Rapid Communications

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 $T_{\rm nem} \sim 156$ K and $T_N \sim 138$ K, respectively. Below $T_{\rm nem}$, 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 $T_{\rm nem}$. These NMR findings indicate that nematic order promotes spin fluctuations in magnetically ordered LaFeAsO, as observed in nonmagnetic 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.

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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) [1–5]. While different classes of FeSCs show very similar softening of the lattice and divergence of the nematic susceptibility when approaching the nematic transition [6,7], there are pronounced differences with respect to the slowing down of spin fluctuations (SFs). In the $BaFe_2As_2$-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 [7–10]. 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 [5,11]. Based on a renormalization group (RG) analysis [12,13], 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 [14–16], 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 $T_{\rm nem} \sim 156$ K and magnetic order at $T_N \sim 138$ 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 $BaFe_2As_2$ 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 $T_{\rm nem}$.

Single crystals of LaFeAsO were grown by using NaAs-flux techniques. The mixture of LaAs, Fe, Fe_2O_3, and NaAs powders with a stoichiometry of LaAs:Fe:Fe_2O_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 de-ionized 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

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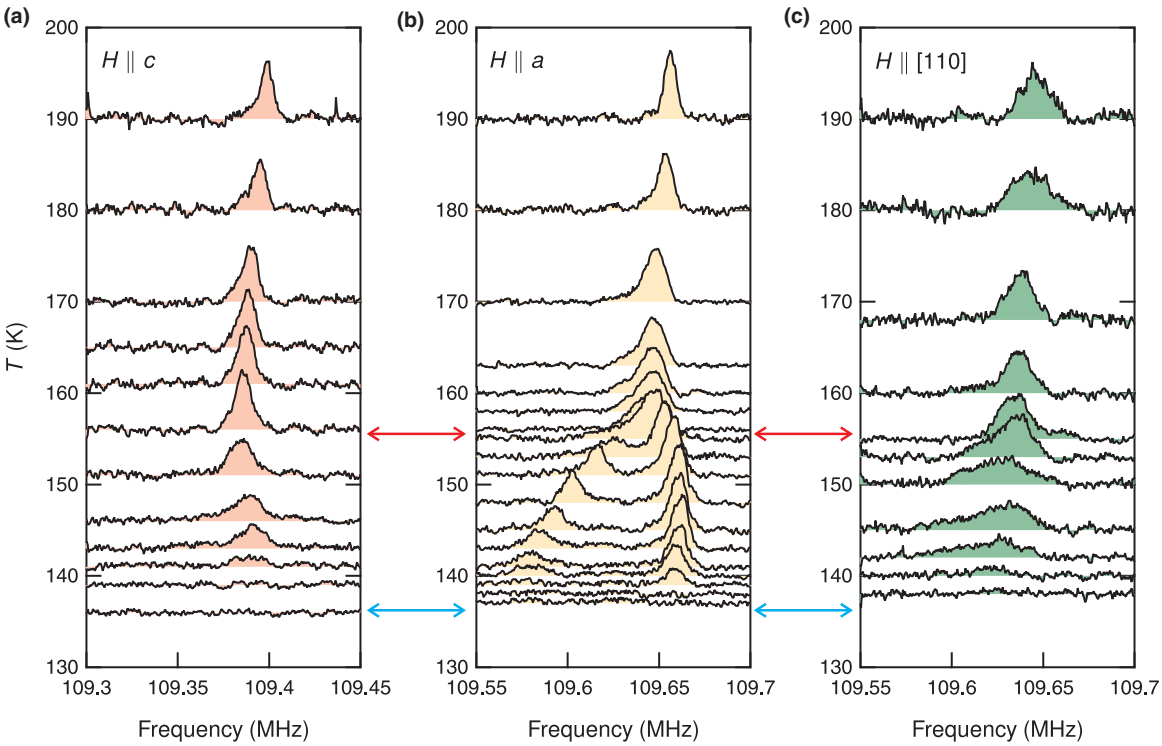

FIG. 1. ^{75}As NMR spectra measured at 9 T applied parallel to the c axis (a), to the a axis (b), and to the [110] direction (c), as a function of temperature. The red and blue horizontal arrows denote the nematic and the magnetic transition temperatures, $T_{\rm nem}$ and T_N, respectively. The ^{75}As line splits below $T_{\rm nem}$ 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 $T_{\rm nem}$ for $H \parallel [110]$ is attributed to a slight misalignment of the sample.

as small as $0.15 \times 0.15 \times 0.01$ 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 μs. 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 [20] as inhomogeneity 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 following fitting function,

$$1 - \frac{M(t)}{M(\infty)} = A(0.9e^{-6t/T_1} + 0.1e^{-t/T_1}),$$

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 $T_{\rm nem}$ 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 ν for each NMR lines is presented in Fig. 2(a) in terms of the NMR shift $\mathcal{K} \equiv (\nu - \nu_0)/\nu_0 \times 100\%$, where ν_0 is the unshifted resonance frequency. In a paramagnetic state, the NMR shift can be written as

$$\mathcal{K} = A_{\rm hf}\chi_{\rm spin} + \mathcal{K}_0 + \mathcal{K}_{\rm quad}, \quad (1)$$

where $A_{\rm hf}$ is the hyperfine coupling constant, $\chi_{\rm spin}$ the local spin susceptibility, $\mathcal{K}_0$ the temperature-independent term, and $\mathcal{K}_{\rm quad}$ the second-order quadrupole shift. For $T > T_{\rm nem}$, 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 $\mathcal{K}_{\rm quad}$, which is the largest for $H \parallel a(b)$, but vanishes for $H \parallel c$. The data reveal that the line splitting occurs at $T_{\rm nem}$ and increases upon lowering temperature. The separation of the two lines, $\Delta\nu_{\parallel a}$, exhibits the $\sqrt{T_{\rm nem} - T}$ behavior of a Landau-type order parameter below $T_{\rm nem}$, as shown in Fig. 2(b). This indicates that $\Delta\nu_{\parallel a}$ represents the $C_4 \rightarrow C_2$ symmetry breaking, or the nematic order parameter. These features near $T_{\rm nem}$ 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

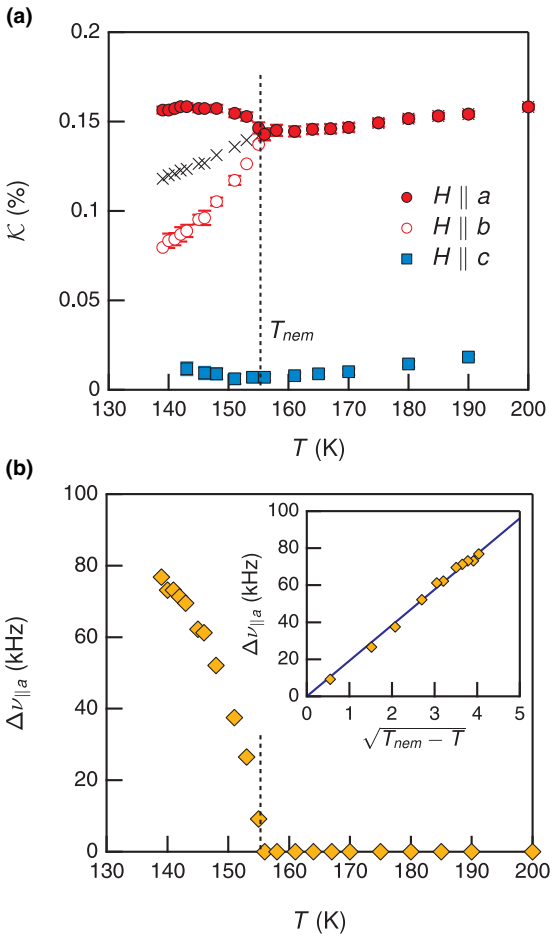

FIG. 2. (a) Temperature dependence of the ^{75}As NMR shift $\mathcal{K}$ for fields parallel to the a (or b) and c axes. The data for $H \parallel ab$ were offset by -0.1 for a better comparison. At $T_{\rm nem}$, $\mathcal{K}_{\parallel a}$ sharply splits into two, but $\mathcal{K}_{\parallel c}$ shows a smooth T dependence. (b) The ^{75}As line splitting $\Delta\nu_{\parallel a}$ as a function of temperature. Inset: $\Delta\nu_{\parallel a}$ is well described by the relation $\sqrt{T_{\rm nem} - T}$ below $T_{\rm nem}$, as is expected for an order parameter at a second-order phase transition.

orthorhombic domains—that is, the direction of the principal axis of the electric field gradient (EFG) in one domain is rotated by 90° 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]

$$\Delta\nu_{\parallel a}^{\rm quad} = \frac{\eta\nu_Q^2}{4\gamma_n H}, \tag{2}$$

where $\eta \equiv |V_{xx} - V_{yy}|/V_{zz}$ is the asymmetry parameter, ν_Q is the quadrupole frequency, and γ_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 $A_{\rm hf}\chi_{\rm spin}$ in Eq. (1) is mainly responsible for the C_4 symmetry breaking at

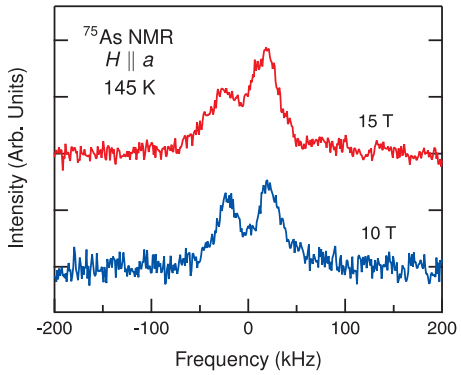

FIG. 3. Comparison of the split ^{75}As spectrum in the nematic phase (at 145 K) for $H \parallel a$ at two different field strengths. Clearly, the distance between the two peaks does not decrease at a larger field, proving that the ^{75}As line splitting is not due to a quadrupole effect. Note that the spectrum is considerably broader than those shown in Fig. 1 because it was obtained in a much larger single crystal used for the spin-lattice relaxation measurements.

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 $T_{\rm nem} \sim 156$ 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 [19,23]. 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 $T_{\rm nem}$ for both $H \parallel a$ and $H \parallel c$. Remarkably, we observed a sharp kink of $(T_1T)^{-1}$ exactly at $T_{\rm nem}$ 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 results [24]. This can be qualitatively understood in terms of the dynamical spin susceptibility $\chi_{\mathbf{q}} \propto (r + q^2)^{-1}$, where $r \sim \xi^{-2}$ with the magnetic correlation length ξ. As the nematic order parameter ϕ becomes nonzero below $T_{\rm nem}$, ξ is renormalized as $\xi^{-2} \to \xi^{-2} - \phi$ [25] and thus $\chi_{\mathbf{q}}$ or $(T_1T)^{-1}$ is strongly enhanced by the onset of nematic order.

Interestingly, Fig. 4(b) reveals that $(T_1T)^{-1}$ deviates from the background (solid lines) at a much higher temperature $T^* \sim 190$ K than $T_{\rm nem}$. Moreover, we find that the FWHM of the ^{75}As line for $H \parallel a$ abruptly increases with respect to the background at T^*, as shown in the inset of Fig. 4(b). These findings are similar to those observed in $NaFe_{1-x}Co_xAs$ [26], where the ^{75}As line broadening with nonzero η sets in at a temperature far above $T_{\rm nem}$. Zhou *et al.* ascribed the development of the nonzero η above $T_{\rm nem}$ to an incommensurate orbital order in the tetragonal phase. An alternative explanation

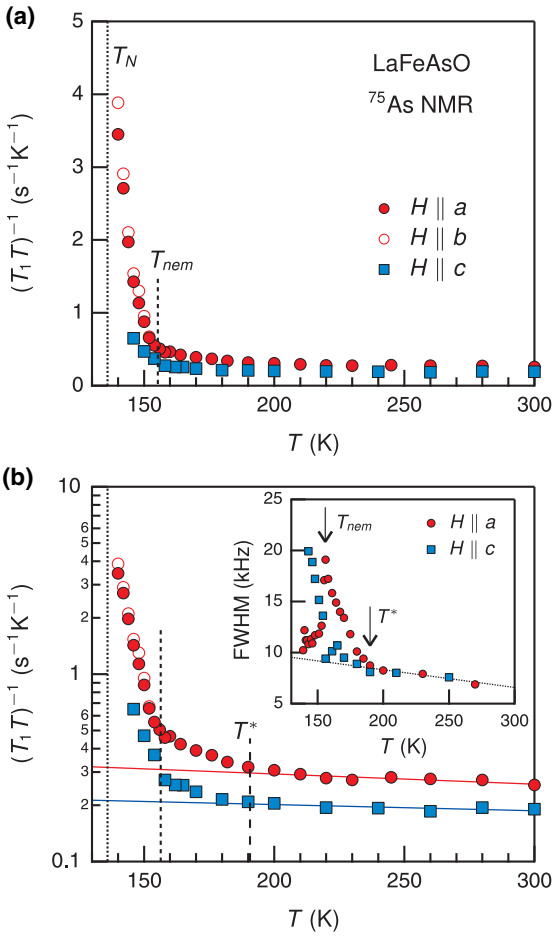

FIG. 4. (a) Temperature dependence of ^{75}As spin-lattice relaxation rate divided by T, $(T_1T)^{-1}$. (b) The same data as in (a) in a semilog scale. $(T_1T)^{-1}$ reveals a clear kink at $T_{\rm nem}$ before diverging at T_N, indicating that SFs are abruptly enhanced by nematic order. The inset shows the temperature dependence of FWHM. The FWHM for $H \parallel a$ starts to increase below a characteristic temperature $T^* > T_{\rm nem}$ with respect to the background. In contrast, the data for $H \parallel c$ do not change through T^*.

may be the occurrence of the lattice softening due to nematic fluctuations [27], which may lead to the local formation of nematic domains. Regardless of its origin, our data indicate that the weak enhancement of SFs below T^* is associated with nematic domains locally generated in some regions of the sample.

In LaFeAsO, a magnetic transition takes place subsequent to a nematic transition, which differs from FeSe where superconducting order develops at a lower temperature without magnetic ordering. Recently, Chubukov *et al.* [12] argued that the hierarchy of orbital, magnetic, and superconducting instabilities is essentially determined by the largest Fermi energy E_F. Namely, for a sufficiently small E_F, the leading instability is towards orbital order as in FeSe, while it is towards a spin density wave (SDW) or superconductivity as in other FeSCs for a large E_F. Despite the large difference of E_F between LaFeAsO and FeSe, however, our NMR results in LaFeAsO and the comparison with those in FeSe [7–9] strongly suggest that nematic order promotes SFs in the same way for both systems. It should be noted that a sharp enhancement of SFs below $T_{\rm nem}$ is also observed in another magnetically ordered system, NaFeAs [28,29]. That is, the proximity of a nematic state to long-range magnetic order does not necessarily indicate that the spin degree of freedom is the driving force for the nematic transition in FeSCs [30,31]. Rather, our NMR findings suggest that nematicity is generally driven by orbital order even in magnetically ordered FeSCs, although it can enhance a magnetic instability. However, this relationship between nematic order and magnetism cannot be established in the $BaFe_2As_2$-type 122 system where magnetic and structural transitions occur simultaneously so that it is not possible to disentangle the orbital and spin degrees of freedom.

In conclusion, by means of ^{75}As NMR, we have investigated the nematic and magnetic properties in high-quality LaFeAsO single crystals. A sharp ^{75}As line splitting observed for $H \parallel a$ below $T_{\rm nem}$ has been proven to arise from the electronically driven twinned nematic domains. The ^{75}As spin-lattice relaxation data reveal that spin fluctuations are sharply enhanced by nematic order, similar to the behavior observed in nonmagnetically 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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