to Eq. 2 for the 11, 111, and 1111 families and Eq. 3 for the 122 family. The fitted parameters are summarized in Table 1.

The angular energy dependence of the materials, with the exceptions of KFe$_2$Se$_2$ and BaFe$_{0.5}$Co$_{0.5}$As$_2$, follows a similar pattern, with the energy difference between the ground stripe state and the least favorable \( \theta = 90^\circ \) configuration varying between 30-60 meV/Fe. Our results for LaFeAsO, BaFe$_2$As$_2$, and KFe$_2$Se$_2$ agree well with previous calculations. The biquadratic interaction constant \( K \) is fairly large and positive in most materials (again excepting KFe$_2$Se$_2$ and BaFe$_{0.5}$Co$_{0.5}$As$_2$) and of the same order as \( J_1 \) and \( J_2 \). One of the factors that influences \( K \) is the Fe-Fe bond length, as \( K \) tends to be larger in compounds which have a greater Fe-Fe distance such as LaFeAsO, NaFeAs and BaFe$_2$As$_2$. The interlayer coupling \( J_\perp \) in the 122 family is about an order of magnitude smaller than \( K \), and the constant varies from material to material.

BaFe$_{0.5}$Co$_{0.5}$As$_2$ and KFe$_2$Se$_2$ are exceptions to the above trends. BaFe$_{0.5}$Co$_{0.5}$As$_2$ was calculated using the VCA and represents electron doping of BaFe$_2$As$_2$. This doping softens the ground state moment by 36% and destabilizes the local moment for angles \( 45^\circ < \theta < 150^\circ \), in which range it collapses. This level of electron doping also suppresses the biquadratic and interplanar interactions, reducing both by an order of magnitude. KFe$_2$Se$_2$, on the other hand, exhibits a negative biquadratic interaction term in agreement with the results of Ref. 10. While it exhibits a negative \( K \), bulk KFe$_2$Se$_2$ is a hypothetical material that cannot be stabilized in experiment, so here it just serves as a proof of concept that a negative \( K \) is possible.

The softening of the moments shown in Fig. 2(b) contributes to \( \Delta E(\theta) \) in a non-trivial way. Modeling the variation of the magnetic moments necessitates the in-
The angular dependence of the energy for compounds belonging to the 11, 111, 122, and 1111 families of superconductors. (b) The angular dependence of the normalized moments belonging to the 11, 111, 122, and 1111 families of superconductors. (c) The angular dependence of the energy for various levels of doping of the 122 compound BaFe$_2$As$_2$. (d) The angular dependence of the normalized moments for different doping levels of the 122 compound BaFe$_2$As$_2$.

FIG. 2. (Color online) The angular energy dependence for various levels of doping of the 122 compound BaFe$_2$As$_2$. A discussion of the validity of using the VCA to address the effect of hole-doping on the biquadratic term is included in the Appendix. As is clear in the figure, the biquadratic interaction constant $K$ strongly depends on the degree of hole-doping in the material. Going from an undoped system to $x = 0.6$ results in a 60% decrease in $K$. Extrapolating the hole doping of BaFe$_2$As$_2$ to the extreme $x = 1$ case, the biquadratic constant $K$ however does not invert and instead nearly vanishes. Because of the similarity of results in other materials, we expect that doping via the VCA would yield similar results in other materials. Of course, in the case of extreme hole doping it is necessary to allow the lattice constant and atomic positions to relax. Here KFe$_2$As$_2$ is an example of extreme hole doping, and if the experimental lattice constants are used, the biquadratic term is 6.3 meV, in contrast to the vanishing biquadratic term inferred from extrapolating the VCA results discussed above. The Fe-Fe and Fe-As(Se) bond lengths, influenced by the hole-doping level, plays a role in determining $K$. This is in...
line with the results of Ref. 16, where \( K \) for KFe\(_2\)Se\(_2\) depended strongly on the internal coordinate \( z_{\text{Se}} \).

Regarding the question of whether it is valid to assume that magnetic interactions can be accurately mapped to a pairwise Hamiltonian by just including an arbitrary number of terms, one can address this issue by comparing the two magnetic patterns shown in Fig. 3. It was pointed out\(^{26}\) that these configurations are degenerate on the mean field level for any Heisenberg model of arbitrary range. Being collinear, the configurations remain degenerate after the inclusion of the biquadratic interaction term, which can be lifted by either magnetoelastic coupling or by integrating out fluctuations.\(^{26}\) We calculated the energy difference between these two configurations for FeTe using the experimental high-temperature structure (tetragonal) and found that the experimentally observed double stripe pattern is lower in energy than the square pattern by 8 meV/Fe, a small, but by no means irrelevant or negligible number. The degeneracy is only lifted on the level of the 4th order (square) ring exchange, which in the localized Hubbard limit is of the order of \( t^4/U^3 \), as compared to the nearest-neighbor superexchange terms which are of the order of \( t^2/U \).

Another consequence of attempting to map to the classical Heisenberg \( J_1-J_2-J_3 \) model is that it does not predict the double stripe or square pattern to be the ground state of FeTe,\(^{16}\) instead predicting spiral phases for large \( J_3 \). In Ref. 26 it was pointed out that for some parameter range collinear structures may be stabilized over the spiral ones because of quantum fluctuations. In contrast, our calculations clearly indicate that the sizeable biquadratic interactions, present in the parent Fe-based HTSC compounds, completely exclude spiral phases already on the mean field level. Moreover, DFT calculations strongly favor double stripes over squares, despite the fact that fluctuations work in the opposite way.\(^{26}\) Our calculations strongly suggest that the fact that the experimental structure in FeTe appears to be double stripe is not related to magnetoelastic coupling, as suggested in Ref. 26, but is instead due to itinerant effects not captured by the Heisenberg Hamiltonian.

Returning to the experiment from Ref. 19, we can use our results to comment upon the experimental data. Our results do not support the proposed noncollinear magnetic configuration in Na-doped BaFe\(_2\)As\(_2\). Why might this be? One possibility is that, as discussed in Sec. 1, there might not be a reentrant \( C_4 \) transition in Na-doped BaFe\(_2\)As\(_2\) and so it would be unnecessary to argue for a change in the magnetic state. The argument for the reentrant \( C_4 \) transition is based on nuclear diffractogram measurements in which an apparent recombination of the nuclear Bragg peaks at low temperatures is observed. However the Bragg peaks are quite broad, and so a reduction, but not a complete removal, of the orthorhombic distortion would also be consistent with the data. Another possibility is that the reentrant \( C_4 \) transition is not accompanied by a noncollinear magnetic configuration. The authors of Ref. 19 put forth a model of the \( C_4 \) transition with two magnetic configurations fitting well to measured x-ray diffraction data: the noncollinear configuration presented in the main body of the paper and also a collinear stripe state. The noncollinear model is preferred as it already has \( C_4 \) symmetry. The authors comment that a linear combination of spin density waves that produce stripes along the \( x \) and \( y \) directions also restores \( C_4 \) symmetry. Without more information, there is no reason to prefer one magnetic configuration over the other.

Therefore, in light of our results, there remains two plausible interpretations of Ref. 19. The first is that the orthorhombic distortion of Na-doped BaFe\(_2\)As\(_2\) is reduced at lower temperatures, but ultimately retains \( C_2 \) symmetry. This is the interpretation we prefer, as it is the simpler way in which \( C_2 \) symmetry would be preserved. A higher resolution measurement of the temperature dependence of the nuclear Bragg peaks is necessary to rule this interpretation out. The second is that the \( C_4 \) transition does occur, but that the magnetic order remains striped and modulates between \( x \) and \( y \) oriented stripe patterns. Additional follow-up studies are necessary to ultimately resolve this question.

### IV. Conclusions

We confirmed that biquadratic coupling is universally present in Fe-based superconductors. It is of the same order of magnitude as the superexchange interactions. In the studied materials, the biquadratic term is modestly affected by the softening of the magnetic moment, is influenced by the Fe-Fe and Fe-As bond lengths, and depends on the doping, which underlines the biquadratic term’s itinerant origin. We find that even in the case of extreme hole doping, no experimentally realized material exhibits a change of sign in the biquadratic term, so the collinear AFM stripe state is energetically preferred in all instances. Therefore, the apparent experimental observa-
tion of a reentrant $C_4$ transition in Na-doped BaFe$_2$As$_2$ is likely to be an artifact due to the inaccessibility of measuring the $C_4$ symmetry at low temperatures with the experimental tools.

Our results show that in the realm of Fe-based superconductors the naive Heisenberg model is a rather poor approximation. The biquadratic exchange plays an essential role and cannot be neglected in any model calculation describing these compounds. In addition there are deviations, as observed for FeTe, from the general pairwise interaction model for linear and biquadratic terms of an arbitrary range. In FeTe it is these terms that stabilize the experimentally observed double stripe in the calculations, and not the magnetoelastic coupling, as conjectured before. It remains to be seen whether these interesting features are specific to the parent compounds of Fe-based HTSCs or are more common than previously expected. Further calculations and studies should aid in answering this question.

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Appendix A: Validity of the virtual crystal approximation (VCA)

We confirmed the validity of the VCA by doing the following test calculations using BaFe$_2$As$_2$. To begin, we directly substituted a Na atom for a Ba atom (the two Ba sites are equivalent via symmetry), keeping the lattice and internal parameters set to the values taken from experiment, and calculated $\Delta E(\pi/2)$. For Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ we obtained $\Delta E(\pi/2) = 11.4$ meV, which is about a factor of two smaller than the VCA $x = 0.5$ result of 21.5 meV.

To see how structural deformations affect $\Delta E(\theta)$, we relaxed the structures in the pseudopotential-based software suite VASP. In VASP we used projector augmented wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof generalized gradient approximation to DFT. Our BaFe$_2$As$_2$ calculations in the main text took the internal parameter $z_{\text{As}}$ from experiment. We want to make a proper comparison between VCA and a relaxed structure with Na substitutions, so in order to do this we relaxed the internal parameter $z_{\text{As}}$ for both undoped BaFe$_2$As$_2$ and doped Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ in VASP and imported the coordinates into ELK. We then calculated $\Delta E(\pi/2)$ for BaFe$_2$As$_2$ in the VCA with $x = 0.5$ using the relaxed atomic positions found for undoped BaFe$_2$As$_2$, and then calculated $\Delta E(\pi/2)$ for Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ using both the relaxed structure for undoped BaFe$_2$As$_2$ and the relaxed structure for Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$. The VCA result with the undoped structure is $\Delta E(\pi/2) = 10.3$ meV. The Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ result using the relaxed undoped structure is $\Delta E(\pi/2) = 3.28$ meV, and the result for using the relaxed structure for Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ is $\Delta E(\pi/2) = 7.58$ meV. If the cell volume of Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ is fixed and both the internal parameter $z_{\text{As}}$, and $a$ and $c$ parameters are relaxed and then imported into ELK, then $\Delta E(\pi/2) = 3.08$ meV for Ba$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$.

Overall the VCA overestimates $\Delta E(\theta)$, but this does not affect the qualitative behavior, i.e., the biquadratic term $K$ does not change sign. Furthermore, using relaxed structures illustrates the sensitivity of the biquadratic interaction to the distance between the Fe and As/Se planes, but these subtle changes do not materially change the overall trends. We conclude that the VCA is an appropriate method for investigating whether doping can affect the qualitative behavior of the biquadratic term.

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In their calculations, the authors of Ref. 16 broke the I4/mmm symmetry and constrained the moments along the c-axis direction to be collinear in order to suppress the interplanar interaction term in Eq. 3. Therefore their $\Delta E(\theta)$ curves are symmetric about $\theta = \pi/2$ while ours are not.