The recent discovery of high transition temperature (high-$T_c$) superconductivity in iron pnictides\textsuperscript{1–4} has spurred huge excitement in the condensed-matter physics community. The FeAs layers, consisting of a square lattice of Fe coordinated by four As, are the crucial component responsible for the superconductivity. The quasi-two-dimensional layered structure is reminiscent of the CuO$_2$ layers in the cuprates, but many dissimilarities exist between iron pnictides and cuprates. For example, doping as high as 22 K.\textsuperscript{4,6} Earlier studies showed that a prototypical parent compound of iron pnictides, BaFe$_2$As$_2$($x=0$), is an itinerant antiferromagnet and exhibits simultaneous first-order structural and magnetic phase transitions at $T_{SDW}=135$ K.\textsuperscript{7–10} 2\% and 4\% Co doping into BaFe$_2$As$_2$ quickly suppresses the ordering temperatures to $T_{SDW}=100$ K and 66 K, respectively.\textsuperscript{11–15} When the doping level is increased to $\sim$8\%, superconductivity appears with optimized $T_c\sim22$ K. Very little is known about the nature of the magnetically ordered state below $T_{SDW}$ in the presence of 2\%–4\% electron doping.

In this Rapid Communication, we will report a microscopic investigation by nuclear magnetic resonance (NMR) on the electronic properties of lightly electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ ($x=0.02,0.04$). We will show that Co doping suppresses the magnetic ordering temperature, $T_{SDW}$. Furthermore, as little as 2\% Co doping transforms the nature of the ground state from the commensurate spin density wave (C-SDW) state observed in the undoped parent compound BaFe$_2$As$_2$ (Refs. 7–9) to a different state, most likely a highly disordered incommensurate spin density wave (IC-SDW) state. We will show that strong spin fluctuations remain below $T_{SDW}$ all the way down to 4.2 K. There is no signature of additional freezing of spin degrees of freedom in contrast with the case of the lightly doped stripe phase of the cuprates.\textsuperscript{16,17}

We grew the single crystals with $x=0,0.02$, and 0.04 from FeAs flux\textsuperscript{4} and determined the actual Co concentration by energy dispersive x-ray spectroscopy. These are the identical pieces that were used for our previous $^{75}$As NMR study in the paramagnetic state.\textsuperscript{12,18} We carried out NMR measurements using the standard pulsed NMR techniques on either one piece of crystal ($x=0,0.04$) or aligned crystals ($x=0.02$, two pieces) with total masses of $\sim$2 to $\sim$20 mg.

In Fig. 1, we present the typical field swept line shapes at a fixed frequency $f=43,503$ MHz for $^{75}$As (nuclear spin $I=\frac{3}{2}$, $\gamma_s/2\pi=7.2919$ MHz/T) with external field $B_{ext}$ applied either along the $c$ axis ($B_{ext}$/$c$) or within the $ab$ plane ($B_{ext}$/$ab$). The nuclear spin Hamiltonian can be expressed as a summation of the Zeeman and nuclear quadrupole interaction terms,

$$H = -\gamma_s h B \cdot I + \frac{h \nu_q}{6} \left( 3I_z^2 - I(I+1) + \frac{1}{2} \eta(I_z^2 + I_y^2) \right),$$

where $h$ is Planck’s constant and $I$ is the nuclear spin. $B$ is the local field at the observed nuclear spin, and the summa-

![Graph](https://example.com/graph1.png)

**FIG. 1.** (Color online) $^{75}$As field swept NMR line shapes of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ measured at $f=43,503$ MHz, for $x=0$($T_{SDW}=135$ K), $x=0.02$($T_{SDW}=100$ K), and $x=0.04$($T_{SDW}=66$ K). $B_{ext}$ was applied along the $c$ axis, except in panel (a) where $B_{ext}$/$ab$. Notice that the positions of the NMR lines in the paramagnetic state only shift from 145 to 77 K in (a) because the hyperfine magnetic field is along the $c$ axis. In (c), NMR lines either split ($x=0$) or broaden ($x=0.02,0.04$).
tion of the external field \( B_{\text{ext}} \) and the hyperfine field \( B_{\text{hf}} \) from the ordered moments. The nuclear quadrupole interaction \( \nu_Q \) is proportional to the electric field gradient (EFG) at the observed As site, and \( \eta \) is the asymmetry parameter of the EFG, \( \eta = |\nu_Q^b - \nu_Q^a|/\nu_Q^c \).

First, we briefly discuss the \(^{75}\text{As} \) NMR results in undoped \( \text{BaFe}_2\text{As}_2 \) \((x=0, \ T_{\text{SDW}}=135 \ \text{K})\). Each \(^{75}\text{As} \) site gives rise to three transitions from \( I_z = 2m+1 \) to \( 2m-1 \) (where \( m=-1, 0, 1 \)) in the paramagnetic state, as shown in Figs. 1(a) and 1(b). The fact that we observe only one set of \(^{75}\text{As} \) NMR signals above \( T_{\text{SDW}} \) is evidence that there is only one type of As site in the undoped parent compound. The satellite transitions \((m=-1, 1)\) are somewhat broader than the central peak \((m=0)\), but are still fairly sharp, implying that \( \nu_Q \) has a well-defined value. From the split between the main peak and the satellite peaks in Fig. 1(a), \( \Delta B = 0.162 \ \text{T} \) we estimate \( \gamma_{\text{As}} B_{\text{ext}}^2 = 1.188 \ \text{MHz} \). From the split in Fig. 1(b), we estimate \( \gamma_{\text{As}} B_{\text{ext}}^2 = 2.3 \ \text{MHz} \). These results confirm that the hyperfine field on the As site is along the principal axis.\(^{9,10}\)

Below \( T_{\text{SDW}} \), the \(^{75}\text{As} \) line only shifts to the lower field side, because the resonance condition is satisfied as \( \gamma_{\text{As}} B_{\text{ext}}^2 + B_{\text{hf}}^2 = f \). These results confirm that the hyperfine field on the As site is along the principal axis.\(^{9,10}\)

FIG. 2. (Color online) \(^{59}\text{Co} \) field swept NMR line shapes of \( \text{Ba(Fe}_{1-x}\text{Co}_x)\text{As}_2 \) measured at \( f=74.103 \ \text{MHz} \) for (a) \( x=0.02 \) at 130 K (paramagnetic), 95 K, and 4.2 K (SDW); (b) \( x=0.04 \) at 100 K (paramagnetic), 65 K, and 4.2 K (SDW). The overall intensities in the SDW state have been amplified by a factor of 2 over those in the paramagnetic state. Solid curves represent Gaussian fits to the data. (c) and (d), \( B_{\text{ext}} \) was applied along the \( ab \) plane, otherwise \( B_{\text{ext}} \) was applied along the \( c \) axis. Notice the scale of the horizontal axis in panel (d) is expanded. The overall intensity in (d) has been amplified by 25 times compared with (c). Open arrows mark where we measured \( T_{I} \).

In Fig. 1(b), we also show the influence of Co doping in the paramagnetic state above \( T_{\text{SDW}} \). The line shapes for the doped samples are very similar to the undoped case, except that the satellite transitions become broader due to additional distribution of \(^{75}\text{As} \) caused by the disorder in the lattice environment. The magnitude of \(^{75}\text{As} \) is by a factor of \( \sim 5 \) smaller than the case of \( \text{LaFeAsO}_{1-x} \) (Ref. 19). This is presumably because \(^{75}\text{As} \) ions are surrounded by 24 + ions only (\( \text{Fe}^{2+} \) and \( \text{Ba}^{2+} \)) in the present case, while \(^{75}\text{As} \) ions in \( \text{LaFeAsO}_{1-x} \) have \( \text{La}^{2+} \) and \( \text{O}^{2+} \) ions nearby, in addition to \( \text{Fe}^{2+} \) ions; the charge disparity would enhance the EFG, hence \(^{75}\text{As} \) in \( \text{LaFeAsO}_{1-x} \). We also note that \(^{75}\text{As} \) is nearly independent of the level of doping, and there is no evidence for correlation between \(^{75}\text{As} \) and \( T_{I} \).

This is in contrast with the case of \( \text{LaFeAsO}_{1-x} \) where \( T_{I} \) appears to have a strong correlation with the \(^{75}\text{As} \) (Ref. 19). On the other hand, we found that the line shapes are qualitatively different between undoped and doped samples below \( T_{\text{SDW}} \), as shown in Fig. 1(c). Unexpectedly, the \(^{75}\text{As} \) lines do not split in 2% and 4% Co-doped samples. Instead, the \(^{75}\text{As} \) NMR lines broaden and become almost featureless. The spin echo signal could be detected everywhere between 4 and 7.5 T, which implies that \( B_{\text{hf}}^c \) at \(^{75}\text{As} \) sites is continuously distributed from 0 to \( \pm 1.32 \ \text{T} \).

In Fig. 2, we present the typical field swept \(^{59}\text{Co} \) (nuclear spin \( I=7/2 \), \( \gamma_{\text{Co}}/2\pi=10.054 \ \text{MHz/T} \) line shapes with \( B_{\text{ext}}/c \) or \( B_{\text{ext}}/ab \). Co is randomly doped into FeAs layers by replacing Fe. The probability for each Co to have four Fe at the nearest neighbor (n.n.) sites is 92.2% for \( x=0.02 \) and 84.9% for \( x=0.04 \), respectively. Thus the Co NMR line shape is dominated by the NMR signals from the Co with four n.n. Fe, and the Co NMR line splits into seven peaks separated by \( \nu_{Q} \). We estimate \( \nu_{Q} = 0.26 \ \text{MHz} \), \( \nu_{ab} = 0.13 \ \text{MHz} \), and \( \eta = 0 \) for both \( x=0.02 \) and 0.04.

Below \( T_{\text{SDW}} \), the \(^{59}\text{Co} \) NMR lines become broader and the seven discrete peaks caused by the quadrupole split \(^{59}\nu_{Q} \) are smeared out. The whole NMR line becomes completely featureless at low temperatures. We observe no signature of residual sharp peaks below \( T_{\text{SDW}} \), hence all \(^{59}\text{Co} \) nuclear spins are under the influence of magnetic ordering. The integrated intensity corrected for the Boltzmann factor agrees well between 4.2 and 100 K, hence we observe all \(^{59}\text{Co} \) nuclear spins at 4.2 K. This conservation of the total intensity rules out any possibility of phase separation or macroscopic inhomogeneity in the sample. Close inspection of the line positions reveals that the center of the broad line progressively shifts to the lower field side with decreasing temperature when we apply \( B_{\text{ext}} \) along the \( c \) axis. For example, the center transition for \( x=0.04 \) at 100 K is at \( B_{\text{ext}} \approx 7.318 \ \text{T} \), which shifts by 0.023 T to 7.295 T at 4.2 K. On the other hand, the \(^{59}\text{Co} \) NMR lines for \( x=0.04 \) split into two broad humps when \( B_{\text{ext}} \) is applied along the \( ab \) plane instead, as shown in Fig. 2(d). The separation between the center of the two broad humps, \( \approx 0.6 \ \text{T} \), is much larger than the small shift, 0.023 T, observed along \( B_{\text{ext}}/c \). This implies that the hyperfine field...
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FIG. 3. (Color online) The temperature dependence of the magnetic broadening $\Delta B_{hf}$ of 59\textsuperscript{Co} NMR lines for $x=0.02$ (○) and $x=0.04$ (●).

at the 59\textsuperscript{Co} site is primarily within the $ab$ plane. Combined with the fact that 75\textsuperscript{As} lines do not exhibit splitting with $B_{ext}/c$, we conclude that Co doping changes the C-SDW spin structure of BaFe$_2$As$_2$.

We fit the broad, featureless 59\textsuperscript{Co} NMR line shapes with $B_{ext}/c$ by assuming that the quadrupole splitting by $59\nu_Q$ does not depend on temperature and all seven transitions become broader by a Gaussian distribution of the hyperfine fields $\Delta B'_{hf}$ below $T_{SDW}$. The fits are reasonable for both $x=0.02$ and 0.04, and we were able to deduce the Gaussian width $\Delta B'_{hf}$ as summarized in Fig. 3. $\Delta B'_{hf}$ continuously increases and finally saturates at base temperature.

In Fig. 4(a), we present the temperature dependence of the static spin susceptibility, $\chi$, for $x=0.02$ and 0.04 as measured by 59\textsuperscript{Co} NMR Knight shift, $K$. We also plot the result for the superconducting $x=0.08$ sample for comparison. In general, we can write $K=K_{spin}+K_{chem}$. $K_{spin}$ is the spin contribution, which is proportional to the local spin susceptibility $\chi$, while $K_{chem}$ is the temperature-independent chemical shift. $K_{chem}$ is not related to $\chi$. Our results indicate that $\chi$ gradually decreases below $\sim 300$ K and begins to level off below $\sim 100$ K. This is consistent with our earlier results based on 75\textsuperscript{As} NMR.\textsuperscript{12} The 59\textsuperscript{Co} NMR linewidth is too broad to determine the concentration dependence accurately.

In Fig. 4(b), we show the temperature dependence of $q$ integrated dynamical spin susceptibility as measured by $\frac{1}{T_1} \propto \sum_q |\mathcal{A}_{hf}(q)|^2 L(q)$ at 59\textsuperscript{Co} sites, where $|\mathcal{A}_{hf}(q)|^2$ is the wave-vector $q$-dependent hyperfine form factor,$^{18}$ $\chi'(q,f)$ is the imaginary part of the dynamical electron spin susceptibility (i.e., spin fluctuations), and $f$ is the NMR frequency ($\sim 10^2$ MHz). $\frac{1}{T_1}$ shows a divergent behavior at $\sim 100$ K for $x=0.02$, and $\sim 66$ K for $x=0.04$. These temperatures agree well with the maximum negative slope observed in in-plane resistivity.\textsuperscript{12} In Ref. 12, we also reported the divergent behavior of $\frac{1}{T_1}$ at 75\textsuperscript{As} sites with $B_{c1}/c$ axis. In this geometry, $75\frac{1}{T_1}$ probes spin fluctuations within the $ab$ plane. On the other hand, Kitagawa et al.\textsuperscript{9} showed that the 75\textsuperscript{As} hyperfine form factor satisfies $|75\mathcal{A}_{hf}(q)|^2=0$ within the $ab$ plane for commensurate spin fluctuations due to cancellation of the transferred hyperfine fields. Therefore, these $\frac{1}{T_1}$ data at 59\textsuperscript{Co} and 75\textsuperscript{As} provide strong evidence for the critical slowing down of the incommensurate spin fluctuations toward a second-order phase transition at $T_{SDW}$. Interestingly, $\frac{1}{T_1}$ decreases roughly linearly with temperature down to the base temperature for both $x=0.02$ and 0.04 except near $T_{SDW}$, and shows qualitatively the same behavior as that of the superconducting sample. Our results suggest that strong spin fluctuations remain even below $T_{SDW}$ in Co-doped samples, which may be an indication that Fe 3$d$ spins of some part of the 3$d$ orbitals remain paramagnetic below $T_{SDW}$ as suggested by Singh et al.\textsuperscript{4,20} based on fermiology. For example, all 3$d$ spins are not ordered in $e_g$ but ordered in $t_{2g}$ orbitals, or vice versa. In passing, we recall that $\frac{1}{T_1}$ at 139\textsuperscript{La} sites in undoped LaFeAsO (Ref. 21) and 75\textsuperscript{As} sites in undoped BaFe$_2$As$_2$ (Refs. 9 and 10) is suppressed by an order of magnitude or more below $T_{SDW}$.

The large in-plane resistivity below $T_{SDW}$ in Co-doped samples\textsuperscript{11,12} is probably related to these strong spin fluctuations. It should also be noted that we find no signature of additional spin freezing at low temperatures in either $\frac{1}{T_1}$ or $\Delta B'_{hf}$. It is worth recalling that in the case of lightly doped La$_{2-x}$Sr$_x$CuO$_{4.5-\delta}$,\textsuperscript{16,17} $\frac{1}{T_1}$ at 139\textsuperscript{La} sites shows additional diverging behavior at $T_{sf}$, much below $T_N$. Furthermore, $B_{hf}$ shows additional enhancement below $T_{sf}$. The spin freezing temperature $T_{sf}$ turned out to be related to glassy freezing of spin and charge stripes. Our present observation is markedly different from the case of the lightly doped cuprates.

In conclusion, we have presented a 59\textsuperscript{Co} and 75\textsuperscript{As} NMR study in the lightly electron-doped, SDW ordered regime of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$. We demonstrated that Co doping suppresses $T_{SDW}$, and changes the spin structure. The continuous growth of the NMR linewidth below $T_{SDW}$ and the strong enhancement of $\frac{1}{T_1}$ at $T_{SDW}$ suggest a second-order phase transition into an SDW phase, most likely incommensurate with the lattice and highly disordered. We did not detect any anomaly from $T_{SDW}$ down to base temperature in either $\Delta B'_{hf}$ or $\frac{1}{T_1}$. This suggests the absence of freezing of stripes or
other analogous phenomena. On the other hand, large \( \frac{1}{T} \) at \( T < T_{SDW} \) hints the residual paramagnetic spins at each Fe site due to the multiorbital nature of FeAs layers. During the final stage of preparing this manuscript, Bernhard et al.\textsuperscript{22} reported \( \mu \)SR observation of static magnetism in a 4\% Co-doped sample only below 15–20 K.

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