NMR Search for the Spin Nematic State in a LaFeAsO Single Crystal

M. Fu,1 D. A. Torchetti,1 T. Imai,1,2 F. L. Ning,3 J.-Q. Yan,4,5,6 and A. S. Sefat1

1Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S4M1, Canada
2Canadian Institute for Advanced Research, Toronto, Ontario M5G1Z8, Canada
3Department of Physics, Zhejiang University, Hangzhou 310027, China
4Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
5Department of Materials Science and Engineering, The University of Tennessee at Knoxville, Knoxville, Tennessee 37996, USA
6Division of Materials Science and Engineering, Ames Laboratory, US-DOE, Ames, Iowa 50011, USA

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We report a 75As single crystal NMR investigation of LaFeAsO, the parent phase of a pnictide high $T_c$ superconductor. We demonstrate that spin dynamics develop a strong twofold anisotropy within each orthorhombic domain below the tetragonal-orthorhombic structural phase transition at $T_{TO} \approx 156$ K. This intermediate state with a dynamical breaking of the rotational symmetry freezes progressively into a spin density wave below $T_{SDW} \approx 142$ K. Our findings are consistent with the presence of a spin nematic state below $T_{TO}$ with an incipient magnetic order.

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The mechanism of high $T_c$ superconductivity in iron pnictides remains enigmatic [1]. Earlier NMR measurements demonstrated that low frequency spin fluctuations associated with the spin density wave (SDW) instability grow toward $T_c$ near optimal doping [2–5], favoring the scenario of spin-fluctuation induced superconductivity. There is, however, a complication: the slowing of the lattice vibrations accompanies that of spin fluctuations [6–8]. For example, neutron scattering measurements showed that LaFeAsO undergoes a tetragonal-orthorhombic structural phase transition at $T_{TO} \approx 156$ K, followed by a SDW ordering at $T_{SDW} = 142$ K [6,9,10]. Moreover, the softening of the lattice begins at as high as $\sim 200$ K, and continues through $T_{TO}$ and $T_{SDW}$ down to $T_{domains} \approx 120$ K [6], where the growth of the orthorhombic domains ends [10,11]. Theoretical analysis of LaFeAsO based on the frustrated $J_1$-$J_2$ model suggests that the Ising symmetry of Fe spins may already be broken below $T_{TO}$ without a three-dimensional magnetic long-range order [12]. Moreover, the intermediate temperature range between $T_{TO}$ and $T_{SDW}$ of LaFeAsO may be identified as a spin nematic state [13].

In such a nematic state, the spin correlations break the tetragonal symmetry, i.e., $(S_i \cdot S_{i+z}) = - (S_i \cdot S_{i+y})$ (we refer readers to Fig. 1 of a review article [14] for a pictorial demonstration of the nematic state). More recent theoretical analysis based on an itinerant electron picture [15] or an orbital fluctuation model [16] also led to analogous conclusions. The prospect of observing such a magnetic analogue of a liquid crystal below $T_{TO}$ with an incipient (“fluctuating”) magnetic order, and its potential link with the mechanism of high $T_c$ superconductivity, has stimulated strong interest among researchers. The past experimental efforts searching for the signature of nematicity were focused primarily on the BaFe$_2$As$_2$ series (e.g., Refs. [17–20]). However, the proximity between the structural and SDW transitions, and/or the twinning of orthorhombic domains, hampered these efforts.

In this Letter, we report a microscopic, 75As NMR investigation of LaFeAsO for a single crystal [21], and compare our results with neutron scattering [10] and magnetic susceptibility $\chi$ measured for the same piece of $\sim 20$ mg crystal. The usage of a single crystal enabled us to resolve complicated changes of NMR line shapes across $T_{TO}$ and $T_{SDW}$ for the first time and find the signature of the spontaneous breaking of the rotational symmetry. We will demonstrate that low frequency spin dynamics indeed exhibit a strong anisotropy within each orthorhombic domain with a twofold symmetry below $T_{TO}$, and the SDW ordered and paramagnetic domains coexist in a broad range of temperature. Our findings uncover the presence of an unconventional intermediate spin state below $T_{TO}$ with the signatures of spin nematicity.

In Fig. 1, we summarize representative field-swept 75As NMR line shapes observed at $f_{NMR} = 58.159$ MHz (nuclear spin $I = 3/2$). When we apply an external magnetic field $B_{ext}$ along the c axis, a sharp paramagnetic (PM) central peak appears at $B_{center}^{ext} \approx 7.96$ T for the $I_z = +1/2$ to $-1/2$ transition, as shown in Fig. 1(b); the resonant condition is $f_{NMR} = (1 + \gamma_s B_{center}^{ext}) / 2\pi = 7.2919$ MHz/T. $75K \sim 0.002(\sim 0.2\%)$ is the Knight shift, which measures the product between the local spin susceptibility and the hyperfine coupling constant. We note that the FWHM of the PM central peak is as sharp as 6.5 KHz (8.9 Oe) at 290 K in the absence of orthorhombic distortion. The narrow linewidth is comparable to that of undoped BaFe$_2$As$_2$ [22,23], and attests to the high homogeneity of our crystal.
Shapes with Coulomb potential arising from electrons and ions near clear quadrupole interaction with the electric field gradient toward arrows), but only below the onset temperature of from the statically SDW-ordered domains (marked by downward arrows), as schematically shown in Fig. 2(a), results in the splitting of the $B_{\text{ext}} \parallel ab$ line shape below $T_{\text{TO}} \approx 156$ K. In Fig. 1(a), we observe an $I_{c} = \pm 3/2$ to $\pm 1/2$ paramagnetic satellite peak near $B_{\text{satellite}} = 6.7$ T (connected by a dotted line). We also found the strongly temperature dependent antiferromagnetic (AFM) central peak arising from the statically SDW-ordered domains (marked by downward arrows), but only below the onset temperature of $T_{\text{SDW}}^{\text{ext}} = 135$ K ($< T_{\text{SDW}}$). The AFM central peak is shifted from the PM central peak at $B_{\text{center}} \approx 7.96$ T in Fig. 1(b) by a static hyperfine field along the c-axis, $\langle B_{\text{hf}}^{c} \rangle$. $\langle B_{\text{hf}}^{c} \rangle$ originates from the ordered Fe magnetic moments $M_{\text{Fe}}$, and $\langle B_{\text{hf}}^{c} \rangle \propto M_{\text{Fe}}[22]$. In Fig. 2(b), we deduce the temperature dependence of $\langle B_{\text{hf}}^{c} \rangle$ from Fig. 1(a), and compare the results with the neutron scattering data of $M_{\text{Fe}}[10]$. The splitting between the central and satellite peaks, $\nu_{Q}^{c} = \gamma_{n}(B_{\text{center}} - B_{\text{satellite}})$, measures the nuclear quadrupole interaction with the electric field gradient (EFG). We summarize the temperature dependence of $\nu_{Q}^{c}$ in Fig. 2(c). The EFG is the second derivative of the Coulomb potential arising from electrons and ions near the observed $^{75}$As sites. Below $T_{\text{TO}} \approx 156$ K, $\nu_{Q}^{c}$ exhibits a sharp downturn, because the EFG is sensitive to the local structural environment. Earlier diffraction measurements showed that the growth of orthorhombic domains finally comes to an end at $T_{\text{domains}} \approx 120$ K [10,11]; $\nu_{Q}^{c}$ also levels off below $T_{\text{domains}}$. In Fig. 1(b), we also show representative NMR line shapes with $B_{\text{ext}}$ applied along the tetragonal $a$ axis within the FeAs planes. Above $T_{\text{TO}}$, all tetragonal domains are equivalent; hence, we observe a single central peak. Below $T_{\text{TO}}$, the elongated $a$ axis of each domain points either along the direction of $B_{\text{ext}}$ or orthogonal to $B_{\text{ext}}$, due to twinning of the orthorhombic domains, as sketched in Fig. 2(a). Moreover, orthorhombic distortion breaks the axial symmetry of the EFG. The difference in the second order effects of the nuclear quadrupole interaction thus results in splitting of the central peak; the peak positions depend on the direction of the elongated $a$ axis relative to $B_{\text{ext}}$. We confirmed that the NMR line splitting in Fig. 1(b) is caused entirely by the difference in the second order nuclear quadrupole effects, which is inversely proportional to $B_{\text{ext}}[24]$. That is, the NMR Knight shift is still axially symmetric, and shows very little temperature dependence below $T_{\text{TO}}$. $73K_{a} = 75K_{b} = 0.22 \pm 0.03\%$. In view of the fact that expansion of the lattice from $T_{\text{TO}}$ to $290$ K results in a larger value of the quadrupole frequency as shown in Fig. 2(c), we tentatively assign the peak near $B_{\text{ext}} \approx 7.91$ T to the orthorhombic domains with $B_{\text{ext}} \parallel a$; the other peak near $B_{\text{ext}} \approx 7.92$ T arises from the orthorhombic domains with $B_{\text{ext}} \parallel b$ instead. From the splitting of an $I_{c} = \pm 3/2$ to $\pm 1/2$ satellite peak, we estimate $\nu_{Q}^{a} \approx 5.2$ MHz and $\nu_{Q}^{b} \approx 3.9$ MHz at $145$ K. We also confirmed that these double peaks collapse into one when we apply $B_{\text{ext}}$ along the [110] direction within the $ab$ plane, because $B_{\text{ext}}$ points along the diagonal direction for all orthorhombic domains in such a geometry.
For bulk averaged measurement techniques such as resistivity, the twinning of orthorhombic domains would result in experimental data averaged over two orthogonal directions within the ab plane, unless one applies a uniaxial stress [17–20]. It is not straightforward, then, to probe the spontaneous breaking of the rotational symmetry. In contrast, NMR is a local probe. Since we have succeeded in resolving the central peaks in Fig. 1(b) for different orientations, we can investigate the in-plane anisotropy of spins within each orthorhombic domain.

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FIG. 3 (color online). (a) Temperature dependence of 1/T1T measured for the PM central peak with Bext along the [110] (●) and the c-axis (△) direction. The solid curves are guides to the eye only. (b) 1/T1T as a function of the field orientation φ as defined in Fig. 2(a), within each orthorhombic domain. The results are symmetrized for φ ≤ 0 due to crystal symmetry. Below TSDW ~ 156 K, 1/T1T exhibits increasingly strong dependence on the in-plane orientation of Bext, which can be modeled by the function 1/T1T = A + B cos2 φ (solid curves). The accidental superposition between different NMR peaks makes accurate measurements of 1/T1T unequivocal below 135–140 K, depending on the direction of Bext.

The anomalous behavior of Fe spins below TSDW is not limited to the in-plane anisotropy of their dynamics. In Fig. 4, we summarize the temperature dependence of the integrated intensities of the NMR signal. An unusual aspect of the signal intensity is that the paramagnetic NMR peaks do not disappear suddenly at TSDW = 142 K, and linger well below TSDW down to Tdomains ~ 120 K. On the other hand, AFM NMR signals from statically SDW ordered domains emerge progressively, only below TSDW = 135 K (< TSDW). Notice that the PM central peak is still clearly observable below TSDW in Fig. 1(b). Our finding that the PM signal intensity is as large as ~60% at TNMRSDW implies that ~60% of the sample volume remains paramagnetic at 135 K. That is, AFM and PM domains coexist even below TSDW, although neutron scattering begins to detect magnetic Bragg peaks below TSDW [10]. In addition, 1/T1T measured for the residual PM peak does not blow up at
become static, to the extent that the PM phase coexists with the AFM phase even below $T_{\text{SDW}}$, as shown in Fig. 1(a). Notice that the negative $B_{\text{ext}}$ from $\sim 7.96$ T to $\sim 3.85$ T does not alter the qualitative features.

$T_{\text{SDW}}$, and continues to increase. If the SDW ordering in our LaFeAsO single crystal was a typical second order phase transition, $1/T_1$ would diverge at $T_{\text{SDW}}$ due to the critical slowing down of spin fluctuations, followed by a sudden disappearance of PM NMR signals below $T_{\text{SDW}}$

The reason NMR and neutron scattering detect different onset temperatures of the SDW is that each experimental probe has a different characteristic measurement time scale [28,29]. Elastic neutron scattering measurements would consider the SDW “static” when fluctuations slow down below the instrument resolution of $\sim 1$ meV. This means that neutron scattering can take an instantaneous picture of Fe spins with a “shutter speed” of $\sim 10^{-11}$ s even if they are still slowly fluctuating. In contrast, AFM NMR signals in Fig. 1(a) become observable only when Fe spins in the SDW become static, to the extent that $\langle B_{hf}^i \rangle$ is time independent over the duration of our spin echo measurements, 40 $\mu$s. If Fe moments are fluctuating faster than $40 \mu$s in some segments of FeAs planes, NMR would see them as motionally averaged out (i.e., paramagnetic). In other words, the different onset temperatures of the SDW ordering between neutron and NMR data indicate that the fluctuations of the SDW continue to slow down from $T_{\text{SDW}} \approx 142$ K to $T_{\text{SDW}}^\text{NMR} \approx 135$ K. The coexistence of PM and AFM domains below $142$ K implies that the fluctuation time scales have a broad distribution throughout the FeAs planes. We also found that $\chi_{ab}$ exhibits an additional kink at $\sim 133$ K, as shown in Fig. 2(d). Since the SQUID measures the time-independent response of spins, the acceleration in the suppression of $\chi_{ab}$ below $T_{\text{SDW}}^\text{NMR}$ is consistent with NMR.

It is interesting to realize that these unusual behaviors of LaFeAsO share similarities with the spin stripes in high $T_c$ cuprates [30], where the concept of nematicity was originally proposed for unconventional superconductors [31]. In the striped cuprates, the spin stripes progressively slow down below a charge ordering at $\sim 70$ K [30] (instead of $T_{\text{TO}}$); elastic neutron scattering, $\mu$SR, and NMR detect the emergence of a static SDW at their respective measurement time scale below $\sim 50$ K [30], $\sim 30$ K [32], and $\sim 1.6$ K [28], respectively. Moreover, PM NMR signals linger well below $\sim 50$ K [28].

The temperature dependence of the AFM NMR signal intensity in Fig. 4 indicates that the volume fraction of the static SDW at the time scale of NMR gradually increases from $T_{\text{SDW}}^\text{NMR} \approx 135$ K toward $T_{\text{domains}} \approx 120$ K. Once the growth of the orthorhombic domains ends at $T_{\text{domains}}$ [10,11], the intensity saturates at $\sim 60\%$ of the paramagnetic intensity above $T_{\text{SDW}}$. The missing signal intensity suggests that $\langle B_{hf}^i \rangle$ is still modulating and/or $T_{\text{SDW}}$ too fast for a spin echo NMR signal to form in $\sim 40\%$ of the sample volume. Our finding is consistent with the earlier $\mu$SR measurements for a powder sample of LaFeAsO; the muon precession with a well-defined frequency of $\sim 23$ MHz takes place only in $\sim 70\%$ of the sample volume, and $\sim 30\%$ of the $\mu$SR signal is strongly damped [33]. It remains to be seen whether these ultraslow dynamics of the SDW in $30\%$–$40\%$ of the sample volume are caused by the motion of the antiphase domain boundaries [29] and/or the finite size effects of the orthorhombic domains.

To summarize, we demonstrated that Fe spin fluctuations in a LaFeAsO single crystal begin to slow down below $T_{\text{TO}} = 156$ K, accompanied by the local breakdown of the rotational symmetry of spin fluctuations in each of the randomly twinned orthorhombic domains. The way that the static SDW develops is also unconventional. The paramagnetic and SDW ordered domains coexist in a wide range of temperature below $T_{\text{SDW}} \approx 142$ K due to a distribution in the fluctuation time scales of the SDW. A large volume of FeAs planes sees freezing of the static SDW only below $T_{\text{domains}} \approx 120$ K. Our findings point towards the presence of a novel spin state between $T_{\text{TO}}$ and $T_{\text{domains}}$ with a dynamically broken rotational symmetry and an incipient magnetic order, i.e., the elusive spin nematic state.

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