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Hedgehog spin-vortex crystal stabilized in a hole-doped iron-based superconductor

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Magnetism is widely considered to be a key ingredient of unconventional superconductivity. In contrast to cuprate high-temperature superconductors, antiferromagnetism in most Fe-based superconductors (FeSCs) is characterized by a pair of magnetic propagation vectors, $(\pi, 0)$ and $(0, \pi)$. Consequently, three different types of magnetic order are possible. Of these, only stripe-type spin-density wave (SSDW) and spin-charge-density wave (SCDW) orders have been observed. A realization of the proposed spin-vortex crystal (SVC) order is noticeably absent. We report a magnetic phase consistent with the hedgehog variation of SVC order in Ni-doped and Co-doped $\text{CaKFe}_4\text{As}_4$ based on thermodynamic, transport, structural and local magnetic probes combined with symmetry analysis. The exotic SVC phase is stabilized by the reduced symmetry of the $\text{CaKFe}_4\text{As}_4$ structure. Our results suggest that the possible magnetic ground states in FeSCs have very similar energies, providing an enlarged configuration space for magnetic fluctuations to promote high-temperature superconductivity.

npj Quantum Materials (2018)3:5; doi:10.1038/s41535-017-0076-x

INTRODUCTION

The many families of Fe-based superconductors (FeSCs) provide a diverse platform for investigating the fundamental nature and applications of high-temperature superconductivity.^{1,2} In these compounds, magnetic order and superconductivity seem intertwined and the ground-state can be tuned by pressure and doping. The FeSCs share a common chemical motif; stacked Fe-pnictide or chalcogenide layers. Magnetism in most FeSCs [e.g., all AeFe_2As_2 ($\text{Ae} = \text{Ca}, \text{Sr}, \text{Ba}$)] is characterized by antiferromagnetic correlations with two symmetry-equivalent propagation vectors, $\mathbf{Q}_1 = (\pi, 0)$ and $\mathbf{Q}_2 = (0, \pi)$ (using the single-iron Brillouin zone notation).^{1,3} Magnetic order with these propagation vectors can be described by the spatial variation of the iron magnetic moments at positions $\mathbf{R}$ (refs. 4–13),

$$\mathbf{m}(\mathbf{R}) = \mathbf{M}_1 \cos(\mathbf{Q}_1 \cdot \mathbf{R}) + \mathbf{M}_2 \cos(\mathbf{Q}_2 \cdot \mathbf{R}). \quad (1)$$

Three types of magnetic order (Fig. 1a–d) are defined by the relationship between the magnetic order parameters $\mathbf{M}_1$ and $\mathbf{M}_2$ (refs. 3,14,15). The orthorhombic stripe-type spin-density wave (SSDW) order (Fig. 1a) has only one nonzero $\mathbf{M}_i$. A spin-charge-density wave (SCDW) (Fig. 1b) is a superposition of the two contributions with $\mathbf{M}_1 = \pm \mathbf{M}_2$. Finally, tetragonal spin-vortex crystal (SVC) orders (Fig. 1c, d) are defined by $|\mathbf{M}_1| = |\mathbf{M}_2|$ with non-collinear vectors $\mathbf{M}_1 \perp \mathbf{M}_2$, both in the Fe-plane.

The existence of two vector order parameters, $\mathbf{M}_1$ and $\mathbf{M}_2$, potentially provides a large configuration space for magnetic fluctuations. They are maximized when different types of magnetic order are close in energy, which may be key to the high-temperature superconductivity in the FeSCs. This makes

FeSCs exceptional, as most unconventional superconductors support only a single magnetic order parameter. Although the majority of iron-based superconductors exhibit only SSDW magnetic order, several hole-doped AeFe_2As_2 ($\text{Ae} = \text{Ca}, \text{Sr}, \text{Ba}$) compounds demonstrate a transition from SSDW to SCDW for compositions near optimal superconductivity.^{14–18} An experimental realization of SVC order would demonstrate the diversity of magnetic ground-states in FeSCs, but has not been reported to date.

Application of a suitable symmetry-breaking field may coax the system to condense into one of the three types of magnetic order as they break distinct symmetries.¹² For example, in-plane uniaxial strain favors SSDW as it breaks tetragonal symmetry in the same way and has been widely employed to study this order.^{19,20} It is difficult to imagine appropriate, externally applicable, symmetry-breaking fields for SCDW or SVC orders. A SVC phase breaks the glide symmetry across the Fe planes,¹² which is present in most FeSCs. Consequently, breaking this glide symmetry could favor SVC order.¹³ In the recently discovered stoichiometric $\text{AeAFe}_4\text{As}_4$ ($\text{Ae} = \text{Ca}, \text{Sr}; \text{A} = \text{K}, \text{Rb}, \text{Cs}$) superconductors,²¹ the alternating Ae and A atom planes inherently break this glide symmetry resulting in two inequivalent As sites (Fig. 1e). Consequently, these compounds could provide a unique opportunity to realize and study a SVC phase. Unfortunately, the parent $\text{AeAFe}_4\text{As}_4$ compounds do not order magnetically.^{21,22} However, recent nuclear magnetic resonance²³ and inelastic neutron scattering²⁴ on $\text{CaKFe}_4\text{As}_4$ revealed magnetic fluctuations near the $(\pi, 0)$, $(0, \pi)$ $\mathbf{Q}$ -vectors. Electron count and experimental properties suggests that $\text{CaKFe}_4\text{As}_4$ can be considered analogous to $(\text{Ba}_{0.5}\text{K}_{0.5})\text{Fe}_2\text{As}_2$

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Received: 11 July 2017 Revised: 11 December 2017 Accepted: 19 December 2017

Published online: 09 February 2018

(ref.²²). In the latter compound, the SSDW is suppressed by hole doping¹ (substituting K into BaFe_2As_2). Inspired by this analogy,²⁵ magnetic order could be induced by electron doping $\text{CaKFe}_4\text{As}_4$. Here, we report that adding electrons via substitution of Co or Ni for Fe in $\text{CaKFe}_4\text{As}_4$ does induce antiferromagnetism consistent with the hedgehog variation of SVC. We stabilize this phase using the chemical structure as a symmetry-breaking field illustrating the multiple competing, nearly-degenerate magnetic phases in FeSCs. This competition may be an important contributor to high-temperature superconductivity as enhanced magnetic fluctuations can boost pairing.

RESULTS

Figure 2a presents the electrical resistance of $\text{CaK}(\text{Fe}_{1-x}\text{Ni}_x)_4\text{As}_4$. With increasing nickel content, a kink at temperature T_N appears and rises to ~ 55 K as the superconducting critical temperature, T_C , is suppressed. The resistance of $\text{CaK}(\text{Fe}_{0.95}\text{Co}_{0.05})_4\text{As}_4$ (Fig. 2b) exhibits a similar trend. The heat capacity of $\text{CaK}(\text{Fe}_{0.951}\text{Ni}_{0.049})_4\text{As}_4$ (insets into Fig. 2a) reveals clear signatures of second-order phase transitions at T_N and T_C . The transition temperatures inferred from these data are plotted in Fig. 3, demonstrating that the phase diagrams of Co-doped and Ni-doped $\text{CaKFe}_4\text{As}_4$ map onto each other if the Ni fraction is scaled by two. This is consistent with an electron doping picture where substituting Ni for Fe supplies twice as many electrons as Co (ref.²⁶). It should be noted that a recent study of $\text{RbEuFe}_4\text{As}_4$ also shows a new phase stabilized by Ni-substitution suggested to be a spin-density wave phase.²⁷

Consistent observation of a transition at T_N in both doping series calls for investigation of its nature. Figure 4a–c shows high-energy x-ray diffraction results from $\text{CaK}(\text{Fe}_{0.951}\text{Ni}_{0.049})_4\text{As}_4$. The peak shapes (Fig. 4c) are unchanged below $T_N = 53$ K indicating an absence of lattice distortions. No superlattice peaks appear in the low-temperature diffraction patterns in the lower halves of Fig. 4a, b. These results suggest that the geometry and multiplicity of the chemical unit cell are unchanged.⁵⁷ ^{57}Fe Mössbauer spectroscopy on crystals of $\text{CaK}(\text{Fe}_{0.951}\text{Ni}_{0.049})_4\text{As}_4$ in Fig. 4d reveals clear structure in the spectra below 55 K demonstrating a hyperfine field, H_{hf} , at the Fe-sites, i.e., magnetic order. A fit of the spectrum at base temperature suggests a H_{hf} distribution centered around 3 T (corresponding to $\sim 0.2 \mu_B$ ordered moment²⁸) and in-plane orientation of the iron moments. The temperature dependence of H_{hf} (Fig. 4f) is characteristic of a second-order phase transition, consistent with heat capacity.⁷⁵ As nuclear magnetic resonance (NMR) is employed to probe the H_{hf} at the inequivalent As1 and As2 sites of the $\text{CaKFe}_4\text{As}_4$ structure. Figure 4e reveals a finite $H_{\text{hf}} \parallel c$ at As1 (close to K) and $H_{\text{hf}} = 0$ at As2. The temperature dependence of H_{hf} at As1 mirrors that at the Fe site (Fig. 4f). The assignment of As1 and As2 is made following ref.²³. As Mössbauer and NMR measurements reveal the behavior of the majority of Fe-atoms, we associate the observed magnetism with the $\text{CaK}(\text{Fe}, \text{Ni})_4\text{As}_4$ phase identified by high-energy x-ray diffraction.

DISCUSSION

Our experimental results are inconsistent with the previously observed magnetic phases in the FeSCs: SSDW and SCDW. First, the Mössbauer spectra cannot be described by the moment motif of the SCDW phase where half the Fe-sites would experience $H_{\text{hf}} = 0$ (Fig. 1b). In addition, the distribution and direction of H_{hf} at As-sites inferred from NMR spectra rules out the SSDW, SCDW, and “loops” SVC phases (see Fig. 1a, b, d and Supplemental Material). Furthermore, the diffraction data in Fig. 4 are inconsistent with an orthorhombic distortion. Of the possibilities depicted in Fig. 1, only SVC-type order remains (Fig. 1c). To systematically consider the possible magnetic phases of $\text{CaK}(\text{Fe}_{0.951}\text{Ni}_{0.049})_4\text{As}_4$, a representation analysis of $\text{CaKFe}_4\text{As}_4$'s magnetic space group, $P4/mmm1'$, was performed, similar to ref.²⁹. There are 96

Fig. 1 Schematics of possible magnetic order types in $\text{CaKFe}_4\text{As}_4$. **a–d** Sketches of four magnetic moment patterns on an Fe–As layer in the $\text{CaKFe}_4\text{As}_4$ structure associated with $\mathbf{Q}_1 = (\pi, 0)$, $\mathbf{Q}_2 = (0, \pi)$ magnetic propagation vectors. The upper yellow square in **a**, **e** represents the projection of the $\text{CaKFe}_4\text{As}_4$ unit cell. The magnetic unit cells are represented by the central yellow squares in **a–d**. The brown arrows represent the magnetic moments at the Fe sites and the blue and green arrows the hyperfine field (H_{hf}) at the inequivalent As1 and As2 sites. In the orthorhombic stripe spin-density wave (SSDW) in **a** all arsenic atoms experience H_{hf} normal to the plane. In the spin-charge-density wave (SCDW), “ C_4 phase”¹⁵, in **b** every other Fe site supports a moment normal to the plane and the As sites experience an in-plane H_{hf} . In the hedgehog spin-vortex crystal (SVC) phase in **c**, the Fe moments display an “all in” or “all out” arrangement centered around the As1 sites generating an out-of-plane $H_{\text{hf}} \neq 0$ at these sites and $H_{\text{hf}} = 0$ at the As2 sites. In the loops SVC in **d** the magnetic moments form loops around As1 and neither As site experiences a H_{hf} . **e** The chemical structure of $\text{CaKFe}_4\text{As}_4$. Note the inequivalent As1 and As2 sites adjacent to K and Ca planes, respectively. **f** Section of the Fe–As sheet with a hedgehog SVC moment arrangement. Spin up currents between the iron atoms, J_s (yellow arrows), generate an electric field, $\mathbf{E}$ (red arrows), which couples to asymmetric shifts of the two arsenic sites. Unlike in the CaFe_2As_2 structure, an asymmetric arrangement of arsenic atoms is imposed by the crystallographic symmetry in $\text{CaKFe}_4\text{As}_4$ providing a symmetry-breaking field that favors the SVC-type phases

Fig. 2 Resistance, magnetic susceptibility, and heat capacity of Co-doped and Ni-doped $\text{CaKFe}_4\text{As}_4$. **a** Temperature dependence of normalized resistance, $R/R_{300\text{K}}$, of $\text{CaK}(\text{Fe}_{1-x}\text{Ni}_x)_4\text{As}_4$ single crystals demonstrating the suppression of the superconducting transition temperature, T_c , and the emergence of a kink-like feature labeled T_N with increasing Ni content, x . The anomaly at T_N appears clearly as a step in the derivative of resistance, dR/dT , and specific-heat, C_p , of $x = 0.049$ (upper left insets). In the magnified portion in the specific-heat inset, data from a $x = 0.017$ sample was subtracted to accentuate the step-like anomaly characteristic of a bulk, second-order transition at T_N . The zero-field cooled (ZFC) volume magnetic susceptibility, $4\pi\chi$, (bottom right inset) demonstrates the suppression of T_c with increasing x and full superconducting shielding for $x \leq 0.049$. The upper right inset shows a magnified view of C_p/T of the $x = 0.049$ sample around T_c . **b** Evolution of resistance and ZFC magnetic susceptibility in $\text{CaK}(\text{Fe}_{1-y}\text{Co}_y)_4\text{As}_4$. T_c is suppressed by Co substitution and the kink-like feature at T_N emerges in the resistance data similar to the effect of Ni substitution

commensurate magnetic structures allowed for the chemical structure²¹ of $\text{CaKFe}_4\text{As}_4$. Possible incommensurate magnetic phases are discussed in Supplemental Information (see Supplemental Information). Only 24 structures retain the original tetragonal chemical unit cell as suggested by the diffraction results. All of these are accessible by a second-order phase transition (see Supplemental Information) and have one common magnitude for all iron moments. However, the ordered Fe moments in eight of these (including ferromagnetism and Néel order) are normal to the Fe-planes, inconsistent with the

Fig. 3 Common phase diagram of Co-doped and Ni-doped $\text{CaKFe}_4\text{As}_4$. Doping $\text{CaKFe}_4\text{As}_4$ with either Co or Ni suppresses the superconducting transition temperature, T_c , and stabilizes a hedgehog spin-vortex crystal below T_N . T_c^R and T_c^M were determined by resistance and magnetization measurements, respectively. The Ni-concentration x , on the upper axis, is scaled by a factor of two with respect to the Co-concentration, y , which maps the transition temperatures of the two series onto each other. This scaling is consistent with an electron doping picture where Ni substitution adds twice as many electrons per atom as Co. Transition temperatures of $\text{CaK}(\text{Fe}_{1-x}\text{Ni}_x)_4\text{As}_4$ determined by heat capacity, Mössbauer spectroscopy, and nuclear magnetic resonance are consistent with this phase diagram. Horizontal error bars represent the standard deviation of 12 composition points for each sample. Vertical error bars indicate transition width

Mössbauer results. The remaining 16 structures are all modifications of SVC order. There are two motif variations,¹³ “hedgehog” with $\mathbf{M}_i \parallel \mathbf{Q}_i$ (Fig. 1c) and “loops” with $\mathbf{M}_i \perp \mathbf{Q}_i$ (Fig. 1d). Each variation can be centered on either As1 or As2 and can have four different stacking patterns along the crystallographic c -axis (see Supplemental Information). Only the hedgehog SVC, with the centering depicted in Fig. 1c, is consistent with the $\mathbf{H}_{\text{hf}}$ at As1 observed by NMR.

We argue that this peculiar, non-collinear magnetic phase is stabilized by the specific crystal structure of $\text{CaKFe}_4\text{As}_4$. The inequivalence of the staggered As sites (Fig. 1e) generates a symmetry-breaking field that couples to the spin vorticity, $\mathbf{M}_1 \times \mathbf{M}_2$, characteristic of SVC order (see Supplemental Materials). One possible mechanism is the electrostatic coupling of the As atoms to spin current loops associated with the magnetic moment motif¹² (Fig. 1f). These spin currents generate an electric field analogous to the magnetic field produced by an electric current.³⁰ The resulting electrostatic force couples the asymmetric shifts of the As atoms to the spin currents. The preference for the hedgehog SVC variation over loops variation is likely a consequence of spin-orbit coupling, which generally favors $\mathbf{M}_i \parallel \mathbf{Q}_i$, observed experimentally in the case of the SSDW order of the parent AeFe_2As_2 compounds³ and theoretically in ref. 9.

Our identification of a hedgehog SVC order in Co-doped and Ni-doped $\text{CaKFe}_4\text{As}_4$ sheds new light on the curious landscape of magnetic phases in FeSCs arising from two magnetic propagation vectors. Previous results indicate that SSDW and SCDW phases have comparable energies in some hole-doped FeSCs.^{14–17} Our

Fig. 4 Experimental insights into the nature of the magnetic phase of $\text{CaK}(\text{Fe}_{0.951}\text{Ni}_{0.049})_4\text{As}_4$ below $T_N = 53$ K. **a, b** Single crystal *HHL* and *HK0* diffraction patterns at 300 K (upper halves) and 30 K (lower halves). No additional diffraction peaks appear at 30 K, counter-indicating a chemical superlattice. The Be sample enclosure produces diffraction rings. **c** 220 and 200 diffraction peaks (integrated azimuthally) vs. plane spacing d . The peak shapes remain unchanged below T_N placing an upper relative limit of 4×10^{-4} on lattice distortions in either direction. **d** ^{57}Fe Mössbauer spectra on a mosaic of 34 single crystals. Broadening of the absorption peak on cooling through T_N indicates a hyperfine field, H_{hf} , produced by an ordered moment at the Fe-sites. The ratios of the peaks in the fitted sextet (solid lines) reveal that these ordered moments lie perpendicular to the crystallographic c -axis. **e** Field-swept ^{75}As (gyromagnetic ratio, $\gamma/2\pi = 7.2919$ MHz/T) nuclear magnetic resonance (NMR) spectra obtained at $f = 43.2$ MHz with applied magnetic field, H , along the crystallographic c -axis (upper three spectra) and with $H \perp c$ (bottom spectrum). Simulated peaks from the two inequivalent As1 and As2-sites are denoted by hues of blue and green, respectively. Above T_N each As site produces a central peak (shaded area) and a pair of electric quadrupole satellites. With $H \parallel c$, the As1 triplet splits into two triplets on cooling through T_N indicating presence of a H_{hf} component parallel to c at half of the As1-sites and antiparallel to c at the other half. The As2 triplet remains un-split. With $H \perp c$, neither triplet is split at 11 K indicating an absence of in-plane hyperfine fields at either As site. **f** The temperature dependence of $|H_{\text{hf}}|$ at the Fe (squares, from Mössbauer) and As1-sites (circles, from NMR), consistent with a second-order magnetic phase transition at T_N . The error bars represent standard fitting error (^{57}Fe) and estimated uncertainty (^{75}As)

observation in effectively hole-doped $\text{CaKFe}_4\text{As}_4$ reveals that SVC order is competitive (with SSDW and SCDW) as well and demonstrates the sensitivity of magnetism in FeSCs. This phenomenon is confirmed by first-principle calculations, which can compare the energies of different magnetic configurations. Previous calculations needed to invoke a SVC-like order to reproduce the structural collapse of $\text{CaKFe}_4\text{As}_4$ under pressure.³¹ Our calculations reveal that SSDW and hedgehog SVC are nearly degenerate for pure $\text{CaKFe}_4\text{As}_4$ but the latter prevails upon electron doping (see Supplemental Information). The near-degeneracy of these magnetic phases provides an enlarged configuration space for magnetic fluctuations which may have profound implications for magnetically mediated superconducting pairing.^{32,33}

Co-doped and Ni-doped $\text{CaKFe}_4\text{As}_4$, then, is the missing link in the evolution of magnetic order in the AeFe_2As_2 systems. Alternating cation layers in the $\text{CaKFe}_4\text{As}_4$ structure generate the appropriate symmetry breaking field to stabilize the predicted SVC phase. Therefore, this family of compounds is an ideal platform to probe the relative stability of SSDW and SVC states. Although the relation between the SVC magnetism and the superconducting state needs to be determined in detail, we note that the spin

resonance observed by neutron scattering in pure $\text{CaKFe}_4\text{As}_4$ suggests similarities to other FeSCs.²⁴

In conclusion, we confidently identified a hedgehog SVC in Co-doped and Ni-doped $\text{CaKFe}_4\text{As}_4$. The chemical structure of $\text{CaKFe}_4\text{As}_4$ and spin-orbit coupling conspire to stabilize this phase further exposing the complex magnetism in FeSCs. This first experimental realization of SVC order in a magnetic superconductor opens a new platform to study multi-component, non-collinear magnetic phases and their interplay with superconductivity.

METHODS

Single crystals of Co-doped and Ni-doped $\text{CaKFe}_4\text{As}_4$ were grown out of a high-temperature solution rich in transition-metals and arsenic similar to the procedure used for the pure compound.^{22,34} Transition-metal arsenides precursors, $M_{0.512}\text{As}_{0.488}$ ($M = \text{Fe}, \text{Co}, \text{Ni}$), were synthesized from ground arsenic lumps (Alfa Aesar 99.9999%) and transition-metal powders [Fe (Alfa Aesar 99.9+ % metals basis), Co (Alfa Aesar 99.8% metals basis), Ni (Alfa Aesar 99.9% metals basis)] in a rotating fused-silica ampoule in a purpose-built tube furnace as described in ref. ³⁵. The iron and cobalt reactions were held at 565 °C for 900 min then 900 °C for 600 min before the furnace was switched off. The nickel version was held at 720 °C for 600 min instead of 900 °C because nickel arsenides melt at lower temperatures. Ground

transition-metal arsenide precursors $M_{0.512}As_{0.488}$, potassium metal globs (Alfa Aesar 99.95%), and distilled calcium metal pieces (Ames Laboratory, Materials Preparation Center 99.9%) were loaded into alumina Canfield Crucible Sets (LSP Industrial Ceramics, Inc.).³⁶ Batches were about 2 g of material with a molar ratio of K:Ca: $Fe_{0.512}As_{0.488}$: $M_{0.512}As_{0.488}$ = 1.2 : 0.8 : 20(1-x) : 20x. This crucible set was sealed in a tantalum metal tube and then in an argon-filled, fused-silica ampoule. These ampoules were heated in a box furnace using the optimum profile described in ref.³⁴. The final temperature varied from 920 to 933 °C depending on how the transition metal ratio shifted the solidification temperature. After 1–2 h at this final temperature the growth assembly was removed from the furnace, inverted into a centrifuge, and spun to decant the remaining liquid off the crystals.³⁶ The metallic plate-like crystals obtained were often smaller than those of undoped $CaKFe_4As_4$ and cleaved easily along the (001) planes.

Chemical analysis of freshly-cleaved crystal surfaces was performed by wavelength-dispersive x-ray spectroscopy on a JEOL JXA-8200 microprobe system. Twelve points were analyzed for each sample. $CaWO_4$, $KAlSi_3O_8$, Co metal, Ni metal and FeAs were used as standards.

Electrical resistance was measured in a standard four-contact geometry with Pt-wires bonded to the samples with silver paint. A Lakeshore Model 370 AC resistance bridge was employed and the temperature environment was provided by a Janis Research SHI-950T 4 K closed-cycle refrigerator.

Magnetization measurements were performed in a Quantum Design, Magnetic Property Measurement System in a clear plastic straw. The samples were zero-field cooled before applying a magnetic field of 50 Oe parallel to the plate-shaped crystals.

The heat capacity data of the samples was measured using a hybrid adiabatic relaxation technique of the heat capacity option in a Quantum Design, Physical Properties Measurement System.

High-energy x-ray diffraction measurements were performed on the six-circle diffractometer at end station 6-ID-D at the Advanced Photon Source, Argonne National Laboratory, using an x-ray energy of $E = 100.34$ keV and a beam size of $100 \times 100 \mu m^2$. The $CaK(Fe_{0.951}Ni_{0.049})_4As_4$ single-crystal sample was mounted on the cold finger of a He closed-cycle refrigerator. The sample was enclosed by a Be dome and He exchange gas was used to ensure the thermal equilibrium. Diffraction patterns were recorded using a MAR345 image plate detector positioned at 1.474 m from the sample. The distance was determined from measurement of powder patterns of CeO_2 standard from the National Institute of Standards and Technology. The detector was operated with a pixel size of $100 \times 100 \mu m^2$, and patterns were recorded while rocking the sample through two independent angles up to $\pm 2.8^\circ$ about the axes perpendicular to the incident beam.

⁵⁷Fe Mössbauer spectroscopy measurements were performed in a SEE Co. conventional, constant acceleration type spectrometer in transmission geometry. The ⁵⁷Co in Rh source was maintained at room temperature. Thirty-four cleaved crystals of $CaK(Fe_{0.951}Ni_{0.049})_4As_4$ were fixed to a paper disk with Apiezon N grease. An effort was made to keep gaps between crystals to a minimum and the part of the disk not covered by crystals was coated with tungsten powder (Alfa Aesar 99.9% metals basis). This mosaic was positioned so that the gamma ray beam was parallel to the crystallographic *c*-axis. The sample temperature was maintained using a Janis SHI-850-5 closed cycle refrigerator with vibration damping. The driver velocity was calibrated using an α -Fe foil. The Mössbauer spectra were fitted using the commercial software package MossWinn 4.0Pre.³⁷ Below T_N , the Mössbauer spectra can be modeled with a single value of hyperfine field (reported in Fig. 4f) and an increased linewidth with respect to the paramagnetic state. Alternatively, they may be described by a temperature independent linewidth and a distribution of hyperfine fields. Both approaches suggest that there is a distribution of H_{hf} at the Fe sites in the magnetic phase.

NMR measurements of $CaK(Fe_{0.951}Ni_{0.049})_4As_4$ (total mass ~5 mg) were carried out on ⁷⁵As ($I = \frac{3}{2}$, $\gamma/2\pi = 7.2919$ MHz/T, $Q = 0.29$ barns) by using a lab-built, phase-coherent, spin-echo pulse spectrometer. The spin echo was observed with a sequence of $\frac{\pi}{2}$ pulse (2.2 μs) - 30 μs - π pulse (4.4 μs). The ⁷⁵As-NMR spectra were obtained at a fixed frequency, $f = 43.2$ MHz, with sweeping the magnetic field up to 8.25 T. The magnetic field was applied parallel or perpendicular to the crystallographic *c*-axis. ⁷⁵As NMR spectra was simulated with two (for $H \parallel c$ above T_N and $H \perp c$) or three ($H \parallel c$ below T_N) sets of peaks with distinct values of H_{hf} and quadrupole interaction, ν_Q . The ratio of the integrated area of As1 to As2 is 1:1 in all the spectra. The ratio of As1 with $-H_{hf}$ to $+H_{hf}$ is also 1:1 in the spectra for $H \parallel c$ below T_N .

The symmetry analysis was performed using the ISOTROPY software suite³⁸ to systematically analyze the possible magnetic orders of $CaKFe_4As_4$ with magnetic space group $P4/mmm1'$. A detailed description of the

analysis is presented in Supplemental Material (see Supplemental Information).

In the first-principles calculations, the effect of electron doping on the magnetic properties of $CaKFe_4As_4$ was studied using the virtual crystal approximation (VCA) and the all-electron full-potential linearised augmented-plane wave basis (Elk FP-LAPW code) (URL <http://elk.sourceforge.net/>, Elk FP-LAPW code). The structure parameters were fixed at the measured room-temperature values for undoped samples.³⁹

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

ACKNOWLEDGEMENTS

The authors would like to acknowledge W. Straszheim for his expertise and assistance with chemical analysis, D. S. Robinson for experimental support of the x-ray scattering study, and T. Kong for assistance during early stages of sample preparation. We also acknowledge discussions with E. Berg, A. Chubukov, and S. Kivelson. Work at the Ames Laboratory was supported by the Department of Energy, Basic Energy Sciences, Division of Materials Sciences & Engineering, under Contract No. DE-AC02-07CH11358. WRM was supported by the Gordon and Betty Moore Foundation's EPIQS Initiative through Grant GBMF4411. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. VB and RV are supported by the Deutsche Forschungsgemeinschaft (DFG) under grant SFB/TRR49. RMF is supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under award DE-SC0012336. PPO acknowledges support from Iowa State University Startup Funds.

AUTHOR CONTRIBUTIONS

P.C.C., S.L.B. and W.R.M. initiated this work; W.R.M. grew the samples; W.R.M., Q.P.D., A. K., S.L.B., A.S., K.K., and A.E.B. performed measurements and analyzed the data; V.B., R. V., P.P.O., C.D.B., and R.M.F. performed the theoretical interpretations and computational work; W.R.M. and A.K. performed the symmetry analysis; R.V., R.M.F., A.I.G., Y.F., A.E.B., and P.C.C. guided the work; W.R.M., A.K., R.M.F., and A.E.B. drafted the manuscript and all authors participated in the writing and review of the final draft.

ADDITIONAL INFORMATION

Supplementary information accompanies the paper on the *npj Quantum Materials* website (<https://doi.org/10.1038/s41535-017-0076-x>).

Competing interests: The authors declare no competing financial interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

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