Frustration-driven $C_4$ symmetric orders in a hetero-structured iron-based superconductor

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A subtle balance between competing interactions in strongly correlated systems can be easily tipped by additional interfacial interactions in a heterostructure. This often induces exotic phases with unprecedented properties, as recently exemplified by high-$T_c$ superconductivity in FeSe monolayers. When the proximity-coupled layer is magnetically active, even richer phase diagrams are expected in iron-based superconductors (FeSCs), which however has not been explored due to the lack of a proper material system. One promising candidate is Sr$_2$VO$_3$FeAs, a naturally-assembled heterostructure of a FeSC and a Mott-insulating vanadium oxide. Here, using high-quality single crystals and high-accuracy $^{75}$As and $^{51}$V nuclear magnetic resonance (NMR) measurements, we show that a novel electronic phase is emerging in the FeAs layer below $T_d \sim 155$ K without either static magnetism or a crystal symmetry change, which has never been observed in other FeSCs. We find that frustration of the otherwise dominant Fe stripe and V Neel fluctuations via interfacial coupling induces a charge/orbital order with $C_4$-symmetry in the FeAs layers, while suppressing the Neel antiferromagnetism in the SrVO$_3$ layers. These findings demonstrate that the magnetic proximity coupling is effective to stabilize a hidden order in FeSCs and, more generally, in strongly correlated heterostructures.

In strongly correlated electron materials, including cuprates, transition metal oxides (TMOs), and iron-based superconductors (FeSCs), competing interactions of spin, charge and orbital degrees of freedom lead to complex and rich phase diagrams, extremely sensitive to external perturbations. Especially impressive is modification of the phase diagram via introducing interfacial interactions, as intensively studied for the heterostructures of high-$T_c$ cuprates or transition metal oxides, showing the enhanced $T_c$ or new emergent phases that cannot be stabilized in their constituent layer alone. The similar effect has also been found in FeSCs, for example, in FeSe monolayers on top of nonmagnetic SrTiO$_3$ showing drastically enhanced $T_c$, arguably higher than 100 K (Ref. [4]). Although the underlying mechanism is yet to be confirmed, the interfacial coupling is considered to be critical and may further enhance $T_c$ in the superlattice [11]. Of particular interest is when the proximity coupled layer is strongly correlated and magnetically active. As found in heterostructures of high-$T_c$ cuprates and magnetic TMOs, additional interfacial spin interaction may also induce novel ground states of FeSCs in proximity of a Mott insulator, which however has not been explored so far.

Sr$_2$VO$_3$FeAs is a unique member of the family of FeSCs, a very rare naturally-assembled superlattice of [SrFeAs]$^{+1}$ and [SrVO$_3$]$^{-1}$ layers, as shown in Fig. 1a. Initially Sr$_2$VO$_3$FeAs was thought to have, because of the V bands, an unusual Fermi surface topology, incompatible with $s^\pm$ superconductivity scenario driven by spin-fluctuation [13]. However, it was soon realized the V 3$d^2$ electrons in the SrVO$_3$ layer are strongly correlated and form a Mott-insulating state [15–17], while the partially-filled Fe 3$d^6$ state in the FeAs layer has the considerable itinerancy and superconducts at $T_c \sim 35$ K [12,14]. These contrasting ground states in Sr$_2$VO$_3$FeAs make this system prototypical for strongly correlated heterostructures based on FeSCs and TMOs. Sr$_2$VO$_3$FeAs has the Fermi surface similar to that in other FeSCs [15,17], and thus is expected to show either the stripe antiferromagnetic (AFM) order with the wave vector $Q=\left(\pi, 0\right)$, or the corresponding nematic phase, or enhanced spin fluctuations at low temperature with the same $Q$. There is in fact a second-order transition observed at $T_0 \sim 155$ K with a sizable entropy loss of $\sim 0.2 R \ln 2 \left( R \right.$ is the gas constant) [19,21]. With no evidence of a static magnetic order or another apparent symmetry breaking, the hidden nature of this phase transition, simi-
lar to the famous “hidden-order” in underdoped cuprates or a heavy fermion system URu₂Si₂, remains elusive and controversial [19–23], posing a challenge to our understanding of the physics of FeSCs in proximity of a Mott insulator.

Here we report that an emergent electronic phase is developed below \( T_0 = 155 \) K in Sr₂VO₃FeAs, which is highly distinct in nature from the transitions found in other FeSCs. Using high-accuracy \(^{75}\text{As}\) and \(^{51}\text{V}\) NMR measurements on high-quality single crystals under various field orientations, we unambiguously show that the transition occurs in the FeAs layer, not the SrVO₃ layer, without breaking either time reversal symmetry and the underlying tetragonal lattice symmetry. This implies that the typical stripe AFM and \( C_2 \) nematic phases in the FeAs layers as well as the Neel antiferromagnetism in the SrVO₃ layer are significantly suppressed by the interfacial coupling between itinerant iron electrons and localized vanadium spins.

Transport and magnetic properties. Our transport and magnetic measurements on high-quality single crystal of Sr₂VO₃FeAs shown in Figs. 1b and 1c confirm that the transition at \( T_0 \) is intrinsic. A weak, but discernible, anomaly is observed at \( T_0 \sim 155 \) K in the resistivity (\( \rho \)), even more pronounced in its temperature derivative \( d\rho/dT \). The magnetic susceptibility \( \chi(T) \) also shows an anomaly at \( T_0 \). Above \( T_0 \), \( \chi(T) \) is several times larger than in typical FeSCs and follows the Curie-Weiss law with a Curie-Weiss temperature \( T_{\text{CW}} \sim -100 \) K (see Supplementary section 2). The effective magnetic moment is consistent with \( S = 1 \) expected for the V \(^{3+}\) ions, suggesting that \( \chi(T) \) is dominated by localized V spins. At \( T_0 \sim 155 \) K, \( \chi(T) \) for both \( H \parallel ab \) and \( H \parallel c \) exhibits a small jump, which corresponds to \( \sim 10^{-3} \) \( \mu_B/\text{f.u.} \), three orders of magnitude smaller than typical values of V \(^{3+}\) ions (\( \sim 1.8\mu_B \)) in vanadium oxides [16] and Fe ions (\( \sim 0.8\mu_B \)) in FeSCs [24]. Such weak anomalies in \( \rho(T) \) and \( \chi(T) \), in contrast to a strong one in the specific heat [19–21], question the previous conjectures of a long-range ordering of either V or Fe spins [19–22], and suggest that this weak ferromagnetic response is only a side effect of the true transition. However, another anomaly at \( T_N \sim 45 \) K in both \( \chi_{ab}(T) \) and \( \chi_c(T) \) turns out to reflect a long-range ordering of Fe, but still not V spins, as discussed below. Notably, neither transition is consistent with the typical stripe AFM or nematic orders for FeSCs.

\(^{75}\text{As}\) and \(^{51}\text{V}\) nuclear magnetic resonance spectroscopy. To gain further insight into the transition at \( T_0 \) on a microscopic level, we measured NMR on \(^{75}\text{As}\) and \(^{51}\text{V}\) nuclei as a function of temperature for field orientations parallel to \( a \) (100), \( c \) (001) and the (110) directions (Fig. 2 and the supplementary Fig. S4). The \(^{51}\text{V}\) probes the V spin order directly and the \(^{75}\text{As}\) is a proxy for the Fe sites, which allows us to probe the two magnetic ions separately. A dramatic change of the \(^{75}\text{As}\) line occurs near \( T_0 \sim 155 \) K as shown in Fig. 2a, consistent with the anomalies in \( \rho(T) \) and \( \chi(T) \). Near 180 K, the \(^{75}\text{As}\) signal starts to lose its intensity rapidly and is not detectable between 150–170 K due to the shortening of the spin-spin relaxation time \( T_2 \) (Ref. [22]). Strikingly, the signal recovers below \( \sim 150 \) K at substantially higher frequencies, in a similar fashion for both field orientations, which contrasts the typical behaviors of \(^{75}\text{As}\) NMR found in other FeSCs (see Supplementary Fig. S5). This is better shown in terms of the Knight shift \( \Delta K \equiv (f-f_0)/f_0 \),
where $\nu_0 \equiv \gamma_n H$ with the nuclear gyromagnetic ratio $\gamma_n$ (see Fig. 2c). $^{75}$As changes abruptly at $T_0 \sim 155$ K without any peak splitting or broadening of the full-width at half-maximum (FWHM) across $T_0$. Conversely, the $^{51}$V line barely shifts below $T_0$ and down to 20 K (Figs. 2b and 2d), while its FWHM gradually increases below $T_0$. The nearly unchanged $^{51}$V NMR line signals that the V spins remain disordered down to low temperatures. This contrasting behavior of the $^{75}$As and $^{51}$V spectra unambiguously proves that the transition at $T_0$ occurs in the FeAs layer, not in the SrVO$_3$ layer, contrary to previous claims [19–24].

Having established that the phase transition at $T_0$ occurs in the FeAs layer, we examined the low-energy Fe spin dynamics, as probed by the $^{75}$As spin-lattice relaxation rate $T_1^{-1}$, which reflects local spin fluctuations. As shown in Fig. 3, at $T \gtrsim 240$ K, $(T_1T)^{-1}$ exhibits a typical Curie-Weiss-like behavior with an anisotropy $T_{1,a}^{-1}/T_{1,c}^{-1} \approx 1.5$. This is expected for a directionally-disordered state with local stripe AFM correlations with $Q = (\pi, 0)$ and has been observed in many FeSCs [29,32] (see Supplementary section 6). With lowering temperature, a critical slowdown of the $(\pi, 0)$ spin fluctuations usually condenses into the $C_2$ stripe AFM phase. For Sr$_2$VO$_3$FeAs, however, this critical growth is arrested at $T \sim 200$ K, showing a broad peak of $(T_1T)^{-1}$ with an unusually large $T_{1,a}^{-1}/T_{1,c}^{-1} \approx 6$, and then the fluctuations harden all the way down to $T_0$. Across $T_0$, $(T_1T)^{-1}$ barely changes and then quickly reaches a constant below $T_0$, behaving as a paramagnetic metal. This completely unexpected behavior in both $75K$ and $(T_1T)^{-1}$ confirms that the transition at $T_0$ in Sr$_2$VO$_3$FeAs is unlike any transitions observed in FeSCs so far.

Let us now discuss possible orders established below $T_0$. First of all, we can eliminate the usual suspects: stripe, double-$Q$ [28,32], and bicollinear [33] AFM orders, observed in other FeSCs. In the first case $Q = (\pi, 0)$ and the Fe spins aligned along the $a$ axis ($s \parallel a$) generate a hyperfine field $H_{hf} \sim 1.5$ T along the $c$ axis. This would be visible in the $^{75}$As NMR spectra as a peak splitting of $\sim 10$ MHz for $H \parallel c$, which is far larger than the FWHM of our spectra ($\sim 0.05$ MHz) and easily detectable. Similarly, for $s \parallel c$, a $^{75}$As peak splitting is expected for $H \parallel a$. Even for $s \parallel b$, in which case no transferred $H_{hf}$ and thus no peak splitting are expected, considerable line broadening due to the directional fluctuations of Fe spins should be seen in experiments. Neither splitting nor broadening is observed in our experiments (Fig. 2a).

For the double-$Q$ AFM state $[28,32]$, a combination of two spin density waves with $Q = (\pi, 0)$ and $(0, \pi)$, the magnetization vanishes at one of the two Fe sublattices and is staggered in the other. Thus, the $^{75}$As peak splitting is expected for either $H \parallel c$ ($s \parallel a$) or $H \parallel a$ ($s \parallel c$), as discussed in the Supplementary section 5, which can be ruled out by experiments. The bicollinear AFM order [33] can also be excluded with even more confidence. In this case,
the (110) and (110) directions are not equivalent [34, 35]. If the generated imbalance between the corresponding orbital Fe-$d_{xz} \pm d_{yz}$ is of the same order as in the stripe- nematic case, a peak splitting for $H \parallel (110)$ should be detected. And, for the nematic partner of the plaquette magnetic order, two inequivalent sites and thus a sizable splitting are expected for every field direction. Yet, none of these signatures appears in our $^{75}$As spectra for $H\parallel a$ (100), c (001) and (110) directions (Figs. 2a, 2b and the Supplementary Fig. S4). Furthermore, our single crystal X-ray diffraction (see Supplementary section 1), as well as the recent ARPES study [17] do not reveal any signature of a $C_4$ symmetry breaking.

Since the transition at $T_0$ retains the $C_4$ symmetry, and in absence of a long range magnetic order, this transition must generate a change in the relative occupations of the $C_4$ orbitals, namely $d_{xy}$, $d_{z^2}$, $d_{x^2-y^2}$, and $d_{xz} \pm id_{yz}$. Given that at high temperature we see clear indications of strong spin fluctuations, we looked for a spin-driven scenario conserving the $C_4$ symmetry; a good candidate is the vestigial (nematic) partner of the double-$Q$ AFM order [34]. It can be visualized (Fig. 4d) as a superposition of two charge/orbital density waves with $Q=(\pi,0)$ and $(0,\pi)$, which preserves the $C_4$ symmetry without unit-cell doubling. This phase has a broken translational symmetry in the Fe-only square lattice, but not in the unit cell doubled to include the As atoms [37]. Formation of the intra-unit-cell charge/orbital density wave affects the Fe-As hybridization and modifies the hyperfine coupling via isotropic Fermi-contact and core-polarization interactions, accounting for the nearly isotropic $^{75}$K Knight shift (Fig. 2). One may note that due to dipole or orbital hyperfine interactions, the Knight shift can split for a field parallel to (110), because half of As sites have paramagnetic neighbors along (110), and half along (110). However, the difference in the $d$ orbital occupations between nonmagnetic and paramagnetic Fe are expected to be small, likely a few % (see Supplementary section 5), in which case the splitting will be below detection, consistent with our experiments.

If we assume nonmagnetic origin, another plausible candidate could be an orbital-selective Mott transition. In this case, the most correlated Fe orbital state, likely $d_{xy}$, experiences a Mott-Hubbard transition, becoming essentially gapped, while the other orbitals remain itinerant. The resulting occupation change in the $d_{xy}$ state of all Fe sites (Fig. 4e), uniformly changes the hyperfine field at the As sites, retaining the $C_4$ symmetry and explaining the nearly isotropic change of $^{75}$K Knight shift (Fig. 2). Indeed a possibility of such transition has been discussed, but, admittedly, not in undoped pnictides, but in more strongly correlated chalcogenides [37] and (strongly underdoped) KFe$_2$As$_2$ [38, 39].

As mentioned, Sr$_2$VO$_3$FeAs experiences another transition at $T_N \approx 45$ K, which can be identified as a spin density wave highly distinct from the typical stripe AFM.
Indeed, \((T_1T)^{-1}\) climbs sharply below 60 K \((\ll T_0)\) for both \(H \parallel a\) and \(H \parallel c\), indicating a critical slow-down of spin fluctuations toward a magnetic ordering at \(T_N \sim 45\) K. However, \(T_1/\pi\) remains isotropic, suggesting that the coupling between Fe spins and As is due to hybridization, which can only generate a magnetic moment on As if As environment is spin-imbalanced. This excludes such AFM orders as stripe, Neel or double-Q, but would be consistent with a longer period AFM order. Also the progressive broadening of \(^{75}\)As spectrum at low temperatures, as shown in Figs. 2a and 2c, suggests a long wavelength, and possibly incommensurate, spin density wave. Neutron diffraction \([22, 23]\), which observed magnetic Bragg peaks at \(Q = (1/8, 1/8, 0)\) below \(T_N \sim 45\) K, is consistent with this conclusion, although it was incorrectly attributed to an ordering of V spins in the previous studies \([16, 19, 24]\). Upon further temperature lowering, \((T_1T)^{-1}\) abruptly drops at \(T_c\). This proves that the superconducting gap opens up on the magnetic Fe sites, and emerges on the background of the remaining, but still strong, spin fluctuations with a \(C_4\) symmetry below \(T_N\). How spin density wave competes or cooperate with superconductivity remains as an important question.

We shall now address an essential question: what suppresses the expected stripe order in the FeAs layer and the Neel order in the SrVO\(_3\) layer? The former can be suppressed via the mechanism in which Neel-type spin fluctuations of the localized magnetic moments are coupled to the itinerant electrons’ stripe spin fluctuation \([10]\). The stripe order, with \(Q = (\pi, \pi, 0)\) for \(0, \pi\), is relatively fragile and can give way to bicollinear, double-Q, and, possibly, plaquette orders, due to AFM fluctuation with additional \(Q\)’s \([36, 40, 41]\). Such magnetic frustration is due to the long range magnetic interactions, reflecting the itinerancy of Fe electrons. Fluctuation at \(Q = (\pi, \pi)\), normally weak in FeSCs, can be enhanced through coupling to the \(Q = (\pi, \pi)\) fluctuations of V spins \([40]\) (Fig. 4a). This destabilizes the \(C_2\) stripe AFM or nematic orders, but encourages the \(C_4\) symmetric vestigial charge/orbital density wave phases \([36, 40]\). Note that in Sr\(_2\)(Mg,Ti)O\(_3\)FeAs and Ca\(_2\)AlO\(_3\)FeAs, isostructural compounds with nonmagnetic oxide layers the standard stripe order is not suppressed \([42, 43]\). Clearly, frustration of stripe Fe and Neel V spin fluctuations, via magnetic proximity coupling, is essential for inducing an unusual hidden phase in Sr\(_2\)VO\(_3\)FeAs.

The coupling between the itinerant Fe electrons and the localized V spins also suppress the Neel order in the SrVO\(_3\) layer. In the SrVO\(_3\) layers, the nearest neighbor superexchange interaction would dominate and generate a stable Neel order. In fact, compared to other V perovskite oxides, such as LaVO\(_3\), SrVO\(_3\)FeAs should have stronger exchange coupling, because of the more straight V-O-V bonds. However, the measured Curie-Weiss temperature of \(T_{CW} \sim -100\) K in Sr\(_2\)VO\(_3\)FeAs is considerably lower than \(T_{CW} \sim -700\) K in LaVO\(_3\) \([44]\). The unexpectedly low \(T_{CW}\) comes from an additional ferromagnetic coupling between the V spins via indirect double-exchange-like interaction mediated by the Fe electrons \([45]\). This frustrates and weakens the AFM superexchange interaction suppressing the long-range V spin order at low temperatures. Indeed, in our detailed LDA+U calculations we found that the calculated magnetic interaction is extremely sensitive to the on-site Coulomb energy \(U\) and the Hund’s coupling \(J\). At \(U - J = 5\) eV, the superexchange interaction, which is inversely proportional to \(U\), is significantly suppressed, while the Fe-mediated one is enhanced, so that the net magnetic interaction becomes weakly ferromagnetic in the planes. For \(U - J = 4\), it changes sign and becomes antiferromagnetic, consistent with a previous report \([10]\). This demonstrates that the SrVO\(_3\) lies on the borderline of competing phases due to a delicate balance between the superexchange and the additional indirect interactions. At the same time, coupling between the stripe fluctuations in the Fe plane at \(Q = (\pi, 0)\) and Neel fluctuations in the V plane \(Q = (\pi, \pi)\) suppresses both
orders even further and prevents V spins form ordering. The interfacial Fe-V interaction is again crucial for the Mott-insulating SrVO₃ layers to remain in a nearly paramagnetic ground state. Our findings therefore manifest that the physics of FeSCs can become even richer in the proximity of other correlated systems and also offers a new avenue for exploring unusual ground state in the correlated heterostructures.

**Methods**

Single crystals of Sr₂VO₃FeAs were grown using self-flux techniques as follows. The mixture of SrO, VO₃, Fe, SrAs, and FeAs powders with a stoichiometry of Sr₂VO₃FeAsFeAs = 1:2 were pressed into a pellet and sealed in an evacuated quartz tube under Ar atmosphere. The samples were heated to 1180°C, held at this temperature for 80 hours, cooled slowly first to 950°C at a rate of 2°C/h and then furnace-cooled. The plate-shaped single crystals were mechanically extracted from the flux. High crystallinity and stoichiometry are confirmed by the X-ray diffraction and energy-dispersive spectroscopy. The typical size of the single crystals is 200×200×10 μm³.

Single crystal X-ray diffraction patterns were taken using an STOE single crystal diffractometer with image plate. Single crystal X-ray diffraction (XRD) reveals a good crystallinity in a tetragonal structure with a = 3.9155(7) Å and c = 15.608(4) Å, consistent with the previous studies on polycrystalline samples. Detailed information about single crystal XRD can be found in the Supplementary Information.

Conventional four-probe resistance of single crystals was measured in a 14 T Physical Property Measurement System. Single crystal magnetizations were measured in a 5 T Magnetic Property Measurement System. The size of one crystal was too small (~ 0.15 mg) to measure the magnetization, thus 8 pieces of Sr₂VO₃FeAs single crystals (1.2 mg) were stacked together. All single crystals were carefully aligned along the c-axis or the ab-plane.

⁵¹V (nuclear spin I=7/2) NMR and ⁷⁵As (I=3/2) NMR measurements were carried out at external magnetic fields of 14.983 T and 11.982 T, respectively. The sample was rotated using a goniometer for the exact alignment along the external field. The NMR spectra were acquired by a standard spin-echo technique with a typical π/2 pulse length 2-3 μs and the spin-lattice relaxation rate was obtained by a saturation method.

Band structure calculations were performed using two standard codes: an all-electron linearized augmented plane wave method implemented in the WIEN2k package [40], and a pseudopotential VASP code [41]. In both cases the gradient-corrected functional of Perdew, Burke and Ernzerhof was used, and special care was taken to ensure proper occupancy of V orbitals in the LDA+U calculations.

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