Competing orders in underdoped \((\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2\)

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Abstract. We report \(^{75}\text{As}\) Nuclear Magnetic Resonance (NMR) measurements in the high-\(T_c\) superconductor \((\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2\) in the underdoped regime. A structural transition at \(T_S \simeq 110\) K is followed by an antiferromagnetic (AFM) order at \(T_N \simeq 102\) K for our \(x=0.16\) single crystal \([1]\). Superconductivity (SC) also appears at \(T_c \simeq 20\) K. We find that the ordered Fe moment \(\langle S \rangle\) is reduced upon hole-doping. Both spectrum analysis and relaxation measurements indicate that pinned vortices are present below \(T_c\) and SC is coexisting with AFM fluctuations.

The newly discovered Fe-based superconductors have stimulated a great interest due to their high-\(T_c\) and rich phase diagrams \([2, 3]\), with similarities to the high-\(T_c\) cuprates. In the \(\text{A} (\text{Fe}_{1-x}\text{T}_x)_2\text{As}_2\) family (\(\text{A} = \text{Ca}, \text{Sr} \text{or Ba and } \text{T} = \text{transition metal}\)) the simultaneous structural/magnetic phase transition that occurs at high temperature in the undoped material splits and is suppressed by chemical doping. Also, superconductivity commonly emerges sometimes coexisting with the AFM state \([4, 5, 6]\). Recently, similar features have been reported for the hole-doped \((\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2\) compound \([1]\). An important and controversial issue is the competition and/or coexistence of AFM and superconductivity in the underdoped regime. Despite the enormous theoretical and experimental effort \([7]\) the nature of the SC in these materials including the pairing mechanism and the symmetry of the order parameter remain unknown. Local probe studies have found evidence for phase separation into AFM domains and SC \([8]\). Moreover, the experimental results reported so far are often contradictory, reflecting large sample and doping dependences \([7]\).

In this work we carried out \(^{75}\text{As}\) NMR measurements to further explore the effect of hole- (out of plane) doping in the electronic and magnetic properties of \(\text{BaFe}_2\text{As}_2\). Particular attention is devoted to the interplay between AFM fluctuations and SC. We found a reduced ordered Fe moment \(\langle S \rangle\) in the underdoped regime, consistent with the suppression of the AFM order with the appearance of SC. Based on the relaxation experiments we conclude that these two broken symmetries are coexisting microscopically and must be related.

Single crystals of \((\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2\) were grown out of Sn-flux. Detailed bulk characterization is described elsewhere \([1]\). A high quality single crystal was mounted on a NMR probe equipped with a goniometer allowing a fine alignment of the crystallographic axes with \(H_{\text{ext}}\). The field-swept \(^{75}\text{As}\) NMR spectra \((I = 3/2; \gamma/2\pi = 7.2919\text{ MHz/T})\) were obtained by summing the Fourier transform of the spin-echo signal stepwise.

Fig. 1(a) and 1(b) present the field-swept \(^{75}\text{As}\)-NMR spectra at constant frequency \(\nu = 62.238\text{ MHz}\) with \(H_{\perp C}\) and \(H_{\parallel C}\), respectively. The spectra at 120 K represent the normal paramagnetic (PM) state while the broad spectra at 4.2 K belong to the coexisting AFM+SC
states. In the PM state, a sharp central transition (+1/2 ↔ −1/2) is observed along with two sets of broader satellite lines (±3/2 ↔ ±1/2) split by the quadrupolar interaction of the As nuclei with the local electric field gradient (EGF). In Fig. 1(d) we show the angular variation of the $^{75}$As spectrum with $H \parallel 9 \ T$ ($\nu = 66.225 \ MHz$) at 120 K. The solid (dotted) lines represent the NMR frequencies $\nu$ given by Eq. 1

$$\nu_{m\rightarrow m-1} = \mu_0 75\gamma(1-K^i)H_{\text{ext}} + \frac{\nu_{zz}}{2}(m-1/2)(3\cos^2\theta - 1 + \eta \sin^2\theta \cos2\phi) + \ 2^{nd}\ order\ correction$$

where the first term is the effective field $H_{\text{eff}}$ and $K^i$ is the knight shift along the $i$-axis. The second term in Eq. 1 is the $1^{st}$ order quadrupolar shift for the three allowed transitions ($\Delta m = \pm 1$). The asymmetry parameter of the EFG is defined as $\eta = (\nu_{xx} - \nu_{yy})/\nu_{zz}$. In the PM state, $\nu_{zz} = \nu_Q$ and $\eta = 0$ due to the high symmetry of the tetragonal phase ($\nu_{xx} = \nu_{yy} = \nu_{zz}/2$). From the fits in Fig. 1(d) we obtained two distinct quadrupole frequencies $\nu_Q^1 \approx 4.30(1) \ MHz$, $\nu_Q^2 \approx 3.06(1) \ MHz$. This means that alloying Ba and K not only induces a substantial distribution of the EFG resulting on the broadening of the satellite lines but also creates two distinct sets of quadrupole splitting. The latter is proportional to the EFG at the As, $V_{zz}$, through the relation: $\nu_Q = cQV_{zz}/2\sqrt{1 + \eta^2}/3$, where $Q$ is the nuclear quadrupole moment of $^{75}$As. $V_{zz}$ arises from the hybridization between the As-4p and the Fe-3d orbitals ($V_{zz}^{\text{intra}}$) with an added contribution from any non-cubic distribution of surrounding ions ($V_{zz}^{\text{inter}}$). These $\nu_Q$’s are larger than $\nu_Q = 2.21 \ MHz$ observed in the undoped compound [9] and confirm previous observations that $\nu_Q$ increases with doping [10, 11]. It also suggests that this sample has no chemically (macroscopically) segregated inhomogeneities [8]. The twinned structural domains are only observed in the orthorhombic ordered phase [9] and is another source for the line broadening observed in the AFM ordered phase.

Below $T_N \approx 102 \ K$, static internal hyperfine fields $H_{\text{int}}$ develop along the $c$-axis at the As sites generated by the commensurate AF ordered Fe moments (see Fig. 1(c)). These $H_{\text{int}}$ split the $^{75}$As-NMR spectra doubling the number of resonance lines since the resonance field is given by $H_{\text{eff}} = H_0 \pm H_{\text{int}}$ (Fig. 1(a)). Alternatively, because of $H_{\text{int}}|c$, when $H \perp c$ the resonance field is given by the magnitude of the vector sum of the mutually orthogonal external and internal fields, $H_{\text{eff}} = \sqrt{H^2 + H_{\text{int}}^2}$, causing the shift of the unsplit $^{75}$As-NMR spectra towards lower fields as displayed in Fig. 1(b) [1].

The $T$ dependence of $H_{\text{int}}$ determined with $H_{\text{ext}}^c \approx 9 \ T$ is shown in Fig. 2(a). The solid (red) line is the best fit to $M(T) = M_0[1 - (T/T_N)^a]$ with $M_0 = 1.052(7)$, $T_N = 102 \ K$ and
The transition at $T_N$ is almost 1st-order-like with the curvature of $M(T)$ much steeper than obtained with $\alpha = 0.5$, the value expected for a 3-D mean field. The reduced value of the critical exponent $\alpha$ is related to the bi-dimensionality of the magnetic fluctuations [13]. From the direct measurement of the magnetic order parameter $H_{\text{int}}$ ($M(T)$) along with the hyperfine coupling constant $A_{hf} \approx 3.93$ T/µB obtained from the Clogston-Jaccarino plot (not shown) we were able to estimate the ordered Fe moment $\langle S \rangle \approx 0.37\mu_B$/Fe for our sample, since $\langle S \rangle \equiv H_{\text{int}}/A_{hf}$. The smaller $\langle S \rangle$ compared to that observed for BaFe$_2$As$_2$ ($\langle S \rangle \approx 0.87\mu_B$/Fe) is consistent with the suppression of $T_N$ and the emergence of SC upon increasing K-doping [1].

In Fig. 2, we also present the $T$ dependence of $1/T_1$ measured at the central transition. The values of the spin-lattice relaxation time $T_1$ were obtained after saturating the nuclear magnetization $M(t)$ and fitting the recovery with the appropriate solutions to the Master equation. $1/T_1$ exhibits a divergence at $T_N \approx 102$ K. Its $T$ dependence can be roughly fitted to the self-consistent renormalization (SCR) theory for weak itinerant AFM [13, 14] given by Eq. 2 with the fitting parameters $a = -0.112(6)$ (s K$^{-1}$), $b = 5.12(4)(s^{-1} K^{-1/2})$ and $c = 0.090(1)$ (s K)$^{-1}$. However, the fast suppression of $1/T_1$ just below $T_N$ can not be well reproduced by Eq. 2 which implies that the nearby structural (tetragonal-orthorhombic) transition may be affecting the spin-fluctuations around $T_N$.

$$1/T_1 = \begin{cases} \frac{aT + bT/\sqrt{T - T_N}}{cT/M(T)}, & T > T_N \\ \frac{1}{cT/M(T)}, & T \leq T_N \end{cases}$$

We carried out the $1/T_1$ measurements using the standard saturation recovery technique but we noted that the signal can be fully inverted after an inversion pulse in the PM phase. However, the full inversion of the line is no longer observed for $T \leq T_N$ when the $^{74}$As spectrum becomes broader due to the distribution of static hyperfine fields in the AFM order. A distribution of $1/T_1$ is also observed below $T_c \approx 20$ K. This is not a surprising result once the vortices induced by $H_{\text{ext}}$ are expected to cause such behavior.

Further insight into the role of the vortices below $T_c$ is obtained from $1/T_2$ vs. $T$ shown in Fig. 3(a). The spin-spin relaxation time $T_2$ were obtained by measuring the decay of the echo intensity as a function of $2\tau_e$ using the typical Hahn-echo sequence: $\pi/2 - \tau_e - \pi - \tau_e - \text{echo signal}$. A single component relaxation function such as Gaussian was not sufficient to fit the relaxation data properly. This is not an issue for high $T$ but, below $T_c \approx 20$ K, the decays are clearly exponential and consist of both components at intermediate $T$, as inferred from Fig. 3(c). In order to separate out these components, we fit the data to the function $M(t) = M(0)[e^{-t/T_{2g}} + (1 - e^{-t/T_{2c}})^2]$ where $T_{2g}$ and $T_{2c}$ are the Gaussian and Lorentzian relaxation times, respectively. We find that $T_{2c}$ has an onset coincident with $T_c$ and associate
the emergence of this new relaxation mechanism with the presence of pinned vortices whose dynamics produce a $z$-component field fluctuations with a Lorentzian spectral density [15]. The increase of $\delta$, and thus the Lorentzian component, is consistent with the drop in $1/T_1$ at $T_c$. This observation independently confirms the microscopic coexistence of frozen vortices and AFM order in the SC state contradicting recent reports [8].

In summary, we have used $^{75}$As NMR experiments to investigate the interplay between AFM and SC in the underdoped (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$. We found a reduced ordered Fe moment $\langle S \rangle \simeq 0.37\mu_B/Fe$ for our sample confirming that AFM order is suppressed upon doping, probably to give way to SC in these materials. This means that these two broken symmetries must be intimately related. We also conclude that the AFM order uniformly coexists with SC in underdoped compositions, at least on a lattice parameter length scale, given that both $1/T_1$ and $1/T_2$ show the anomalies associated with the AFM order ($T_N$) and SC ($T_c$) probed locally by the same $^{75}$As nuclei.

Acknowledgments

Work at NHMFL was performed under the auspices of the NSF through the Cooperative Agreement No. DMR-0654118 and the State of Florida. Work at Unicamp was supported by Fapesp, CNPq and Capes.

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