59Co and 75As NMR Investigation of Lightly Doped Ba(Fe1−xCo2)xAs2 (x = 0.02, 0.04)

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We investigate the electronic properties of Ba(Fe1−xCo2)xAs2 (x = 0.02, 0.04) in the lightly electron-doped regime by 59Co and 75As NMR. We demonstrate that Co doping significantly suppresses the magnetic ordering temperature to the SDW state, T_{SDW}. Furthermore, ordered moments below T_{SDW} exhibit large distribution. Strong spin fluctuations remain even below T_{SDW}, persisting all the way down to 4.2 K. We find no signature of additional freezing of spin degrees of freedom unlike the case of the lightly hole-doped stripe phase of the cuprates.

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The recent discovery of high transition temperature (high-Tc) superconductivity in iron-pnictides 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 CuO2 layers in the high-Tc cuprates, but many dissimilarities exist between iron-pnictides and cuprates. Further studies showed that a prototypical parent compound (x = 0) is an itinerant antiferromagnet, and exhibits simultaneous first order structural and magnetic phase transitions at T_{SDW} ∼ 135 K [7, 8, 9, 10]. 2% and 4% Co doping into BaFe2As2 induces superconductivity with Tc as high as 22 K [11, 12]. Earlier studies showed that a prototypical parent compound of iron-pnictides, BaFe2As2 (x = 0) is an itinerant antiferromagnet, and exhibits simultaneous first order structural and magnetic phase transitions at T_{SDW} ∼ 135 K [7, 8, 9, 10]. 2% and 4% Co doping into BaFe2As2 quickly suppresses the ordering temperatures to T_{SDW} ∼ 100 K and 66 K respectively [11, 12, 13, 14, 15]. When the doping level is increased to ∼ 8 %, superconductivity appears with optimized Tc ∼ 22 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(Fe1−xCo2)xAs2 (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 BaFe2As2 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 [16, 17].

We grew the single crystals with x = 0, 0.02 and 0.04 from FeAs flux [4] and determined the actual Co concentration by EDS (Energy Dispersive X-Ray Spectroscopy). These are the identical pieces that were used for our previous 75As NMR study in the paramagnetic state [12]. 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 2 ~ 20 mg.

FIG. 1: (Color Online). 75As field swept NMR lineshapes of Ba(Fe1−xCo2)xAs2 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 K 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).

In Fig. 1, we present the typical field swept lineshapes at a fixed frequency f = 43.503 MHz for 75As (nuclear spin I = 3/2, γn/2π = 7.2919 MHz/Tesla) with external field B_{ext} applied either along the c-axis (B_{ext}/c) or within
gives rise to three transitions from $I^z$ to $I^z + 1$ due to the quadrupole interaction. The asymmetry parameter of the EFG, $\eta$, is the summation of the external field $B_{\text{ext}}$ and the hyperfine field $B_{hf}$.

For $B_{\text{ext}}//ab$, the $75\text{As}$ NMR lineshape in the paramagnetic state at $T = 77\text{K}$ is nearly independent of the level of doping, and there is no evidence for correlation between $75\nu_Q$ and $T_c$. This is in contrast with the case of LaFeAsO$_1$-$\delta$, where $T_c$ appears to have a strong correlation with the $75\nu_Q$.

In Fig. 1(b), we also show the influence of Co doping in the paramagnetic state above $T_{SDW}$. The lineshape for the doped samples are very similar to the undoped case, except that the satellite transitions become broader due to additional distribution of $75\nu_Q$. 

FIG. 2: (Color Online). $^{59}\text{Co}$ field swept NMR lineshapes of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ measured at $B = 74.103$ 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 compared with those in the paramagnetic state. Solid curves represent Gaussian fit to the data. In (c) and (d), $B_{\text{ext}}$ was applied within 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 $T_1$. 

The nuclear spin Hamiltonian can be expressed as a summation of the Zeeman and nuclear quadrupole interaction terms,

$$H = -\gamma_n h B \cdot I + \frac{h \nu_Q}{6} \left\{ 3I_z^2 - I(I+1) + \frac{1}{2} \eta (I_+^2 + I_-^2) \right\}, \tag{1}$$

where $\hbar$ is Planck’s constant, and $I$ is the nuclear spin. $B$ is the local field at the observed nuclear spin, and the summation of the external field $B_{\text{ext}}$ and the hyperfine field $B_{hf}$ 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, $\eta = |\nu_Q - \nu_Q'|/\nu_Q'}$.

First, we briefly discuss the $75\text{As}$ NMR results in undoped BaFe$_2$As$_2$ ($x = 0$, $T_{SDW} = 135\text{K}$). Each $75\text{As}$ site gives rise to three transitions from $I_z = \frac{2m+1}{2}$ to $\frac{2m-1}{2}$ (where $m = -1, 0, 1$) in the paramagnetic state, as shown in Fig. 1(a) and (b). The fact that we observe only one set of $75\text{As}$ NMR signals above $T_{SDW}$ 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), $\Delta B \sim 0.162$ Tesla, we estimate $75\nu_Q = 75\gamma_n \Delta B = 1.188$ MHz. From the split in Fig. 1(b), we estimate $75\nu_Q = 2.3$ MHz. Thus $\eta \approx 0$ at 145 K for $75\text{As}$, as expected for the tetragonal symmetry. At $77\text{K}$, the $75\text{As}$ NMR lines with $B_{\text{ext}}//c$ split into two sets as shown in Fig. 1(c). This is because the hyperfine field at $75\text{As}$ site from the ordered moments, $\pm B_{hf}$, is along the $c$-axis. For $B_{\text{ext}}//ab$, the $75\text{As}$ line only shifts to the lower field side, because the resonance condition is satisfied as $75\gamma_n B_{hf} = \frac{1}{2} \nu_Q$. These results confirm that the hyperfine field on the As site is along the $c$-axis.

The relatively sharp peaks at 77 K in the ordered state indicate that the ordered moments are commensurate with the lattice and the hyperfine field has only two discrete values, e.g. $B_{hf} = \pm 1.32$ Tesla at 77 K.

In Fig. 1(b), we also show the influence of Co doping in the paramagnetic state above $T_{SDW}$. The lineshape for the doped samples are very similar to the undoped case, except that the satellite transitions become broader due to additional distribution of $75\nu_Q$ caused by the disorder in the lattice environment. The magnitude of $75\nu_Q \sim 2.3$ MHz is by a factor of 5 smaller than the case of LaFeAsO$_1$-$\delta$. This is presumably because $75\text{As}$ ions are surrounded by 2+ ions only (Fe$^{2+}$ and Ba$^{2+}$) in the present case, while $75\text{As}$ ions in LaFeAsO$_1$-$\delta$ have La$^{3+}$ and O$^{2-}$ ions nearby, in addition to Fe$^{2+}$ ions; the charge disparity would enhance the EFG, hence $75\nu_Q$ in LaFeAsO$_1$-$\delta$. We also note that $75\nu_Q \sim 2.3$ MHz is nearly independent of the level of doping, and there is no evidence for correlation between $75\nu_Q$ and $T_c$. This is in contrast with the case of LaFeAsO$_1$-$\delta$, where $T_c$ appears to have a strong correlation with the $75\nu_Q$.

On the other hand, we found that the lineshapes are qualitatively different between undoped and doped samples below $T_{SDW}$, 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 Tesla, which implies that $|B_{hf}|$ at $75\text{As}$ sites is continuously distributed from 0 to $\approx 1.32$ Tesla.

In Fig. 2, we present the typical field swept $^{59}\text{Co}$ nuclear spin I = 5/2, $\gamma_n/2\pi = 10.054$ MHz/Tesla) lineshapes 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 lineshape 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 $59\nu_Q$. We estimate $59\nu_Q \sim 0.26$ MHz, $59\nu_Q^{ab} \sim 0.13$ MHz and $\eta = 0$ for both $x = 0.02$ and 0.04.

Below $T_{SDW}$, 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 $T_{SDW}$, hence all $59\text{Co}$ nuclear spins are under the influence of magnetic ordering. The integrated intensity corrected for the Boltzmann factor agree well between 4.2 K 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 $B_{ext}$ along the $c$-axis. For example, the center transition for $x = 0.04$ at 100 K is at $B_{ext} \sim 7.318$ Tesla, which shifts by 0.023 Tesla to 7.295 Tesla at 4.2 K. On the other hand, the $59\text{Co}$ NMR lines for $x = 0.04$ split into two broad humps when $B_{ext}$ is applied along the $ab$-plane instead, as shown in Fig. 2(d). The separation between the center of the two broad humps, $\sim 0.6$ Tesla, is much larger than the small shift, 0.023 Tesla, observed along $B_{ext}/c$. This implies that the hyperfine field at the $59\text{Co}$ site is primarily within the $ab$-plane. Combined with the fact that $^{75}\text{As}$ 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 $59\text{Co}$ NMR lineshapes 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 $\Delta B_{hf}^c$ as summarized in Fig. 3. $\Delta B_{hf}^c$ 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 $59\text{Co}$ NMR Knight shift, $K$. We also plot the result for the superconducting $x = 0.08$ sample for comparison [18]. In general, we can write $K = K_{\text{spin}} + K_{\text{chem}}$. $K_{\text{spin}}$ is the spin contribution, which is proportional to the local spin susceptibility $\chi$, while $K_{\text{chem}}$ is the temperature-independent chemical shift. $K_{\text{chem}}$ 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 $^{75}\text{As}$ NMR [12]. The $59\text{Co}$ 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 $1/T_1 \propto \sum_q |A_{hf}(q)|^2 S(q,f)$ at $59\text{Co}$ sites, where $|A_{hf}(q)|^2$ 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 ($\lesssim 10^7$ MHz). $1/T_1$ 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 for in-plane resistivity [12]. In ref [12], we also reported the divergent behavior of $75\text{Co}$ NMR with $B_{ext}/c$-axis. In this geometry, $75\text{Co}$ NMR probes spin fluctuations within the $ab$-plane. On the other hand, Kitagawa et al [3] showed that the $^{75}\text{As}$ hyperfine form factor satisfies $|A_{hf}(q)|^2 = 0$ within the $ab$-plane for commensurate spin fluctuations due to cancellation of the transferred hyperfine fields. Therefore, these $1/T_1$ data at $59\text{Co}$ and $^{75}\text{As}$ pro-

![Graph](image_url)
vide strong evidence for the critical slowing down of the incommensurate spin fluctuations toward a second order phase transition at $T_{SDW}$. Interestingly, $\frac{1}{T_{sf}}$ 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 3d spins of some part of the 3d orbitals remain paramagnetic below $T_{SDW}$ as suggested by Singh et al. [4,20] based on Fermiology. For example, all 3d spins are not ordered in Ce sites in undoped LaFeAsO [21] and As sites in undoped BaFe$_2$As$_2$ [11,12] is probably related to these strong spin fluctuations. It should also be noted that we find no significant enhancement below $T_{SDW}$ down to base temperature in either $\frac{1}{T_{sf}}$ or $\Delta B_{hf}$. It is worth recalling that in the case of lightly doped La$_{2-x}$Sr$_x$CuO$_4$ [16,17], $\frac{1}{T_{sf}}$ at $T_{sf}$ shows additional diverging behavior at $T_{sf}$, much below $T_s$. 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 $^{59}$Co and $^{75}$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 continuous enhancement of $\frac{1}{T_{sf}}$ at $T_{sf}$ 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 $\frac{1}{T_{sf}}$. This suggests the absence of freezing of stripes or other analogous phenomena. On the other hand, large $\frac{1}{T_{sf}}$ at $T \ll T_{SDW}$ hints the residual paramagnetic spins at each Fe site due to the multi-orbital nature of FeAs layers. During the final stage of preparing this manuscript, Bernhard et al. reported $\mu$SR observation of static magnetism in a 4% Co doped sample only below 15 ~ 20 K [22].

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