Orbital order and spin nematicity in the tetragonal phase of the electron-doped iron pnictides NaFe$_{1-x}$Co$_x$As

R. Zhou,1 L. Y. Xing,1 X. C. Wang,1 C. Q. Jin,1 and Guo-qing Zheng1,2

1Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
2Department of Physics, Okayama University, Okayama 700-8530, Japan

(Received 8 June 2015; revised manuscript received 14 January 2016; published 1 February 2016)

In copper-oxide and iron-based high-temperature (high-$T_c$) superconductors, many physical properties exhibit in-plane anisotropy, which is believed to be caused by a rotational symmetry-breaking nematic order, whose origin and its relationship to superconductivity remain elusive. In many iron pnictides, a tetragonal-to-orthorhombic structural transition temperature $T_s$ coincides with the magnetic transition temperature $T_N$, making the orbital and spin degrees of freedom highly entangled. NaFeAs is a system where $T_s = 54$ K is well separated from $T_N = 42$ K, which helps simplify the experimental situation. Here we report nuclear magnetic resonance (NMR) measurements on NaFe$_{1-x}$Co$_x$As ($0 \leq x \leq 0.042$) that revealed orbital and spin nematicity occurring at a temperature $T^*$ far above $T_s$ in the tetragonal phase. We show that the NMR spectra splitting and its evolution can be explained by an incommensurate orbital order that sets in below $T^*$ and becomes commensurate below $T_s$, which brings about the observed spin nematicity.

DOI: 10.1103/PhysRevB.93.060502

Understanding the normal state out of which high-$T_c$ superconductivity (SC) develops is an important task in condensed-matter physics. In copper-oxide high-temperature superconductors, the normal state deviates from the conventional state described by Landau Fermi liquid theory. In particular, below a certain temperature $T^*$, a so-called pseudogap state emerges, breaking the rotation symmetry of the underlying lattices [1,2]. In iron-pnictide or iron-selenide high-$T_c$ superconductors, many physical properties in the normal state also show strong anisotropy (nematicity), breaking the fourfold rotation ($C_4$) symmetry [3–5]. For example, in the parent Fe-pnictide BaFe$_2$As$_2$, electronically driven nematicity was discovered in the in-plane resistivity below a tetragonal-to-orthorhombic structural transition temperature $T_s$ [3,6]. Soon after the transport measurements, angle-resolved photoemission spectroscopy (ARPES) found that the degeneracy of the Fe-3$d_{xz}$ and 3$d_{yz}$ orbitals is lifted [4]. Later on, nematicity was also found in other properties ranging from the magnetoelastic property in chemically pressurized BaFe$_2$As$_2$ [5], to spin dynamics in carrier-doped BaFe$_2$As$_2$ [7], and to a local electronic structure around defects even above $T_s$ [8,9]. Theoretically, both spin [10] and orbital origin [11–14] have been proposed for the cause of the experimentally observed nematicity. In the BaFe$_2$As$_2$ family, however, antiferromagnetism (AF) sets in simultaneously at $T_s$ or slightly below [15]. As a result, it is unclear whether the transition is driven by spin degree of freedom [10] or by orbital degree of freedom [11–14]. Neither is it clear whether the nematicity is caused by a static [5] or a fluctuating order [7]. Therefore, identifying the origin of the nematicity has become an urgent issue, since it is believed that the interaction leading to such a nematicity may also be responsible for the high-$T_c$ superconductivity [16,17].

NaFeAs is a unique system where $T_s = 54$ K is well above $T_N = 42$ K. Only 2.7% of Co substituting for Fe gives rise to the maximum $T_c = 21$ K [18], which makes the system a clean one with much less doping-induced disorder than other systems. In this Rapid Communication, we report evidence pointing toward orbital order at a temperature $T^*$ (as high as 90 K) that is far above $T_s$ in NaFe$_{1-x}$Co$_x$As by $^{75}$As and $^{23}$Na NMR spectroscopy. We further revealed a spin nematicity in this system by the spin-lattice relaxation rate ($1/T_1$) measurements, and show that it can be understood as a direct consequence of the orbital order.

The single crystals of NaFe$_{1-x}$Co$_x$As used for the measurements were grown by the self-flux method [8]. In order to prevent sample degradation, the samples were covered by Stycast 1266 in a glovebox filled with high-purity Ar gas [19]. The typical sample size is 3 mm $\times$ 3 mm $\times$ 0.1 mm. The Co content $x$ was determined by energy-dispersive x-ray spectroscopy. The $T_s$ was determined by dc susceptibility measured by a superconducting quantum interference device. The nuclear magnetic resonance (NMR) spectra were obtained by integrating the spin echo as a function of frequency at $H_0 = 11.998$ T. The $T_1$ was measured by using the saturation-recovery method, and determined by a good fitting to the theoretical curve [20].

The $^{75}$As or $^{23}$Na nucleus with spin $I = 3/2$ has a nuclear quadrupole moment $Q$ that couples to the electric field gradient (EFG) $V_{\alpha\alpha} (\alpha = x, y, z)$, relating to the nuclear quadrupole resonance (NQR) frequency tensors $v_0 = 4\pi^2 I(m/2) V_{\alpha\alpha}$. Therefore, both $^{75}$As- and $^{23}$Na-NMR are good probes for a structural phase transition as shown in NaFeAs where the principal axes are along the crystal axes [21]. In addition, the As site is very close to the Fe plane so that the As-$p$ and Fe-$d$ orbitals strongly hybridize, which makes $^{75}$As NMR also a sensitive and unique probe for detecting an orbital order since a disparate occupation in As-$p$ orbitals will produce an asymmetric EFG.

When a magnetic field $H_0$ is applied along the $i$ axis ($i = a$ or $b$), the NMR resonance frequency $f$ is expressed by [22]

$$f_{m\rightarrow m-1,i} = \gamma_N H_0 (1 + K_i) + \frac{1}{2} v_0 (m - \frac{1}{2}) (n_i \eta - 1) + a_m \delta f_i,$$

where $K_i$ is the Knight shift, $m = 3/2$, 1/2, and $-1/2$, and $n_i = \mp 1$. $\eta \equiv |(\nu_a - \nu_d)/(\nu_a + \nu_d)|$ is the asymmetry parameter of the EFG, which measures a nematicity in the $ab$ plane. Finally, $a_m \delta f_i$ is the second-order quadrupolar shift when $H_0$ is applied.
One apparent possibility for the $^{75}$As-NMR lines broadening (splitting) is that there are some small local orthorhombic domains existing above $T_s$ formed by tiny uniaxial pressure from disorders [9,24] or uniaxial strains due to epoxy encapsulation. However, this can be ruled out since $^{23}$Na-NMR spectra do not change below $T^*$ and there is no angular dependence in the tetragonal phase [19]. The other is that orbitals order in the real tetragonal phase. In this case, the origin of EFG asymmetry is the Fe orbital order parameter $\Delta$. For example, for the orbital splitting found in ARPES [4], one can write $\Delta \propto (n_{5z^2}^d - n_{5z^2}^d)$, where $n$ is the electron density. It will produce a population disparity between $4d_p$ and $4p_z, (n_{5z^2}^d - n_{5z^2}^d)$, through Fe-As orbital hybridization. Such disparity was explained by electronic mechanism [10-14], as well as by local-density approximations calculation [25]. At the moment, we cannot rule out other forms of $\Delta$ that can produce a finite $(n_{5z^2}^d - n_{5z^2}^d)$. The As-NQR frequency tensor $\nu_{x,y,z}$ is related to $n_{5z^2}^p$ as [26]

$$
\begin{align*}
\nu_x & = \nu_0 - \frac{3\nu_x^2}{2} |\nu_x^2| \\
\nu_y & = \nu_0 - \frac{3\nu_y^2}{2} |\nu_y^2| \\
\nu_z & = \nu_0 - \frac{3\nu_z^2}{2} |\nu_z^2|
\end{align*}
$$


(3)

where $\nu_0$ is the NQR frequency when there is one electron (hole) in each $4p$ orbital. It follows that $|\nu_x - \nu_y| = \frac{3}{2} |n_{5z^2}^p - n_{5z^2}^p|$, therefore $\eta_{5z^2} \propto |n_{5z^2}^p - n_{5z^2}^p| \propto \Delta$.

Below we show that an incommensurate orbital order in the tetragonal phase, which becomes commensurate below $T_s$, can consistently account for the observed results. Generally speaking, in a commensurate density-wave state, the NMR line reflects the small number of physically non-equivalent nuclear sites in the unit cell so that the linewidth is small. In an incommensurate state, however, since the translational periodicity is lost, the number of non-equivalent nuclear sites is larger which gives rise to a larger linewidth. A modulation due to orbital order will cause an additional term in the resonance frequency at As site $(x,y)$. Let this term be a cosine function as $\cos(\frac{2\pi}{4} q_x x + \gamma_{x} + \cos(\frac{2\pi}{4} q_y y + \gamma_{y}))$, where $q_x$ and $q_y$ are the two-dimensional (2D) wave vectors and $\gamma_{x,y}$ is the phase. Then, for commensurate order, the additional term becomes $\cos(\theta_x + \cos \theta_y)$, which is site independent. For incommensurate order, however, this term is site dependent, which leads to a broadening of the spectrum. By convoluting with a Gaussian function [19], we can reproduce the spectra as shown in Fig. 1(a).

Below $T_s$, the $^{75}$As-NMR spectra become narrower and each peak is well resolved. Moreover, no NMR intensity loss is observed below $T_s$ or $T^*$[19]. All these imply that all the $^{75}$As-NMR sites have the same environment. That is, the orbital order becomes commensurate. The doping dependence of the spectra is shown in Fig. 2. As for $x = 0$, a peak splitting was also found above $T_i$ for $x = 0.0089$, 0.018, and 0.027, which get well resolved at $T_s$. For $x = 0.042$, however, no change of the spectra was found down to $T = 20$ K.

More quantitative data are shown in Fig. 3 where the evolution of $\eta$ is demonstrated.

The $\eta_{Na}$ develops continuously below $T^*$, showing a saturation tendency approaching $T_i$. In contrast, $\eta_{Na}$ shows up
FIG. 2. $T$ evolution of the $^{75}$As-NMR satellite peaks. For $x = 0, 0.0089, 0.018$, and 0.027, the peaks are broadened below $T^*$, and split below $T_s$. For $x = 0.042$, however, no clear change in the spectrum is detected down to $T = 20$ K.

only below $T_s$, the absolute value is much smaller than $\eta_{\text{As}}$, indicating that it is purely due to the structural transition. There are two contributions to the observed $\eta : \eta = \eta_{\text{lattice}} + \eta_{\text{orbital}}$, where $\eta_{\text{lattice}}$ is due to surrounding lattice and $\eta_{\text{orbital}}$ is due to orbital order on Fe site. By first-principles calculation, we find that the observed $\eta_{As}$ is well explained by the change in $\eta_{\text{lattice}}$; the discrepancy is about 10%. Another remarkable feature of $\eta_{As}$ is that it increases steeply again below $T_s$, which cannot be accounted for by the calculated $\eta_{\text{lattice}}$. The red circles in Fig. 3(c) show the net increase after subtracting the effect due to the lattice change. A clear kink can be seen at $T_s$, which is true even after multiplying the calculated result by a factor of 1.1–1.15. The increase is consistent with the incommensurate-to-commensurate transition. In the incommensurate state, $|n_{4\pi} - n_{4\pi}'|$ is inhomogeneous and $\eta_{As}$ probes the averaged $|n_{4\pi} - n_{4\pi}'|$. In the commensurate state, $\eta_{As}$ measures the homogeneous $|n_{4\pi} - n_{4\pi}'|$, which can be larger [19].

Finally, it is worthwhile pointing out that $\eta_{As}$ shows a linear relationship with $\sqrt{T - T^*/T^*}$ for all samples in the vicinity of $T^*$, as shown in Fig. 3(d), suggesting that the nematic order undergoes a Landau-like second-order phase transition. The $T^*$ and $T_s$ results obtained by NMR are summarized in the phase diagram shown in Fig. 4.

Next we turn to the spin dynamics of this system, which was also clearly seen below $T^*$ in $1/T_1$. Figure 5(a) shows the $1/T_1$ results for $x = 0, 0.0089, 0.018$. Below $T^*$, $1/T_1$ measured at the positions corresponding to $H_0 \parallel [100]$ is $a$ axis and

FIG. 4. The obtained phase diagram. For $x < 0.027$, $T_s$ agrees well with that from resistivity [19]. For $x = 0.027$, the $T_s$ coincides with $T_c$ so that direct comparison with resistivity is unavailable. To distinguish with other compositions, the data point is represented by an open triangle. Ortho and Tetra represent the orthorhombic and the tetragonal phase, respectively.
H\| [010]_b (b axis) shows opposite T dependence. Here we assign the direction with larger NQR frequency tensor to the a axis. Figure 5(b) shows the ratio of the two T_1. As in Ba(Fe_1-x[Ni,Co])_2As_2 [15,29], 1/T_1 arises from the antiferromagnetic spin fluctuations and the contribution due to the intraband (density of state at the Fermi level), but the former is dominant [19]. We show below that the anisotropy of 1/T_1 is a natural consequence of the orbital order.

The magnetic order on the Fe atoms below T_N is of stripe type with ordering vectors Q_X = (\pi,0) [23]. Above T_N, however, magnetic fluctuations from Q_Y = (0,\pi) also exist and have equal amplitude to those from Q_X. Since As sits above or below the center of the square formed by four irons, 1/T_1 of 75As along the orthorhombic a direction or b direction sees antiferromagnetic spin fluctuations from both Q_X and Q_Y as follows [32]:

(4) \( \frac{1}{T_1} Q_x \propto A^2 \chi''_a \)

(5) \( \frac{1}{T_1} Q_x \propto A^2 (\chi''_a + \chi''_b) \)

and

(6) \( \frac{1}{T_1} Q_x \propto A^2 \chi''_a \)

Here A is the hyperfine coupling constant and \( \chi''_j \) (j = a,b,c) is the imaginary part of the staggered susceptibility. The measured (1/T_1), (i = a,b) can then be written as

\[
\left( \frac{1}{T_1} \right)_i = N_X \left( \frac{1}{T_1} \right)_i Q_x + N_Y \left( \frac{1}{T_1} \right)_i Q_y.
\]

where N_X (N_Y) is the relative weight of contribution from Q_X (Q_Y), with N_X + N_Y = 1. It then follows

\[
\frac{1}{T_1} = \frac{1}{T_1} Q_x + \frac{1}{T_1} Q_y = \frac{\chi''_a + \chi''_b}{2} + \frac{\chi''_b}{N_Y} \frac{1}{T_1} Q_y.
\]

which measures a change in the ratio \( \frac{\chi''_b}{\chi''_a} \). The 1/T_1 ratio will always be a unity as long as N_X = N_Y. On the other hand, in the limit of N_X ~ 1 and N_Y ~ 0, the ratio will be 2, since polarized inelastic neutron scattering found that the anisotropy in the low-energy spin excitations above T_N is small, if any [33].

As seen in Fig. 5(b), the observed ratio \( \frac{\chi''_b}{\chi''_a} \) increases below T*, indicating that N_X increases and N_Y decreases. These results are a natural consequence of orbital order with the occupation of Fe-3d_{xz,yz} becoming larger than Fe-3d_{xy} which changes the FS nesting condition so that spin fluctuations with Q_X become dominant [34]. This is because Q_X connects the Fermi pocket centered at \( \Gamma = (0,0) \) with that centered at \( M_X = (\pi,0) \) consisting of the d_{xz} orbital, and Q_Y connects the Fermi pocket with that centered at \( M_Y = (0,\pi) \) consisting of the d_{yz} orbital [see Fig. 5(c)]. Finally, we note that an anomaly is found at T_a in 1/T_1 of both directions, which is consistent with a change in the character of orbital order, but the detailed analysis of the anomaly and theoretical explanation are a topic of future investigation.

Previously, electronic nematicity was found in BaFe_2As_2 [4,5,15] and FeSe [35–39] systems, but it occurs right at T_a. Above T_a, only fluctuations were observed [40,41]. In Ni-doped BaFe_2As_2, although anisotropy was found in the spin susceptibility above T_a, the system was under a uniaxial pressure and it was attributed to a fluctuating order [7]. By contrast, no external driving force was applied in the present case, thus the observation of a static order at the time scale of \( 10^{-8} \) s is unprecedented.

In summary, we have presented the systematic NMR measurements on single crystals of NaFe_1-xCo_xAs. The 75As spectra were broadened at T* far above T_a and get well split below T_a. The EFG asymmetry parameter \( \eta \) emerges below T* and increases abruptly below T_a. However, the 23Na-NMR spectra showed no change until T_a. EFG analysis can be explained by an incommensurate orbital order formed in the tetragonal phase which becomes commensurate below T_a. A spin nematicity is also found below T* which can be understood as a direct consequence of the orbital order.

We thank T. Xiang for helpful discussion and comments, M.-H. Julien and S. Onari for a critical reading of the manuscript, and S. Maeda and T. Oguchi for advice and help in the EFG calculation, Z. Li and J. Yang for assistance in some of the measurements. This work was partially supported by CAS Strategic Priority Research Program, Grant No. XDB07020200 and by a 973 project National Basic Research Program of China, Grant No. 2012CB821402.


