Nematicity and magnetism in LaFeAsO single crystals probed by $^{75}$As nuclear magnetic resonance

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We report a $^{75}$As nuclear magnetic resonance study in LaFeAsO single crystals, which undergoes nematic and antiferromagnetic transitions at $T_{\text{nem}} \approx 156$ K and $T_{N} \approx 138$ K, respectively. Below $T_{\text{nem}}$, the $^{75}$As spectrum splits sharply into two for an external magnetic field parallel to the orthorhombic $a$ or $b$ axis in the FeAs planes. Our analysis of the data demonstrates that the NMR line splitting arises from an electronically driven rotational symmetry breaking. The $^{75}$As spin-lattice relaxation rate as a function of temperature shows that spin fluctuations are strongly enhanced just below $T_{\text{nem}}$. These NMR findings indicate that nematic order promotes spin fluctuations in magnetically ordered LaFeAsO, as observed in non-magnetic and superconducting FeSe. We conclude that the origin of nematicity is identical in both FeSe and LaFeAsO regardless of whether or not a long range magnetic order develops in the nematic state.

Understanding nematic order and its relationships to magnetism and superconductivity remain among the most important questions in the current study of Fe-based superconductors (FeSCs). While different classes of FeSCs show very similar softening of the lattice and divergence of the nematic susceptibility when approaching the nematic transition [1–5], there are pronounced differences with respect to the slowing down of spin fluctuations (SFs). In the BaFe$_2$As$_2$-type system, the dynamic spin susceptibility as revealed from NMR spin-lattice relaxation rate data scales with the softening of the elastic constant above the nematic transition [6]. This was interpreted as evidence for theoretical scenarios where nematic order is driven by an antiferromagnetic instability. On the other hand, the nonmagnetic compound FeSe does not show any slowing down of SFs above the nematic transition [7, 8]. This, as well as the absence of long-range magnetic order in FeSe, has been taken as evidence for an alternative origin of nematic order, related to orbital degrees of freedom [9, 10]. Based on a renormalization group (RG) analysis [11, 12], a possible scenario for such an orbital order as the leading instability was derived. According to this model the origin of the orbital order in FeSe is the small Fermi energies of the electron and hole bands. While the changes of the electronic structure due to nematic order obtained by the RG analysis are consistent with recent high resolution angle-resolved photoemission spectroscopy (ARPES) studies [14, 15], it is impossible to prove this scenario from the available data on FeSe. Several alternative scenarios were suggested for the nematic order in FeSe, for example, related to the frustration of the magnetic exchange interactions [17, 18].

In order to shed more light on the possible origin of nematic order in FeSCs, we carried out a NMR investigation on a prototypical FeSC, LaFeAsO, which shows a clear separation between nematic order at $T_{\text{nem}} \approx 156$ K and magnetic order at $T_{N} \approx 138$ K. The temperature dependence of $^{75}$As NMR spectra and spin-lattice relaxation rates measured in our LaFeAsO single crystals reveals remarkable similarities to that in FeSe, suggesting that the scaling behavior found in BaFe$_2$As$_2$ is not generic for FeSCs. In contrast, qualitatively the interplay between nematicity and magnetism as seen by NMR is almost identical in FeSe and LaFeAsO. The only difference is that, in the latter, the impact of orbital order on SFs is much stronger and the pronounced slowing down of SFs is followed by long range magnetic order 15 K below $T_{\text{nem}}$.

Single crystals of LaFeAsO were grown by using NaAs-flux techniques. The mixture of LaAs, Fe, Fe$_3$O$_3$, and NaAs powders with a stoichiometry of LaAs:Fe:Fe$_3$O$_3$:NaAs = 3:1:1:4 was double-sealed with a Ta tube (or stainless steel tube) and an evacuated quartz tube. The entire assembly was heated to 1150°C, held at this temperature for 40 h, cooled slowly to 700°C at a rate of 1.5°C/h and then furnace-cooled. The NaAs flux was rinsed off with deionized water in a fume hood and the plate-shaped single crystals were mechanically extracted from the remaining by-products.

$^{75}$As (nuclear spin $I = 3/2$) NMR measurements were carried out on LaFeAsO single crystals at an external field of 9 T and in the range of temperature 130 – 300 K. It turned out that the $^{75}$As NMR spectrum becomes significantly narrower for smaller crystals, indicating that local inhomogeneity or disorder increases rapidly in proportion to the size of the crystal. Since the coupling of $^{75}$As nuclei to nematicity is generally very small in
FeSCs, the sufficiently narrow NMR spectrum is crucial for the detailed investigation of nematicity. For this reason, we collected and aligned five single crystals as small as 0.15 × 0.15 × 0.01 mm$^3$ to achieve a measurable signal intensity while maintaining a minimal linewidth. The alignment of samples is satisfactory, based on the much narrower $^{75}$As line than that observed in a previous NMR study [19] (see Fig. 1). The aligned single crystals were reoriented using a goniometer for the accurate alignment along the external field. The $^{75}$As NMR spectra were acquired by a standard spin-echo technique with a typical $\pi/2$ pulse length 2–3 $\mu$s. For the nuclear spin-lattice relaxation ($T_1^{-1}$) measurements, we used a large single crystal with a dimension of $2 \times 2 \times 0.1$ mm$^3$ as homogeneity does not affect the average spin-lattice relaxation rate. $T_1^{-1}$ was obtained by fitting the recovery of nuclear magnetization $M(t)$ after a saturating pulse to the following fitting function,

$$1 - \frac{M(t)}{M(\infty)} = A \left(0.9e^{-t/T_1} + 0.1e^{-t/T_1}\right)$$

where $A$ is a fitting parameter.

Figure 1 shows the $^{75}$As spectrum as a function of temperature for three different field orientations along the $c$, $a$ (or $b$), and [110] directions, respectively. The full width at half maximum (FWHM) of the line remains very narrow (less than 20 kHz), evidencing a high quality of the samples. Below $T_{nem}$ we observed a clear splitting of the $^{75}$As line for $H \parallel a$. In strong contrast, the $^{75}$As line for $H \parallel c$ remains a single line until it disappears due to the antiferromagnetic (AFM) ordering at $T_N$. We also confirmed that the $^{75}$As line does not split when $H$ is applied parallel to the $ab$ plane in the diagonal direction ($H \parallel [110]$). Therefore one can conclude that the split lines for $H \parallel a$ arise from the two fully twinned nematic domains in the orthorhombic structural phase.

The temperature dependence of the resonance frequency $\nu$ for each NMR lines is presented in Fig. 2(a) in terms of the NMR shift $K \equiv (\nu - \nu_0)/\nu_0 \times 100$ % where $\nu_0$ is the unshifted resonance frequency. In a paramagnetic state, the NMR shift can be written as

$$K = A_{hf}\chi_{spin} + K_0 + \mathcal{K}_{quad},$$

where $A_{hf}$ is the hyperfine coupling constant, $\chi_{spin}$ the local spin susceptibility, $K_0$ the temperature independent term, and $\mathcal{K}_{quad}$ the second order quadrupole shift. For $T > T_{nem}$, the NMR shift for both field directions is weakly temperature dependent. Note that the large anisotropy of the NMR shift between the field orientations along $a$ and $c$ is accounted for by the term $\mathcal{K}_{quad}$ which is the largest for $H \parallel a(b)$, but vanishes for $H \parallel c$.

The data reveal that the line splitting occurs at $T_{nem}$ and increases upon lowering temperature. The separation of the two lines, $\Delta \nu_{\parallel a}$, exhibits the $\sqrt{T_{nem} - T}$ behavior of a Landau-type order parameter below $T_{nem}$, as shown in Fig. 2(b). This indicates that $\Delta \nu_{\parallel a}$ represents the

![FIG. 1. $^{75}$As NMR spectra measured at 9 T applied parallel to the $c$ axis (a), to the $a$ axis (b), and to the [110] direction (c), as a function of temperature. The red and blue horizontal arrows denote the nematic and the magnetic transition temperatures, $T_{nem}$ and $T_N$, respectively. The $^{75}$As line splits below $T_{nem}$ for $H \parallel a(b)$, but it remains a single line for $H \parallel c$ and $H \parallel [110]$, proving spontaneous $C_4 \rightarrow C_2$ symmetry breaking. The notable broadening below $T_{nem}$ for $H \parallel [110]$ is attributed to a slight misalignment of the sample.](image)
FIG. 2. (a) Temperature dependence of the $^{75}$As NMR shift $K$ for fields parallel to the $a$ (or $b$) and $c$ axes. The data for $H \parallel ab$ were offset by $-0.1$ for a better comparison. At $T_{\text{nem}}$, $K_{\parallel a}$ sharply splits into two, but $K_{\parallel c}$ shows a smooth $T$-dependence. (b) The $^{75}$As line splitting $\Delta v_{\parallel a}$ as a function of temperature. Inset: $\Delta v_{\parallel a}$ is well described by the relation, $\sqrt{T_{\text{nem}} - T}$ below $T_{\text{nem}}$, as is expected for an order parameter at a second order phase transition.

$C_4 \rightarrow C_2$ symmetry breaking, or the nematic order parameter. These features near $T_{\text{nem}}$ are identical to the case of FeSe, except for the presence of the AFM transition at $T_N \sim 138$ K.

The immediate question then arises which degree of freedom, among lattice/spin/orbital, is responsible for the splitting of the $^{75}$As line. A previous NMR study in LaFeAsO single crystals [19] interpreted that the $^{75}$As line splitting is a direct consequence of the quadrupole effect in the twinned orthorhombic domains — that is, the direction of the principal axis of the electric field gradient (EFG) in one domain is rotated by $90^\circ$ in the other, giving rise to the different second order quadrupole shift in the two domains. If this is the case, the separation between $^{75}$As split lines should be given by [21]

$$\Delta v_{\parallel a}^{\text{quad}} = \frac{\eta v_Q^2}{4\gamma_n H},$$

where $\eta \equiv |V_{xx} - V_{yy}|/V_{zz}$ is the asymmetry parameter, $v_Q$ is the quadrupole frequency, and $\gamma_n$ is the nuclear gyromagnetic ratio. Accordingly, the line splitting should be inversely proportional to the external field $H$. As shown in Fig. 3, however, we verified that the splitting does not decrease linearly in field, but even slightly increases, as $H$ is increased from 10 to 15 T. This unambiguously proves that the line splitting cannot be ascribed simply to the quadrupole effect. Rather, similar to the discussion made in the $^{77}$Se NMR study of FeSe [8, 9], it is natural to consider that the local spin susceptibility, $A_\text{hf}\lambda_{\text{spin}}$ in Eq. (1), is mainly responsible for the $C_4$ symmetry breaking at the As sites, proving that the nematic transition is electronically driven [22].

Having established that the lattice distortion is not a primary order parameter for nematicity, now we discuss the possible role of the spin degree of freedom for the nematic transition. For this purpose, we measured the spin-lattice relaxation rate $T_1^{-1}$ as a function of temperature, as the quantity $(T_1T)^{-1}$ probes SFs averaged over the Brillouin zone at very low energy. The results are shown in Fig. 4(a). $(T_1T)^{-1}$ is nearly constant for both field orientations with a weak anisotropy at high temperatures. At near $T_{\text{nem}} \sim 156$ K, however, it starts to upturn accompanying a strong anisotropy and diverges at $T_N$ for $H \parallel a$, being consistent with previous NMR studies [19, 22]. The strong development of SFs in the nematic phase raises the question whether SFs drives nematicity or it is a consequence of nematic ordering. In order to answer the question, we measured $(T_1T)^{-1}$ very carefully near $T_{\text{nem}}$ for both $H \parallel a$ and $H \parallel c$. Remarkably, we observed a sharp kink of $(T_1T)^{-1}$ exactly at $T_{\text{nem}}$ for both field orientations, which is better shown in a semilog plot [Fig. 4(b)]. This observation indicates that nematic ordering drastically enhances SFs in LaFeAsO, which is consistent with inelastic neutron scattering re-
As in (a) in a semi-log scale. (T, (T/T)⁻¹) reveals a clear kink at T_{nem} before diverging at T_N, indicating that SFs are abruptly enhanced by nematic order. The inset shows temperature dependence of FWHM. The FWHM for H || a starts to increase below a characteristic temperature T* > T_{nem} with respect to the background. In contrast, the data for H || c does not change through T*.

In conclusion, by means of ⁷⁵As NMR, we have investigated the nematic and magnetic properties in high quality LaFeAsO single crystals. A sharp ⁷⁵As line splitting observed for H || a below T_{nem} has been proven to arise from the electronically driven twinned nematic domains. The ⁷⁵As spin-lattice relaxation data reveal that spin fluctuations are sharply enhanced by nematic order, similar to the behavior observed in non-magnetically ordered FeSe. We conclude that the leading instability for nematicity is identical for both FeSe and LaFeAsO, irrespective of whether long-range magnetic ordering occurs in the nematic state.

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